ASTRONAUTICS INFORMATION

LITERATURE SEARCH NO. 482

ORGANIC SEMICONDUCTORS, II: PROPERTIES, SYNTHESIS, AND APPLICATION

1964

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA

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ORGANIC SEMICONDUCTORS, II:
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COMPILED BY
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JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY PASADENA CALIFORNIA

1964

FOREWORD

This Literature Search updates and supplements Astronautics Information Literature Search No. 341, "Organic Semiconductors: Properties and Applications." Most of the entries refer to material published or papers presented in the period July 1961 through September 1963. Translations of foreign articles formerly referenced in the original language are cited. Literature Search No. 482 has been prepared at the request of the technical staff of the Jet Propulsion Laboratory and is published for distribution to interested organizations working in the field of astronautics.

The references are classified in four broad subject areas: **Conductivity and Semiconductivity**, **Photoconductivity**, **Excited States**, and **Dielectric Effects.** Entries in each of the four areas are further grouped to comprise general references, theory, experiment, synthesis, and application. Within each of these groups the material is arranged alphabetically by source. An author index is included.

Several subjects which were only sampled in Literature Search No. 341, such as organic liquids, biological molecules, and electron spin resonance, are more fully covered here. Ion, exciton, and electron conduction processes are considered for both extrinsic and intrinsic semiconductors. Various types of emission and absorption spectra are discussed in the section on **Excited States.** Many of these entries may be considered as basic theory for **Conductivity and Semiconductivity** and **Photoconductivity.** A sampling of available studies is presented in the **Dielectric Effects** section.

The following reference sources were consulted in the preparation of this document: *Solid State Abstracts (SSA)*, *Physics Abstracts (PA)*, *International Aerospace Abstracts (IAA)*, *Chemical Abstracts*, *Chemical Titles*, *Current Chemical Papers*, National Aeronautics and Space Administration *Scientific and Technical Aerospace Reports (STAR)*, Defense Documentation Center *Technical Abstract Bulletin*, and JPL Library acquisitions, including periodicals, both foreign and domestic, pertinent to the fields of chemistry, electronics, and optics.

The compiler wishes to acknowledge the assistance of Dr. Alan Rembaum and Dr. Jovan Moacanin of the Jet Propulsion Laboratory.

CONTENTS

CONDUCTIVITY AND SEMICONDUCTIVITY
GENERAL REFERENCES

1. PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON SEMICONDUCTOR PHYSICS. PRAGUE, 1960
Academic Press, Inc., New York, N.Y., and
London, England, 1961

The conference, which was organized by the Czechoslovak Academy of Sciences, took place from August 29 to September 2, 1960. It was held under the auspices of IUPAP and was supported by the Czechoslovak Government and UNESCO. About 760 scientists from 25 countries attended the conference, which was devoted to fundamental problems in the physics of semiconductors, both from the experimental and theoretical point of view. Topics covered included: band structure and related problems; transport phenomena including scattering processes, hot electrons, and galvanomagnetic effects; recombination; radiation damage; optical properties; optical and magneto-optical effects; photoconductivity; surface phenomena; resonance; thermal properties and thermoelectricity; ionic crystals; and semiconducting materials. (*PA*, 1962, #21,113)

2. ORGANIC SEMICONDUCTORS
Garrett, C. G. B.
In "Proceedings of the International Conference on Semiconductor Physics, Prague, August 29–September 2, 1960," pp. 844–848
Academic Press, Inc., New York, N.Y., and
London, England, 1961

Various organic materials display an electrical conductivity that increases with increasing temperature; many of these show photoconductivity as well. Among well-defined substances, one can distinguish two classes of organic semiconductors: molecular crystals such as anthracene, and charge-transfer complexes such as perylene-iodine. The properties of materials falling into these two classes are reviewed. (*PA*, 1962, #23,304)

3. ELECTRICAL CONDUCTIVITY OF ORGANIC SEMICONDUCTORS
Inokuchi, H., Akamatu, H.
In "Solid State Physics--Advances in Research and Applications," Volume 12, pp. 93–148
Seitz, F., Turnbull, D., Editors
Academic Press, Inc., New York. N.Y., 1961

The article covers the following: introduction, including historical survey of electrical conduction in organic compounds, concept of organic semiconductors, classes of the organic semiconductors, and structural aspect of the organic semiconductors; preparations and purifications of organic semiconductors; electrical resistivity of organic semiconductors, including preparation of conductivity cells, survey of the resistivity measurements, pressure dependence for resistivity, single crystals, results with thin films, and phthalocyanines; photoelectric phenomena, including photoconductivity and photovoltaic effect in organic semiconductors; discussion of the energy gap, with the energy band model, the tunnel effect, and the exciton; and semiconductive properties of the aromatic-halogen molecular complexes and of the alkali metal-aromatic complexes. The molecular formulas of semiconductive organic compounds and the commercial names of vat dyestuffs are presented in appendices.

4. CONDUCTION AND BREAKDOWN IN LIQUID DIELECTRICS
Sharbaugh, A. H., Watson, P. K.
In "Progress in Dielectrics, Volume IV," pp. 199–248
Birks, J. B., Hart, J., Editors
Academic Press, Inc., New York, N.Y., and
Heywood & Company, Ltd., London, England, 1962

This is a review, mainly of work since 1957, on the conduction and breakdown of purified organic liquids. The topics considered include low-field and high-field conduction, electrical breakdown measurements, miscellaneous high-field phenomena, and mechanisms of electrical breakdown. 89 references. (*PA*, 1962, #19,572)

5. GIANT MOLECULES AND SEMICONDUCTORS
Brillouin, L.
***Cahiers de Physique*. v. 15 pp. 413–425, October 1961**

A discussion is presented of the relationship between the behavior of large biological molecules (proteins and nucleic acids) and that of semiconductors. The work of many authors is reviewed, and it is shown that their results suggest a close similarity between these molecules and semiconducting circuits. 42 references. (*PA*, 1962, #6430)

6. ELECTRICAL PROPERTIES OF ORGANIC SOLIDS
Kearns, D. R.
1960
California, University of, Berkeley
Thesis

7. ORGANIC CONDUCTORS RESEARCH
***Chemical and Engineering News*, v. 40, no. 9, pp. 86–95,**
February 26, 1962

The survey includes a discussion of conduction mechanisms and conduction in anthracene, polymers (including polydiketones and the polyacene quinone radical polymers), ionic photoconductor dyes, the charge-transfer complexes (including 7,7,8,8-tetracyanoquino-dimethane and iodine-perylene), diamonds and graphite. Work being done at various agencies is pointed out, and the SSSR contributions to the field are noted.

8. **POLYMERIC SEMICONDUCTORS**
Rembaum, A., Moacanin, J.
To be published in "Progress in Dielectrics, Volume VI"
Heywood & Company, Ltd., London, England
(in publication 1964)

9. **SYMPOSIUM ON ELECTRICAL CONDUCTIVITY IN ORGANIC SOLIDS**
Kallmann, H., Silver, M., Editors
Interscience Publishers, Inc., New York, N.Y., 1961
(Review by C. A. Klein available in *Solid-State Electronics*, v. 5, pp. 418–419, 1962)

Proceedings are presented of a conference (Duke University, Durham, North Carolina, April 1960) sponsored by the Office of Ordnance Research, U.S. Army; the Office of Naval Research, U.S. Navy; and the Office of Scientific Research, U.S. Air Force. The conference was devoted entirely to this "new" area in solid-state research. The following papers are presented:

"Charge-Transport Processes in Organic Materials," by H. Kallmann and M. Pope, pp. 1–25 (For abstract see Entry #669, AI/LS 341.)

"Photoconductivity in Aromatic Hydrocarbon Crystals," by O. Simpson, pp. 27–38 (For abstract see Entry #712, AI/LS 341.)

"Photoelectric Properties of Semiconducting Organic Dyes," by A. Terenin, pp. 39–59 (For abstract see Entry #162, AI/LS 341.)

"Observations on Aromatic Hydrocarbons in Connection with Their Electrical Conductivity," by N. Riehl, pp. 61–68 (For abstract see Entry #676, AI/LS 341.)

"The Photovoltaic Behaviors of Aromatic Hydrocarbons," by H. Inokuchi, Y. Maruyama, and H. Akamatu, pp. 69–76 (For abstract see Entry #713, AI/LS 341.)

"Pulsed Photoconductivity in Anthracene," by R. G. Kepler, pp. 77–81 (For abstract see Entry #715, AI/LS 341.)

"A-C and D-C Photoconductivity in Anthracene Single Crystals," by M. Pope and H. Kallmann, pp. 83–104 (For abstract see Entry #717, AI/LS 341.)

"Spatial Distribution of Trapped Electrons in Anthracene," by M. Silver and W. Moore, pp. 105–111 (For abstract see Entry #731, AI/LS 341.)

"Trapping Centers and Electronic Conduction Processes in Anthracene and 9,10-Dichloroanthracene," by A. Bree, P. J. Reucroft, and W. G. Schneider, pp. 113–125 (For abstract see Entry #716, AI/LS 341.)

"The Diffusion of Excitons and Charges in Molecular Crystals," by J. N. Murrell, pp. 127–145 (For abstract see Entry #732, AI/LS 341.)

"Molecular-Orbital Theory and Crystals," by J. A. Pople, pp. 147–162 (For abstract see Entry #733, AI/LS 341.)

"Weak Transitions in Molecular Crystals," by D. P. Craig and S. H. Walmsley, pp. 163–181 (For abstract see Entry #734, AI/LS 341.)

"Emission Spectra in Crystalline Naphthalene," by H. Sponer, pp. 183–191 (For abstract see Entry #735, AI/LS 341.)

"Absorption and Luminescence Spectra and the Spectral Dependence of Photoemission and Photoconduction in Aromatic Hydrocarbon Crystals," by L. E. Lyons, pp. 193–203 (For abstract see Entry #736, AI/LS 341.)

"Paramagnetic Resonance of Phosphorescent Naphthalene Molecules," by C. A. Hutchison, Jr., pp. 205–218 (For abstract see Entry #737, AI/LS 341.)

"Dispersion Forces in Molecular Crystals," by D. S. McClure, pp. 219–238 (For abstract see Entry #738, AI/LS 341.)

"Electronic States of Aromatic Solids," by D. Fox, pp. 239–245 (For abstract see Entry #739, AI/LS 341.)

"Ionic Organic Photoconductors," by R. C. Nelson, pp. 247–256 (For abstract see Entry #710, AI/LS 341.)

"The Electrical Conductivity of Solid Free Radicals and the Electron Tunneling Mechanism," by D. D. Eley and M. R. Willis, pp. 257–276 (For abstract see Entry #670, AI/LS 341.)

"The Chemical Aspects of Semiconductive Compounds," by H. Akamatu and H. Inokuchi, pp. 277–290 (For abstract see Entry #671, AI/LS 341.)

"Photoconduction and Photovoltaic Effects in Carotenoid Pigments," by B. Rosenberg, pp. 291–308 (For abstract see Entry #711, AI/LS 341.)

"Semiconductive Properties of Molecular Complexes," by R. Sehr, M. M. Labes, M. Bose, H. Ur, and F. Wilhelm, pp. 309–324 (For abstract see Entry #672, AI/LS 341.)

"Electric and Magnetic Properties of Some Low-Resistance Organic Semiconductors," by J. Kommandeur and L. S. Singer, pp. 325–336 (For abstract see Entry #673, AI/LS 341.)

"Electrical and Thermal Properties of Poly-Copper Phthalocyanine," by A. Epstein and B. Wildi, pp. 337–357 (For abstract see Entry #674, AI/LS 341.)

"Long Scintillation-Decay Times in Anthracene," by P. E. Gibbons and D. C. Northrop, pp. 359–368 (For abstract see Entry #740, AI/LS 341.)

"Biological Aspects," by J. Gergely, pp. 369–383 (For abstract see Entry #675, AI/LS 341.)

"Energy Transfer by Aqueous Solutions of Human Serum-Albumin (SAH): Photosensitized Reactions," by P. Douzou, J. C. Francq, R. Goldstein, and J. M. Thuillier, pp. 385–394 (For abstract see Entry #741, AI/LS 341.)

"The Influence of Electrode Material on the Photoconductivity in Anthracene," by H. Boroffka, pp. 395–398 (For abstract see Entry #714, AI/LS 341.)

10. ORGANIC SEMICONDUCTORS
Juster, N. J.
***Journal of Chemical Education*, v. 40, no. 10, pp. 547–555, October 1963**

A review is presented including discussion of the terms involved, the different mechanisms of semiconduction, the organic materials which show photoconduction or dark conductivity, and possible uses of conductive organics. 48 references.

11. SEMICONDUCTING POLYMERIC MATERIALS
Topchiev, A. V.
***Journal of Polymer Science, Part A: General Papers*, v. 1, no. 2, pp. 591–597, February 1963**

This paper deals with theoretical and experimental data on polymeric products with semiconducting properties. The data show the possibility of producing, on the basis of polymers, particularly polyacrylonitrile, substances characterized by high electroconductivity and exponential dependence of the latter on temperature. Possible changes in electrophysical properties of the materials are discussed. A quasimetallic model of a polymeric semiconductor is described.

12. SOME RELATIONS OF STRUCTURE OF SYNTHETIC SOLID POLYMERS TO THEIR ELECTRICAL PROPERTIES
Baker, W. O.
Introductory Paper presented at the International Symposium on Macromolecular Chemistry, Paris, France, July 1–6, 1963, sponsored by the International Union of Pure and Applied Chemistry, under the patronage of Monsieur le Ministre d'État chargé de la Recherche Scientifique, under the auspices of the Délégation Générale à la Recherche Scientifique et Technique, and the National Committee for Chemistry
(To be published in *Journal of Polymer Science, Part C: Polymer Symposia*)

13. ORGANIC SEMICONDUCTORS
Kuroda, H.
***Kagaku No Ryoiki*, v. 17, pp. 113–120, 1963**

A review is presented.

14. ZUR ELEKTRISCHEN LEITFÄHIGKEIT VON HOCHPOLYMEREN (ELECTRICAL CONDUCTIVITY OF HIGH POLYMERS
Kallweit, J. H.
***Kolloid-Zeitschrift*, v. 188, no. 2, pp. 97–114, April 1963**

15. ORGANIC SEMICONDUCTORS
Eley, D. D.
***M & B Laboratory Bulletin*, v. 5, pp. 51–57, 1963**

A review is presented. 41 references.

16. ORGANIC SEMICONDUCTORS
Brophy, J. J., Buttrey, J. W., Editors
The Macmillan Co., New York, N.Y., 1962

This book presents (1) a brief, semi-technical survey of the highlights of the Inter-Industry Conference on Organic Semiconductors; (2) an up-to-date collection of reports on major research activities; (3) a concise summary of the present state of knowledge; (4) technical papers on the details of electrical conduction processes in various organic materials; and (5) suggestions for possible new applications of organic semiconductors in electronic devices.

The following papers are presented:

"Charge Carrier Mobility and Production in Anthracene," by R. G. Kepler, pp 1–20

"Electronic Transport in Anthracene and Other Organic Systems," by O. H. LeBlanc, Jr., pp. 21–26

"Carrier Generation and Electrode Contact Effects in Photoconducting Anthracene," by M. Silver, pp. 27–35

"Comparison of Measurements on Single Crystal and Compressed Microcrystalline Molecular Complexes," by P. L. Kronick and M. Labes, pp. 36–44

"Electronic Conduction and Exchange Interaction in a New Class of Conductive Organic Solids," by R. G. Kepler, P. E. Bierstedt, and R. E. Merrifield, pp. 45–48

"Electronic Conduction in Charge Transfer Molecular Crystals," by E. Menefee and Y.-H. Pao, pp. 49–78

"Electronic Properties of Organic Compounds: I. Heterocyclic Compounds," by S. Aftergut and G. P. Brown, pp. 79–88

"Electronic Properties of Organic Compounds: II. Theoretical Considerations on the Effect of Impurities," by G. P. Brown and S. Aftergut, pp. 89–99.

"Effect of Impurities on the Electrical Conductivity of Simple Polycyclic Aromatic Hydrocarbons," by Y. Okamoto, F. T. Huang, A. Gordon, W. Brenner, and B. Rubin, pp. 100–107

"Photoconductivity and Intermolecular Interaction in Non-ionic Aromatic Crystals," by M. Y. Kleinerman and S. P. McGlynn, pp. 108–114

"An Open Shell Self-Consistent Field Method for Aromatic and Olefinic Organic Molecules," by O. W. Adams and P. G. Lykos, pp. 115–122

"The Thermal Conductivity of Molecular Crystals," by R. W. Keyes, pp. 123–133

"Semiconduction in Polymers," by H. A. Pohl, pp. 134–141

"Studies of Some Semiconducting Polymers," by H. A. Pohl, J. A. Bornmann, and W. Itoh, pp. 142–158

"Electrical Conductivity in Pyrolyzed Polyacrylonitrile," by W. D. Brennan, J. J. Brophy, and H. Schonhorn, pp. 159–168

"Current Noise in Pyrolyzed Polyacrylonitrile," by J. J. Brophy, pp. 169–179

"Electrical Properties of Pyrolytic Graphites," by C. A. Klein, pp. 180–239

"A Management Appraisal of Organic Semiconductors," by J. F. Bourland, pp. 240–243.

17. CONDUCTION PHENOMENA IN SOLID DIELECTRICS

Lipsett, F. R., Rolfe, J.
In "Digest of Literature on Dielectrics—1959," Volume 23, pp. 101–131
Frisco, L. J., Callinan, T. D., Editors
National Academy of Sciences, National Research Council, Washington, D.C., 1960 (available as Publication 799)

18. CONDUCTION PHENOMENA IN SOLID DIELECTRICS

Davisson, J. W., Pasternak, J.
In "Digest of Literature on Dielectrics--1961," Volume 25, pp. 147–2[illegible]6
Parks, A. M., Editor
National Academy of Sciences, National Research Council Washington, D.C., 1962 (available as Publication 1034)

For organic materials, ordinary conduction is considered on pages 173 through 176; photoconductivity on pages 196 through 198; electroluminescence on page 199; and electrets on page 212.

19. ELECTRONIC PROPERTIES OF SOLID POLYMERS

Pohl, H. A., Huggins, M. L.
March 1962
National Academy of Sciences, National Research Council, Washington, D.C.
Technical Report, "Unsolved Problems in Polymer Science," pp. 182–187, ASD TR-62-283, AF 33(616)-1861
AD-282-067

A general review is presented of electrical conductivity of polymers. These polymers generally possess a conductivity intermediate between metals and insulators, i.e., in the range of 10^{-3} to 10^{12} ohm^{-1}cm^{-1}, and exhibit electronic, in contrast to ionic, conduction. Some of them are noted as photoconductors. Problems still to be solved are pointed out, such as the following: (1) development of materials that would be suitable for photosynthesis, i.e., would have both catalytic and power-conversion capabilities; (2) development of materials that would be suitable for ion exchange and at least as conductive as sea water, thereby possibly permitting fresh water preparation by an economical means; (3) development of materials that would be suitable for electron exchange (redox operation) and would be conductive; and (4) development of interpretative understanding of organic semiconductive processes that would carry over into useful understanding of various important biological processes, such as the photoinduction of cancer, enzyme action, photosynthesis, and vision.

20 PROGRAM AND ABSTRACTS: ORGANIC CRYSTAL SYMPOSIUM, OCTOBER 10, 11 AND 12, 1962

National Research Council, Ottawa, Canada, 1962

This symposium was sponsored by the National Research Council of Canada; United States Army Research Office, Durham, North Carolina; and United States Office of Naval Research, Washington, D.C. The sessions included: Optical Properties; Charge-Transfer Complexes and Excitons; Experimental Techniques; Electrical Properties (Theory, Anthracene); Magnetic Properties; and Charge-Transfer Complexes and Other Organic Systems.

21. POLYMER SEMICONDUCTORS

Azernikov, V.
***Nauka i Zhizn*, no. 2, pp. 8–10, February 1961**
(Translations available as JPRS 4874 and JPRS:4592, Joint Publications Research Service, Washington, D.C., and OTS:61-27958 and OTS:61-[illegible]111, U.S. Dept. of Commerce, Office of Technical Services, Washington, D.C.)

22. ORGANIC SEMICONDUCTORS

Brophy, J. J.
***Physics Today*, v. 14 no. 8, pp. 40–41, August 1961**
(See also Entry #16)

A report is given of a two-day conference held in April 1961 in Chicago under the cosponsorship of the Armour Research Foundation and the magazine *Electronics*. The audience of nearly 300, drawn from widely diverse organizations, was treated to eight invited addresses and fourteen contributed papers. The object of the program was to present a concise summary of the present understanding of a field in which major research activities are only two years old. (*PA*, 1961, #17,676)

23. THE PHYSICO-CHEMICAL ASPECTS OF ORGANIC SEMICONDUCTORS
Pohl, H. A.
February 1, 1962
Princeton University, Plastics Lab., N.J.
Technical Report 64C, DA 36-039-sc-89143
AD-273,720
(Also available through U.S. Dept. of Commerce, Office of Technical Services, Washington, D.C.)

A literature review of studies on organic semiconductors is presented. There are certain aspects of the electronic behavior of both monomeric and polymeric semiconductors which need considerable enlightenment. These include the origin of the activation energy observed for the conduction processes, the high conductivities of incompletely crystalline materials, and the low sensitivity to impurity (and possibly to morphology) exhibited by large numbers of organic semiconductors. In comparing the organic semiconductors with the best examples of the inorganic ones, it should be noted that while overall conductivities for either class of material can be made quite large and comparable with the conductivities of some metallic substances, the organic semiconductors have not yet been prepared with the high mobilities characteristic of the highest quality inorganic semiconductors. Certain attributes of the presently available organic semiconductors such as high pressure sensitivity of certain organic resistors may offer some advantage.

24. ORGANIC SEMICONDUCTORS
Krentsel, B. A.
***Priroda*, v. 50, no. 1, pp. 51–55, January 1961**
(Translations available as JPRS:9480, Joint Publications Research Service, Washington, D. C., June 19, 1961 and OTS:61-28617, U.S. Dept. of Commerce, Office of Technical Services, Washington, D.C.)

25. ORGANIC SEMICONDUCTORS
Garrett, C. G. B.
***Radiation Research*, Supplement 2, pp. 340–348, 1960**
(Proceedings of Bioenergetics Symposium, Brookhaven National Laboratory, Upton, N.Y., October 12–16, 1959, sponsored by the U.S. Atomic Energy Commission)

The following sections appear in the article: Introduction; Survey of Experimental Results; Theoretical Models; and Surface Effects vs. Volume Effects.

26. ORGANIC SEMICONDUCTORS
Gutmann, F., Netschey, A.
***Reviews of Pure and Applied Chemistry*, v. 12, pp. 2–15, March 1962**

The sections of this review are: Introduction; Band Structure in Molecular Crystals; Mobility; Energy Gap; Excitons; Tunneling, Other Hypotheses; and Semiconductivity and Structure.

Information on the temperature dependence of electrical conductivity of organic semiconductors, representing much of the literature published before 1961, is tabulated. 45 references.

27. ORGANIC SEMICONDUCTORS
Traynard, P.
***Revue de l'Institut Français du Pétrole et Annales des Combustibles Liquides*, v. 18, pp. 62–82, 1963**

A review is presented. 17 references.

28. USSR WORK ON SEMICONDUCTORS
***Zhurnal Vsesoyuznogo Khimicheskogo Obshc'estva imeni D.I. Mendeleeva*, v. 5, no. 5, October 1960**
(Translations available as JPRS: 9293, Joint Publications Research Service, Washington, D.C., May 26, 1961, and OTS: 61-23009, U.S. Dept. of Commerce, Office of Technical Services, Washington, D.C.)

This report contains selected papers of USSR work on semiconductors. The following articles are included: "The Chemistry of Semiconductors and Electron Mechanisms of Chemical Reactions"; "Organic Dyestuffs-Semiconductors and Their Photoelectric Characteristics"; "The Semiconductor Properties of Polymer Materials"; "New High-Temperature Semiconductors and Their Application"; "The Chemistry of Diamond-like Semiconductors"; "Chemical Reactions on the Surface of Germanium, Silicon, and Their Electronic Analogues"; "Vitreous Semiconductors"; "Physicochemical Analysis of Semiconductors"; "Radioactivation Analysis of Pure Materials and Prospects of its Development"; and "Physicochemical Problems of Dielectrics."

THEORY

29. CALCULATION OF MOLECULAR ORBITAL ENERGIES OF MACROMOLECULES WITH CONJUGATED DOUBLE BONDS
Koutecký, J., Zahradník, R.
In "Proceedings of the International Conference on Semiconductor Physics, Prague, August 29–September 2, 1960," p. 849
Academic Press, Inc., New York, N.Y., and London, England, 1961

The energies of eight types of macromolecules (43 substances) were calculated by the simple MO-LCAO method. The results of the calculations show that the energy difference between the highest filled energy level and the lowest empty level is, in the case of certain of the molecules studied, of the same order of magnitude as the energy gap in normal semiconductors. (*PA*, 1962, #23,020)

30. GIANT MOLECULES AND SEMICONDUCTORS

Brillouin, L.
In "Horizons in Biochemistry," pp. 295–318
Kasha, M., Pullman, B., Editors
Academic Press, Inc., New York, N.Y., and
London, England, 1962

The purpose of this report is to give the viewpoint of a theoretician, who has been at the origin of the whole theory of semiconductors, and to discuss in very general terms the conditions required for a possible application of the theory of semiconductors to macromolecules.

31. SEMICONDUCTIVITY IN BIOLOGICAL MOLECULES

Eley, D. D.
In "Horizons in Biochemistry," pp. 341–380
Kasha, M., Pullman, B., Editors
Academic Press, Inc., New York, N.Y., and
London, England, 1962

The paper deals with semiconductor behavior, including specific conductivity, electron transfer in crystals, the potential box (electron gas) model, the energy gap, Ohm's Law and κ_0 and mobility; the molecular types of solid free radicals, charge-transfer complexes, porphyrins, proteins, nucleic acids, and nucleoproteins; photoconduction; and biological systems, including cytochrome systems, chloroplasts, carcinogenesis, energy conversion in retinal rods, and irradiation of proteins.

It is suggested that an important function of adsorbed water is to transfer electrons to biological molecules such as proteins and nucleic acids, so as to form *n*-type laminae. The interaction of quinones and other electron acceptors, such as a free radical source with proteins in lipoidal environments, then forms *p*-type laminae. The juxtaposition of these structures, as in transistors, will allow a wide range of electron conduction behavior, and permit the localization of oxidation and reduction behavior in chloroplasts, mitochondria, etc. This localization may be coupled with stereochemical considerations to give a high degree of specificity. This new hypothesis may serve to unify the three concepts of Szent-Györgyi, and is offered as a subject for further experimentation.

32. QUANTUM CHEMISTRY IN MOLECULAR BIOLOGY

Kasha, M.
In "Horizons in Biochemistry," pp. 583–599
Kasha, M., Pullman, B., Editors
Academic Press, Inc., New York, N.Y., and
London, England, 1962

In this essay a number of topics in quantum chemistry have been singled out for evaluation and comment as an indication of the potential which these topics offer for detailed molecular electronic mechanisms in biological phenomena. A number of important topics, such as ligand-field theory of metal ions, the intricacies of intramolecular electronic excitation, and numerous others have been omitted from discussion here. Among the topics covered are basic theories of energy transfer and electron transfer, including the exciton theory of energy transfer (excitation transfer), charge-transfer interaction (donor-acceptor interaction), and electronic semiconductivity in molecular aggregates: and molecular memory models.

33. A THEORY OF EXCITON TRANSFER IN ANTHRACENE

Zalewski, K.
***Acta Physica Polonica*, v. 20, no. 4, pp. 313–319, 1961**
(in English)

A continuity equation describing the motion of localized excitons in an anthracene crystal is proposed. The intermolecular transition probabilities are computed in the dipole approximation with a semiempirical adjustment, as used by Dexter. Simpson's experiment is discussed and his phenomenological theory reexamined. (*PA*, 1961, #17,473)

34. ELECTRONIC STRUCTURE OF DEOXYRIBONUCLEIC ACID. I. APPROXIMATE CALCULATION OF THE π-ELECTRON OVERLAP BETWEEN ADJACENT NUCLEOTIDE BASES. PROBABLE CONSEQUENCES

Ladik, J.
***Acta Physiologica Academiae Scientiarum Hungaricae*,**
v. 11, pp. 239–258, 1960

The approximate quantum mechanics π-electron overlap integrals between the parallel nucleotide bases of deoxyribonucleic acid (DNA) at 3.36 Å from one another indicate the existence of a π-electron interaction which cannot be neglected. The biological effect of physical or chemical changes localized in small parts of DNA is explained by taking into account the mobility of the electrons along the long axis.

35. STATES INVOLVING CHARGE TRANSFER IN ORGANIC SYSTEMS

Benderskii, V. A., Blyumenfeld, L. A.
***Akademiya Nauk SSSR, Doklady*, v. 144, no. 4, pp. 813–816,**
June 1, 1962

It is hypothesized that the local states, which determine the magnetic and electric properties in two-component acceptor-donor crystals, organic polymers, and low-molecular weight compounds with conjugated bonds, are responsible for the charge transfer between molecules or between individual segments in the molecule, thus explaining the formation of carriers in dissociative complexes involving charge transfer. The potential curves of a complex formed from two molecules in neutral and polar conditions were studied. The local state in a polar complex represents an increasing dislocation in which the molecules are located closer to each other than in neutral crystals. The electric conductivity of molecular crystals was studied by calculating the dissociation and polarization energy of the local state involving a charge transfer, and it was found that the dissociation energy decreased rapidly with the size of the molecule and increased polarization energy, indicating the appearance of charge carriers in molecular crystals. The concentration of carriers, p, was found by the equation $p = N_0 \exp(-\epsilon_0 / 2kT) + n \exp(-E_d / 2kT) + \gamma[N_0 / (1 + W_1 / W_2)] \exp(-\epsilon_0' / 2kT)$, where $\gamma \approx 1$, and W_1 and W_2 are the probability factors of deactivation and dissociation of the excitons.

36. ELECTRIC CONDUCTIVITY AND ELECTRON SPIN RESONANCE SIGNAL IN POLYMERS WITH CONJUGATED DOUBLE BONDS

Levich, V. G., Markin, V. S., Chirkov, Yu. G.
***Akademiya Nauk SSSR, Doklady*, v. 149, no. 4,**
pp. 894–896, April 1, 1963

Expressions for electrical conductivity are presented, corresponding to a model of a long-chain molecule with conjugated double bonds. Thermal vibrations and heterogeneities in the chain represent the resistance to displacement of an electron along the chain. The electron spin resonance of the model chain is discussed.

37. THE NATURE OF SEMICONDUCTION IN SOME ACENE QUINONE RADICAL POLYMERS

Opp, D. A., Pohl, H. A.
American Chemical Society, Washington, D.C.
Paper 86, Division of Physical Chemistry, presented at the 140th Meeting, ACS, Chicago, Ill., September 3–8, 1961

The polymers prepared by condensation of various substituted aromatic hydrocarbons with various aromatic acid anhydrides are semiconductors which conduct electronically and not ionically. Determination of various electronic properties, such as the Seebeck coefficient, the conductivity, and its changes with temperature, pressure, and electrical field strength afforded clues as to the nature of the processes basic to electronic conduction in such molecular solids.

Evidence for the existence of *eka*-conjugation in the various organic polymers showing enhanced electronic semiconduction is discussed. *Eka*-conjugation is said to arise when the degree of conjugation is such that appreciable amounts of biradical (or exciton) state appear at room temperature. The energy of formation of the excited states (in ev) can be approximated by the electron-in-a-box model as, $\Delta E \cong E^3 \cong \pi^2 n^2 (n_2^2 - n_1^2) / 8ma^2 \cong 14.4 / x^2$, where x is the number of conjugated double-single bonds associated, and the average bond length is 1.40A, $n_2 = 2$, $n_1 = 1$, m = mass of electron, a = width of potential well. Carrier motion is considered to occur by hopping mechanism. The basic reactions important for carrier formation are considered to be:

$$(1)\quad \mathrm{R} \leftrightharpoons .\mathrm{R}.\ ;\ \Delta F_1 \cong E^3 \cong kT$$

$$(2)\quad .\mathrm{R}. + \mathrm{R} \leftrightharpoons .\mathrm{R}:^- + \mathrm{R}^+\ ;\ \Delta F_2 = \Delta H_2 + T\Delta S_2$$

giving

$$(3)\quad n_i = (s / 2) \exp[(-\Delta F_2 + E^3) / 2kT]$$

where n_i is the concentration of carriers of either sign, s is the concentration of unpaired electrons (spins / cm^3), and ΔF_2 is the free energy of formation of carriers. There is evidence for a hopping process of very low saddle height energy, E_s, with the mobility μ varying as $\mu = (\text{const.})T^2 \exp(-E^s/kT)$, and involving carrier-exciton interactions in the field-favored direction, i.e.,

$$(4)\quad \mathrm{R}^- + .\mathrm{R}. \rightarrow .\mathrm{R}. + \mathrm{R}^-$$

$$(5)\quad \mathrm{R}^+ + .\mathrm{R}. \rightarrow .\mathrm{R}. + \mathrm{R}^+.$$

38. CONDUCTION AND RELAXATION IN POLYAMIDES

McCall, D. W.
American Chemical Society, Washington, D.C.
Paper 20, Division of Polymer Chemistry, presented at the 144th Meeting, ACS, Los Angeles, Calif.,
March 31–April 5, 1963

An attempt is made to give a self-consistent discussion of the conduction, polarization and relaxation processes in polyamides. The melting range is usually broad, presumably because of a distribution of crystallite sizes, and the crystalline regions show a structure change well below the melting point. The latter change is associated with rotation about the chain axes. The amorphous material exhibits a glass transition, which is sensitive to water, and a separate relaxation region associated with water dipole motions is observed at lower temperatures. At still lower temperatures a transition involving both crystalline and amorphous regions appears and this is ascribed to rotation about the chain axes. Ionic conduction in the amorphous regions gives rise to a substantial dc conductivity above the glass temperature, and an accompanying low frequency polarization (Maxwell-Wagner) is observed. The nature of the conduction mechanism is discussed.

39. ON THE ELECTRICAL PROPERTIES OF POLYMERS AND THEIR PRECURSORS

Huggins, C. M.
American Chemical Society, Washington, D.C.
Paper 30, Division of Polymer Chemistry, presented at the 144th Meeting, ACS, Los Angeles, Calif.,
March 31–April 5, 1963

Considerable data exist on the electrical conductivity of some polymeric systems, but it has not been possible to make quantitative correlations with chemical or physical structures. Several techniques of measuring the conductivity itself are discussed, and it is shown that only under the most optimum circumstances will the measurement reflect the "true" bulk conductivity. The difficulties inherent in making theoretical arguments based on even the best of these conductivity data have minimized progress on the study of polymers.

This report describes the separation of the two main factors controlling conductivity, carrier generation and mobility, with emphasis on hypothesized mechanisms in typical conducting polymers. For a consideration of carrier transport in a usual polymer, it is first necessary to ascertain the effect of random molecular orientation on the mobilities as well as any self-polarization trapping. For a model compound, measurements of photo-induced carrier generation and mobility are made on crystalline and amorphous β-carotene, a highly efficient photoconductor which can be considered to be a precursor to a linear conjugated hydrocarbon. The technique of transient space-charge-limited photocurrents is used to measure generation, mobility, and the effects of structure and impurities on carrier trapping.

40. ELECTRONIC TRANSPORT IN ORGANIC CRYSTALS

LeBlanc, O. H., Jr.
American Chemical Society, Washington, D.C.
Paper 31, Division of Polymer Chemistry, presented at the 144th Meeting, ACS, Los Angeles, Calif., March 31–April 5, 1963

Electronic drift mobilities have been reported by several workers, most notably by Kepler who has made a thorough study of hole and electron mobilities in anthracene, including anisotropy, temperature dependence over a wide range, and pressure dependence. The drift mobilities are of the order of 1 cm^2/v-sec and decrease with increasing temperature. Similar results are obtained in other crystals.

The Hall effect has been observed in metal-free and copper phthalocyanine. The sign of the effect is that for majority electrons in the former and for majority holes in the latter, with Hall mobilities of $\sim$0.4 and $\sim$200 cm^2/v-sec, respectively.

These results can be interpreted in a straightforward, self-consistent fashion with band formalism. From this point of view the transport mechanism in organic crystals is qualitatively the same as that in valence semiconductors; quantitative differences arise from the extremely narrow bandwidths in organic crystals. Whether the band model really describes what goes on in these crystals, or whether it is just a phenomenological scheme that more or less accidentally gives reasonable results, is still very much a moot question.

41. A CHEMICAL INTERPRETATION OF THE SEMICONDUCTIVITY OF AMORPHOUS CARBONS

Weiss, D. E.
***Australian Journal of Chemistry*, v. 14, p. 157, 1961**

Qualitative relations are set up between change in conductivity of C with carbonization temperature and the supposed structural features of the C. The p-type semiconductivity of C prepared at 600–800°C is thought to be due to an electronic interaction between carbonyl and ether groups, through an aromatic residue.

42. SEMICONDUCTIVITY OF HEAT-TREATED ORGANIC COMPOUNDS

Brooks, J. D.
***Australian Journal of Chemistry*, v. 14, pp. 645–646, 1961**

The generality is questioned of Weiss's explanation of semiconductivity of higher-temperature carbons as the interaction of ether and carbonyl groups. The high-temperature semiconductivity of carbonized poly(vinylidine chloride) and carbonized violanthrene is explained as pairing of σ-electrons of broken bands with adjacent π-electrons.

43. THE ORGANIZATION OF CELLULAR ACTIVITY

Kuyper, Ch. M. A.
Elsevier Publishing Company, Amsterdam, The Netherlands, and New York, N.Y., 1962

44. ELECTRONIC PROCESSES IN PARAFFINIC HYDROCARBONS. PART 2. VALIDITY OF A BAND MODEL

McCubbin, W. L.
***Faraday Society, Transactions of the*, v. 59, pt. 4, no. 484, pp. 769–774, April 1963**

(For Part 1, see Entry #141.) Recent investigations on the validity of a band model for organic materials have concentrated on unsaturated hydrocarbons. Because the approach normally used makes no clear distinction between charge generation and charge transfer mechanisms, conclusions frequently rest on assumptions which are sufficient but not necessary. The present calculation answers only the question: how fast does a positive charge—entirely free from the negative charge with which it may at one time have been associated—move from one paraffin molecule to another? The result shows that it is valid to describe charge transport in terms of a band model.

An apparent contradiction arises from the experimental result that the conductivity of liquid paraffin greatly exceeds that of the solid at the melting point. By an extension of the ideas embodied in the above-mentioned calculation, it is possible to give a straightforward explanation in terms of band theory.

45. ON THE THEORY OF IMPURITY LEVELS IN AMORPHOUS SEMICONDUCTORS

Gubanov, A. I.
***Fizika Tverdogo Tela*, v. 3, no. 8, pp. 2336–2341, August 1961**
(Translated from the Russian in *Soviet Physics—Solid State*, v. 3, no. 8, pp. 1694–1697, February 1962

Various hypotheses are proposed to explain the absence of impurity conduction in amorphous semiconductors. It is shown by theoretical analysis of these hypotheses that the absence of impurity conduction in amorphous semiconductors can only be explained by a shift in local levels as the result of a reorientation of the atoms in the vicinity of the defect.

46. THEORY OF CHARGE TRANSPORT ON THE SURFACE OF SEMICONDUCTOR FILAMENTS

Chobanu, G.
***Fizika Tverdogo Tela*, v. 3, no. 8, pp. 2434–2441,**
August 1961
(Translated from the Russian in *Soviet Physics—Solid State*,
v. 3, no. 8, pp. 1767–1772, February 1962)

The effective (rms) mobility of carrier charges in a semiconductor filament of cylindrical symmetry is computed, taking into account the presence of a region with a space charge at the surface of the filament. The computation is carried out by means of the solution of the Boltzmann transport equation. The obtained formulas are applied to the case when the space charge has a potential of parabolic form.

47. LOCAL FLUCTUATION LEVELS IN AMORPHOUS SEMICONDUCTORS

Gubanov, A. I.
***Fizika Tverdogo Tela*, v. 4, no. 10, pp. 2873–2879,**
October 1962
(Translated from the Russian in *Soviet Physics—Solid State*,
v. 4, no. 10, pp. 2104–2108, April 1963)

A theoretical study is made of the formation in amorphous bodies of local electron levels due to fluctuations in the position of atoms. These electron or hole fluctuation traps may be responsible for the absence of impurity conduction in glassy semiconductors.

48. ON THE OBSERVATION OF TRANSIENT SPACE-CHARGE-LIMITED CURRENTS IN INSULATORS

Silver, M., Mark, P., Olness, D., Helfrich, W., Jarnagin, R. C.
***Journal of Applied Physics*, v. 33, no. 10, pp. 2988–2991,**
October 1962

The conditions for the observation of space-charge-limited (SCL) transient current pulses in insulators are examined. A parameter $\alpha = 2t_r/\tau$ (t_r = space-charge-free transit time and τ = response time of the circuit) is defined, whose value determines the extent to which the pulses are distorted from their ideal shape. For $\alpha > 100$, the pulses are undistorted. For $20 < \alpha < 100$, the pulse shape becomes distorted from the ideal case, and for $\alpha < 20$, pulses begin to be indistinguishable. It is shown that carrier transport in any insulator may be investigated by transient SCL current measurements provided that trapping is not too severe and that ohmic contact formation (either transient or steady-state) is possible. (*PA*, 1962, #23,259)

49. ERRATUM: OPTICAL AND OTHER ELECTRONIC PROPERTIES OF POLYMERS

Tinoco, I., Jr.
***Journal of Chemical Physics*, v. 34, no. 3, p. 1067,**
March 1961

Corrections are made in the equations of a previous paper (Entry #686, AI/LS 341) as a result of the criticism by Professor R. Feynman, California Institute of Technology, that the former equations were not adequate to give the correct oscillator strength or polarizability for a polymer.

50. BAND STRUCTURE AND TRANSPORT OF HOLES AND ELECTRONS IN ANTHRACENE

LeBlanc, O. H., Jr.
***Journal of Chemical Physics*, v. 35, no. 4, pp. 1275–1280,**
October 1961

Previous mobility measurements indicate that the band approximation can be used to describe the behavior of injected holes and electrons in anthracene, and the present theoretical investigation appears to confirm this. The structures of the bands appropriate to a hole or electron are calculated with the tight binding approximation. Hückel linear combinations of Slater-type atomic orbitals are used for the molecular basis functions. Both bands are highly anisotropic and each is found to be approximately 0.56 kT wide at room temperature. Mobility tensors are derived using a simplified treatment of scattering which assumes isotropic scattering parameters. The calculated mobilities exhibit roughly the anisotropy that has been observed experimentally. Magnitudes of the scattering parameters are estimated from the observed mobilities, and these are found to be reasonable (e.g., free path > lattice distances). (*PA*, 1961, #17,451)

51. RESONANCE TRANSFER MODEL OF ELECTRON AND HOLE CONDUCTION IN ANTHRACENE

Kearns, D.
***Journal of Chemical Physics*, v. 35, no. 6, pp. 2269–2270,**
December 1961

A resonance transfer model is applied to the experimental results of Kepler. Variation of electron and hole mobilities as the reciprocal temperature agrees with experiment, but both have the same dependence on temperature from the theory which conflicts with experiment. Anisotropy of hole mobility in the model shows good agreement with experiment but differences occur in the case of electron mobility. (*PA*, 1962, #4027)

52. SEMICONDUCTIVE PROPERTIES OF TETRACYANOETHYLENE COMPLEXES AND THEIR ABSORPTION SPECTRA

Kuroda, H., Kobayashi, M., Kinoshita, M., Takemoto, S.
***Journal of Chemical Physics*, v. 36, no. 2, pp. 457–462,**
January 15, 1962

The absorption bands characteristic of the solid molecular complexes of tetracyanoethylene are attributed to the charge transfer interaction between tetracyanoethylene and donor molecules. In the complexes with polycyclic aromatic hydrocarbons, the energy gap associated with the semiconductivity agrees well with the energy of the charge-transfer excitation in the crystalline state, while the former is much smaller than the latter in the complexes with polymethylbenzenes and azulene. (*PA*, 1962, #4040)

53. ELECTRICAL CONDUCTIVITY OF PROTEINS. II. SEMICONDUCTION IN CRYSTALLINE BOVINE HEMOGLOBIN

Rosenberg, B.
***Journal of Chemical Physics*, v. 36, no. 3, pp. 816–823,**
February 1, 1962

Evidence is presented to show that crystalline bovine hemoglobin is a semiconductor in the dry state. The semiconduction activation energy is 2.3 ev. This is similar to the values obtained for a number of other proteins, chromoproteins, and biological structures which have proteins as the main constituent. The effect of adsorbed water is to increase the conductivity enormously. The dependence on the amount of adsorbed water is exponential, in agreement with the results of Baxter and Spivey. In the "wet" state, the protein is still a semiconductor, but the semiconduction activation energy is lower. The dependence of the activation energy on the amount of adsorbed water is given by

$$E_W = E_D - \delta m.$$

It has been proved that this is the only effect of water in causing the increase in conductivity. The value of σ in the semiconduction formula is $7 \times 10^3 [\Omega\text{-cm}]^{-1}$ and is independent of the adsorbed water content. The effect of water adsorption on the conductivity is reversible when the water is desorbed. Experimental evidence, which strongly indicates that the conductivity process in the wet protein is electronic rather than ionic, has been given previously by the author. A theory is developed which shows that the effect of adsorbed water in increasing the dielectric constant of the protein lowers the work necessary to separate the charges due to the increase in the polarizability of the medium. This leads to a prediction that the dependence of the dielectric constant on the adsorbed water content should be of the form

$$\kappa' = \kappa/(1 - \kappa\chi m).$$

Some previous measurements of Medley and King are in semiquantitative agreement with this. The theory also predicts that for higher adsorbate concentrations, the conductivity should become constant (saturation effect). Again, the measurements of Medley and King confirm this. This saturation effect allows an estimate to be made of the radius of the polarization (R) and the ionization energy minus the electron affinity ($I - A$) for the protein. $R \cong 2.8 \times 10^{-8}$ cm and $I - A \cong 10$ ev. Both values are in reasonable agreement with expectations. (*PA*, 1962, #6473)

54. ERRATUM: BAND STRUCTURE AND TRANSPORT OF HOLES AND ELECTRONS IN ANTHRACENE

LeBlanc, O. H., Jr.
***Journal of Chemical Physics*, v. 36, no. 4, p. 1082,**
February 15, 1962

(For original article, see Entry #50.) A mistake in one of the equations is pointed out. Corrected values of the resonance integrals are given. (*PA*, 1962, #8186)

55. THEORY OF HOLE INJECTION AND CONDUCTIVITY IN ORGANIC MATERIALS

Kallmann, H. P., Pope, M.
***Journal of Chemical Physics*, v. 36, no. 9, pp. 2482–2485,**
May 1, 1962

The relationship between current and applied voltage is calculated for a process in which a given number of charge carriers of one sign is injected into matter which contains only a negligible density of charges of the opposite sign. Diffusion effects are taken into account approximately. The current–voltage relationship depends strongly on the image force exerted on the injected carriers near the electrode. The calculated current–voltage curve agrees qualitatively with that observed in anthracene under light excitation. The voltage at which saturation is approached can be calculated and depends upon a recombination velocity of the injected charge with the injecting electrode, and upon the image force. Different saturation voltages for various electrodes can be explained by a difference in recombination velocities. The dependence of the saturation voltage upon the intensity of the saturation current is also explained. For anthracene, the recombination between holes and a water electrode is expressed as a velocity much greater than thermal velocities. (*PA*, 1962 #14,521)

56. TUNNELING MODEL FOR ELECTRON TRANSPORT AND ITS TEMPERATURE DEPENDENCE IN CRYSTALS OF LOW CARRIER MOBILITY

Keller, R. A., Rast, H. E., Jr.
***Journal of Chemical Physics*, v. 36, no. 10, pp. 2640–2643,**
May 15, 1962

A tunneling model is used to explain electron transport in crystals of low carrier mobility. Temperature is incorporated into the model by allowing the barrier width to vary sinusoidally as a result of lattice vibrations. The maximum amplitude of vibration is proportional to $T^{1/2}$. The resulting expression for the mobility exhibits a linear temperature dependence. The model can also be used to estimate the width of the conduction band. The calculated results are compared with experimental results on anthracene, and the agreement is quite good for the mobility but not as good for the temperature dependence.

57. ELECTRON CONDUCTION IN CHARGE-TRANSFER MOLECULAR CRYSTALS

Menefee, E., Pao, Y.-H.
***Journal of Chemical Physics*, v. 36, no. 12, pp. 3472–3481,**
June 15, 1962

Molecular crystals consisting of strong electron donors and strong electron acceptors in ordered array often possess electronic properties which are not found in other types of organic solids. Molecular orbital calculations are carried out for the triethylammonium (tetracyanoquino dimethane)$_2$ crystal. The LCAO-MO method combined with a crystal-field splitting calculation results in a reasonably accurate value for the activation energy observed for electron conduction. On a basis of the results of this calculation, it would be concluded that this type of organic solid should not be expected to exhibit the properties of conventional inorganic semiconductors. However, the results do provide a basis for some hypotheses concerning electron conduction processes and possible photoconduction mechanisms in these solids. (*PA*, 1962, #16,673)

58. CALCULATED ELECTRON MOBILITY AND ELECTRICAL CONDUCTIVITY IN CRYSTALS OF LINEAR POLYENES

Tobin, M. C.
***Journal of Chemical Physics*, v. 37, no. 5, p. 1156, September 1, 1962**

Using the theory of Bardeen and Shockley, the mobility and electrical conductivity of a crystal of long-chain linear polyene molecules were calculated to be 1.4 cm^2/v sec and 0.12 ohm^{-1} cm^{-1}. (*PA*, 1963, #4926)

59. ELECTRONIC CONDUCTIVITY IN MOLECULAR CRYSTALS: AN ALTERNATIVE TO THE BLOCH-FUNCTION APPROACH

Keller, R. A.
***Journal of Chemical Physics*, v. 38, no. 5, pp. 1076–1083, March 1, 1963**

Bloch functions are not good basis functions for molecular crystals in high electric fields. When the interaction with the electric field is large with respect to next-neighbor interactions, it is better to use wave-functions which are localized over molecular sites as basis functions. A treatment of electronic mobility and diffusion in molecular crystals is developed using quantum mechanical transition probabilities between localized energy levels and considering only nearest-neighbor interactions. The asymmetry of the potential function, caused by the electric field, and the conservation of energy during transport are considered. The mobility is found to be independent of temperature, and the diffusion constant proportional to temperature. The magnitude of the diffusion constant calculated from phonon-induced transitions is quite reasonable (4.6×10^{-3}). Photon-induced transitions do not appear to be important.

60. DARK CONDUCTIVITY OF CATIONIC DYE PHOTOCONDUCTORS

Nelson, R. C.
***Journal of Chemical Physics*, v. 39, no. 4, pp. 859–863, August 15, 1963**

A theory is put forth to account for the dark conduction in cationic dyes, which assumes thermal excitation from ground state to conductive excited state, followed by trapping of the hole at the anion. It is applicable in principle to any case in which charge carriers are separated by an intrinsic thermal process which is followed by deep trapping of the minority carrier. Where such processes take place, measurements of thermally excited conduction will in general lead to one of three results when interpreted by simple equilibrium theory: the correct activation energy will be found, but the mobility inferred will be impossibly high; or, the mobility will be of the correct order of magnitude, but the activation energy will be too low; or both will be incorrect. The theory is applied to data for dark conduction in eight triphenylmethane dye halides, and it accounts for the observed thermal activation energies in terms of optical energy levels, and leads to mobilities which are similar and of acceptable magnitude.

61. BAND STRUCTURE AND TRANSPORT OF HOLES AND ELECTRONS IN HOMOLOGS OF ANTHRACENE

Thaxton, G. D., Jarnagin, R. C., Silver, M.
***Journal of Physical Chemistry*, v. 66, no. 12, pp. 2461–2465, December 1962**

Calculations of the band structure and of the mobility of excess holes and of excess electrons in homologs of anthracene have been completed. Following LeBlanc, the tight binding approximation was used and applied to naphthalene, tetracene, and pentacene. Calculated mobility tensors and bandwidths indicate the mobility properties of excess charge carriers in all four molecular crystals to be much alike. Experimental results for the crystals other than anthracene are not yet available.

62. CONDUCTANCE MECHANISM IN ORGANIC SEMICONDUCTOR POLYMERS

Airapetyants, A. V., Voitenko, R. M., Davydov, B. E., Krentsel, B. A.
Preprint 70, presented at the International Symposium on Macromolecular Chemistry, Paris, France, July 1–6, 1963, sponsored by the International Union of Pure and Applied Chemistry, under the patronage of Monsieur le Ministre d'État chargé de la Recherche Scientifique, under the auspices of the Délégátion Générale à la Recherche Scientifique et Technique, and the National Committee for Chemistry
(To be published in *Journal of Polymer Science, Part C: Polymer Symposia*)

A previous study of the dependence of differential thermal EMF and temperature showed that the character of this dependence is governed by the nature of the polymer when experiments are conducted in air. The present paper describes how the adsorption of oxygen influences the electrophysical properties of semiconducting materials derived from polyacrylonitrile. The desorption of oxygen is accompanied by an increase in conductivity and by a decrease in the energy of activation of polymeric semiconductors. The desorption of oxygen is also accompanied by a decrease in thermal EMF (positive sign) which at definite temperatures characteristic of each semiconductor passes through zero and changes its sign. The desorption of oxygen thus causes the transition of the hole-containing semiconductor (as the sign of thermal

EMF shows) into electronic materials. The dependence between the thermal EMF of deaerated polymeric semiconductors and temperature indicates the existence in the studied examples of partially or completely degenerated current carriers; their concentration does not depend on the temperature, and the exponential increase of conductivity is determined by exponential increases of the efficient mobility of the carriers. Moreover, the assumption that carriers degenerate is confirmed by the nature of the dependence between the thermal EMF and electroconductivity.

63. ELECTRONS AND HOLES IN ALTERNANT HYDROCARBONS

McLachlan, A. D.
Molecular Physics, v. 4, no. 1, pp. 49–56. January 1961

The theory of creation and destruction operators is used to give a new, simpler proof of the well-known pairing relation between electronic states of alternant hydrocarbon positive and negative ions. The method is like one that Heisenberg used to explain why the atomic spectra of elements such as C (with two electrons in the 2p shell), and O (with two holes) are so similar. It depends on the analogy between electrons in an orbital ψ' and holes in the paired antibonding orbital ψ' of the π-electron shell. A modified pairing relation holds also in a magnetic field. Applications of the operators to other problems are suggested. (*PA*, 1961, #14,071)

64. THE MOBILITY OF HOLES AND ELECTRONS IN ORGANIC CRYSTALS

Murrell, J. N.
Molecular Physics, v. 4, no. 3, pp. 205–208, May 1961

Overlap integrals between the molecular orbitals of different anthracene molecules in the crystal lattice are calculated. In the c' direction the highest occupied orbitals overlap to a greater extent than the lowest vacant orbitals (a ratio of 4.7:1). This result explains the experimental fact that holes are more mobile than electrons in this direction. It is predicted that in the *ab* plane the mobilities of the holes and electrons should be approximately equal, and considerably greater than in the c' direction. (*PA*, 1962, #585)

65. ELECTRICAL CONDUCTION IN DIELECTRICS

Armstrong, H.
In "Digest of Literature on Dielectrics—1960," Volume 24, pp. 121–127
Callinan, T. D., Parks, A. M., Editors
National Academy of Sciences, National Research Council, Washington, D.C., 1961 (available as Publication 917)

In a section on polymers and organic substances, Murphy's work on cellulose, silk, and water is reported. Conductivity of nearly dry cellulose is represented as the sum of two terms, one representing ionic conduction, the second depending upon absorbed water. Conductivity of the materials containing appreciable amounts of water is expressed by a separate formula: $\sigma = \sigma_s\ (\alpha/\alpha_0)^n$, where σ_s is conductivity at saturation, α the amount of water in percent of dry weight, α_0 the amount of water at saturation, and n a constant dependent on the structure of the material.

66. IONIZED STATES AND CHARGE TRANSPORT IN CRYSTALLINE CHARGE-TRANSFER COMPLEXES [ABSTRACT]

Tobin, M. C.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 46–49
National Research Council, Ottawa, Canada, 1962

It has often been reported that crystalline charge-transfer complexes have dark conductivities orders of magnitude higher than either component. This seems to be due in good part to a lessened activation energy.

Lyons and Fox have pointed out that for intrinsic conduction, only ionized exciton states of an organic crystal may be involved, since these are the only ones which can be markedly affected by an electric field. Lyons hypothesizes that an ionized exciton migrates to a trap, where the trapping energy leads to dissociation. Fox, however, shows that the energetics of the lowest conducting state are such that conduction in organic crystals might often be intrinsic. In both pictures, a major factor is the polarization energy of an isolated charge in a crystalline lattice. To examine these questions, the ionic energy levels in a hypothetical, ideal crystal of a charge-transfer complex is considered, using Lyon's approach. Limitations of the applicability of the arguments are pointed out.

67. POLARONS IN MOLECULAR CRYSTALS [ABSTRACT]

Siebrand, W.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 56–60
National Research Council, Ottawa, Canada, 1962

In conventional band theory the electronic overlap term of the total Hamiltonian is considered in zeroth order, producing Bloch-type energy bands, whereas the interaction of the conducting electrons (or holes) with nuclear vibrations is treated as a perturbation giving rise to scattering. In narrow band-type semiconductors, such as molecular crystals, the order in which these terms have to be taken into account may be reversed. The electron–phonon interaction then will lead to formation of polarons, i.e., electrons in self-induced potential wells, and the electronic overlap will produce polaron bands corresponding to the motion of a polaron as a whole. In this note recent developments in polaron theory are applied in a qualitative way to molecular crystals.

68. TECHNIQUES AND INTERPRETATION OF TRANSIENT MEASUREMENTS [ABSTRACT]

Mark, P.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 75–79
National Research Council, Ottawa, Canada, 1962

The salient features of SCL current transients in insulators, first reported independently by Many, et al., and by Helfrich and Mark, are illustrated. At $t = 0$ (it is assumed that the applied voltage rises instantaneously to its steady state value), the injected space charge resides on the surface of the crystal viewed as a capacitor. As t increases, the crystal begins to fill with space charge, located behind a well-defined carrier front which advances through the crystal from the injecting electrode by the action of the applied field. As the crystal fills with space-charge, its capacitance increases with time. This also causes the current to increase until the carrier front arrives at the exit electrode (which may be either ohmic or blocking) at the time $t_o = 0.786\ t_r$ ($t_r = d^2/\mu v$, the uniform field transit time): t_o is less than t_r because the average field seen by the carrier front as it traverses the crystal is always greater than the uniform field v/d. A cusp appears in the current at t_o because at t_o the space charge in the crystal is concentrated near the exit electrode, while in the steady state it is concentrated near the injecting electrode. As t increases beyond t_o, the redistribution of the injected space-charge causes the current to decay from the cusp to its lower steady state value. The exact shape of the transient in the interval $0 \leqslant t \leqslant t_o$ can be obtained analytically and has the form

$$j(t) = 0.445\ j_{ss}\left[1 - \frac{t}{2t_r}\right]^{-2} (\text{amp/m}^2).$$

For $t > t_o$, numerical methods are required to calculate the decay to the steady state.

69. ELECTRON-LATTICE INTERACTIONS IN ORGANIC SEMICONDUCTORS [ABSTRACT]

Glarum, S. H.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 84–89
National Research Council, Ottawa, Canada, 1962

To assess the potential of organic materials for semiconductor applications it is necessary to know their carrier mobility characteristics. In an electric field mobile charges drift through a lattice, and a steady state is reached in which the potential energy gained by these charges is converted into lattice vibrational energy. Any *a priori* calculation of drift mobilities must take into account the electronic and vibrational states of the lattice, as well as their interactions. At present, information concerning the properties of organic lattices is so limited that such a calculation is not practical, and to approach the problem theoretically oversimplified models are needed.

As limiting cases of carrier motion, two models are usually considered—a band (delocalized) model and a hopping (localized) model. In the former case one visualizes carriers as traveling in a wave-like fashion, traversing many lattice sites before being scattered, while in the latter case carriers are envisioned as hopping in a random fashion from molecule to molecule. The purpose of this discussion is to investigate charge mobilities in both cases in terms of existing semiconductor theory under conditions expected to occur in organic molecular crystals. What may be expected from organic semiconductors in the way of high carrier mobilities? Most favorable conditions arise when bands are wide and the lattice is isotropic. Even then, however, it is difficult to conceive of situations where the mobility exceeds 10–30 cm²/v/sec, provided the tight-binding approximation holds.

One objection to this conclusion might be that the arguments presented have assumed a simple lattice of translationally equivalent molecules rather than a real lattice structure. In the latter case it is possible to find configurations which give much smaller effective masses at band edges, and therefore a mobility higher than that to be expected for a simple lattice. In organic molecular lattices, however, these advantages are small, for the deformation potential is inversely proportional to the effective mass. This effect, combined with the effects of lattice anisotropy, suggests that little is to be gained in seeking favorable lattice structures. It should also be remembered that in this band model, multiphonon processes, vibrational modulations of localized site energies, defect and impurity scattering, and librational lattice modes have been ignored—all factors which may be important, and which will further reduce the mobility below that calculated. Unless it can be shown that bandwidths in the ev region may occur in organic crystals, so that the tight-binding approximation is no longer adequate, the conclusions as to the magnitude of electron mobilities in organic semiconductors are probably correct.

70. THE PHYSICAL SIGNIFICANCE OF THE ACTIVATION ENERGY FOR CONDUCTANCE IN AROMATIC HYDROCARBONS [ABSTRACT]

Forster, E. O.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 125–127
National Research Council, Ottawa, Canada, 1962

The activation energy E as obtained from the change of conductance with temperature has been used as an important parameter in elucidating the conduction mechanism of organic substances. No satisfactory explanation has been advanced to account for the fact that the value of E does not change monotonically with increasing size of the aromatic molecules. To elucidate this problem, available data for E (using the form $\exp(-E/kT)$) have been compared with such molecular parameters as resonance energy, (RE), and energy values (E^*) for the transition from the ground state to the lowest excited state (${}^3E_1$) (both for solutions of the respective molecule in nonpolar solvents and for the solid material). These quantities are compared for a series of linear polyacenes, and a similar comparison is also made for compounds derived from naphthalene. Included are values of E_r, a predicted activation energy which was calculated from the empirical relation $E_r = 0.067\ p$, where p is the number of peripheral π-electrons, and 0.067 is a constant selected so as to fit the experimental data for benzene. The existence is suggested of two basic conduction mechanisms in aromatic molecules. One mechanism, applicable to polyacenes with less than 18 peripheral π-electrons, involves the injection of an electron at the cathode. The second mechanism, applicable to polyacenes having more than 18 peripheral π-electrons, involves the intrinsic formation of charge carriers, a possibility already considered by Fox. For molecules with 18 peripheral π-electrons, either mechanism can dominate or both can operate simultaneously.

71. MOLIONIC LATTICES [ABSTRACT]

Pott, G. T., Kommandeur, J.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," p. 169
National Research Council, Ottawa, Canada, 1962

In most cases the conductivity observed in solid organic and semi-organic donor-acceptor complexes is accompanied by a strong electron spin resonance signal. In some cases the number of spins is temperature dependent; in others it is not. In all cases a temperature independent number of spins is found below a certain temperature.

To explain this phenomenon it is supposed that at 0°K the crystal lattice of the complexes is built up of ions and neutral molecules in such a fashion that the lattice energy is a minimum. By calculations it is concluded that such a minimum is possible. For other arrangements the lattice energy will be slightly higher. Then, at normal temperatures there will be a statistical distribution over the several states of the lattice, which under certain conditions will lead to conductivity. At low temperatures the whole lattice is in the lowest state and a constant number of spins is expected. If the energy differences between the various states of the lattice are large, there will be no temperature dependence of the number of spins.

72. THE TEMPERATURE DEPENDENCE AND ACTIVATION ENERGY OF ELECTRICAL CONDUCTION IN HIGH POLYMERS

Warfield, R. W., Petree, M. C.
September 19, 1958
Naval Ordnance Laboratory, White Oak, Md.
NAVORD R-6246
(Also available as OTS: PB-145,826, U.S. Dept. of Commerce, Office of Technical Services, Washington, D.C.)

The temperature dependence of the electrical resistivity of a number of high polymers has been determined. By means of an Arrhenius plot, the activation energy for the conduction process in these polymers has been calculated, and the results have been interpreted in terms of an ionic diffusion process. The activation energy for the conduction process appears to be a very sensitive index of the extent of polymerization.

73. ELECTRONIC PROPERTIES OF IMIDAZOLE

Aftergut, S., Brown, G. P.
***Nature*, v. 191, no. 4786, pp. 379–380, July 22, 1961**

An energy gap of 2.6 ev was obtained for imidazole using the equation $\rho = \rho_0 \exp(E/2kT)$. This value was compared with an estimated value of 5 ev for benzene, and it was concluded that the hydrogen bonding of imidazole affects the semiconduction. (*PA*, 1961, #17,745)

74. ELECTRONIC PROPERTIES OF GRAPHITE AND ITS CRYSTAL COMPOUNDS IN THE DIRECTION OF THE *c*-AXIS

Ubbelohde, A. R.
In "Proceedings of the 5th Conference on Carbon, Pennsylvania State University, University Park, June 19–23, 1961," Volume I, pp. 1–7
Pergamon Press, Ltd., London, England, and The Macmillan Co., New York, N.Y., 1962

Band theory can now be used to give a fairly satisfactory account of electronic properties of graphite and of its crystal compounds in the direction of the *a*-axis but, as yet, yields a much less complete account of corresponding properties in the direction of the *c*-axis. Important information includes the resistivity and thermoelectric power of various graphites, and of crystal compounds derived from them.

For near-ideal graphites, the thermoelectric power shows a large anisotropy numerically, and also has opposite signs in the direction of the *c*- and *a*-axes. Formation of crystal compounds either with electron donors or electron acceptors suppresses the difference in sign, and generally reduces the numerical anisotropy. Changes in resistivity and in its temperature coefficient give additional information. Traps and scattering effects may function anisotropically, for transport of charge in the direction of the *a*-axis and *c*-axis.

75. THEORY OF THE ELECTRON TRANSPORT PROPERTIES OF SINGLE-CRYSTALLINE GRAPHITE

McClure, J. W., Smith, L. B.
In "Proceedings of the 5th Conference on Carbon, Pennsylvania State University, University Park, June 19–23, 1961," Volume II, pp. 3–10
Pergamon Press, Ltd., London, England, and The Macmillan Co., New York, N.Y., 1963

Calculations, expressed as functions of the temperature and impurity content, are presented for the electrical resistivity, magnetoresistance, Hall effect, and thermoelectric power of graphite single crystals.

76. THEORY OF TRANSIENT SPACE-CHARGE-LIMITED CURRENTS IN SOLIDS IN THE PRESENCE OF TRAPPING

Many, A., Rakavy, G.
***Physical Review*, v. 126, no. 6, pp. 1980–1988, June 15, 1962**

The problem of transient space-charge-limited currents in insulating and conducting crystals is treated mathematically. With a number of simplifying assumptions, solutions are derived for the time-dependent current and space-charge distribution following the onset of injection, the latter taking place via an ohmic contact under an applied voltage-pulse. Exact analytical solutions are given for the two limiting cases of no trapping and fast trapping. For flow in an insulator under slow trapping, approximate expressions are derived which are valid for trapping times larger than twice the transit time. For shorter trapping times the equations of flow are solved numerically and the solutions presented in graphical form.

77. ELECTRICAL CONDUCTIVITY OF GRAPHITE

Sugihara, K., Sato, H.
***Physical Society of Japan, Journal of the*, v. 18, no. 3, pp. 332–341, March 1963**

Theoretical calculations are given for the electrical conductivity of graphite in the hexagonal layer planes. The resistivity increases with temperatures as $T^{1.2}$ between 25 and 77°K. In the long wavelength limit, the lattice vibrations of graphite are approximately grouped into two modes, polarization being in the layer plane in mode 1, and parallel to the c-axis in mode 2.

Contributions to the relaxation process due to the scattering of carriers by the two modes are comparable in order of magnitudes. The ratio of the electron-phonon coupling constants which gives the best agreement to the temperature dependence of the observed conductivity has been found to be $C_1 . C_2 = 6:1$, where C_i denotes the coupling constant between carriers and the i-th mode phonons.

The Hall coefficient is strongly field-dependent and the present theory could not explain the positive sign of the Hall coefficient in the low field limit. Thus, in discussing the Hall coefficient a more refined theory seems to be necessary.

78. DIRECT STRUCTURAL EVIDENCE FOR WEAK CHARGE-TRANSFER BONDS IN SOLIDS CONTAINING CHEMICALLY SATURATED MOLECULES

Hassel, O., Roemming, C.
***Quarterly Reviews*, London, v. 16, no. 1, pp. 1–18, 1962**

In order to be able to draw advantage from the more direct interferometric methods, particularly those with X-rays or neutron beams, it was felt that crystal structure analyses should be carried out on solid addition compounds expected to exhibit weak charge-transfer bonds. Since 1954 a number of papers dealing with compounds corresponding to "loose" complexes have appeared, and the aim of this article is to sum up the results so far obtained regarding the atomic arrangements in the solid state and to discuss their significance for the charge-transfer bond.

79. DONOR-ACCEPTOR INTERACTION

McGlynn, S. P.
***Radiation Research*, Supplement 2, pp. 300–323, 1960**
(Proceedings of Bioenergetics Symposium, Brookhaven National Laboratory, Upton, N.Y., October 12–16, 1959, sponsored by the U.S. Atomic Energy Commission)

This work has as its main purpose the delineation of those properties of donor-acceptor complexes which would seem to be of importance to the biochemist and biophysicist. Limitations of space, however, have made necessary the omission of any explicit discussion of infrared and Raman spectra, dipole moments, magnetic susceptibility, adsorption, self-complexes, metallic π-complexes of unsaturates, and the spectrophotometric determination of equilibrium constants.

Besides the introduction, the following sections are included: Basis of Electron Donor-Acceptor Interactions (with both intramolecular and intermolecular donor-acceptor interaction); Charge-Transfer Transition (with energy, solvent effects, polarization, intensity, and pressure effects included); Energy and Charge Transport in Donor-Acceptor Complexes; Possible Biological Importance of Charge-Transfer Complexes; and Effect of Complexing on Reaction Rates. Several pages of references follow the text.

80. TRANSFER MECHANISMS OF ELECTRONIC EXCITATION ENERGY

Förster, Th.
***Radiation Research*, Supplement 2, pp. 326–339, 1960**
(Proceedings of Bioenergetics Symposium, Brookhaven National Laboratory, Upton, N.Y., October 12–16, 1959, sponsored by the U.S. Atomic Energy Commission)

The following sections are included: Experiments on Energy Transfer in Biological Systems; Possible Transfer Mechanisms; General Principles of Resonance Transfer; Theory of Slow Resonance Transfer; and Resonance Transfer in Proteins.

81. ENERGY MIGRATION IN AGGREGATED PIGMENT SYSTEMS AND BIOLOGICAL ENERGY CONVERSION

Tollin, G.
***Radiation Research*, Supplement 2, pp. 387–406, 1960**
(Proceedings of Bioenergetics Symposium, Brookhaven National Laboratory, Upton, N.Y., October 12–16, 1959, sponsored by the U.S. Atomic Energy Commission)

Sections of the report follow: Introduction; Energy Migration by Exciton Transfer; Energy Migration by Charge-Carrier Motion; Energy Conversion in Photosynthesis; and Problems for the Future.

82. **ROLE OF ELECTRON AND EXCITON TRANSFER IN CARCINOGENESIS**
Mason, R.
***Radiation Research*, Supplement 2, pp. 452–461, 1960**
(Proceedings of Bioenergetics Symposium, Brookhaven National Laboratory, Upton, N.Y., October 12–16, 1959, sponsored by the U.S. Atomic Energy Commission)

83. **A MOLECULAR THEORY OF ELECTROMAGNETIC WAVE PROPAGATION IN TWO-COMPONENT ANISOTROPIC POLYMER SYSTEMS**
Bullough, R. K.
***Royal Society of London, Philosophical Transactions of the, Series A—Mathematical and Physical Sciences*, v. 254, no. 1044, pp. 397–440, 1962**

The principal refractive indices of such a system are calculated and given explicitly in terms of generalized radial distribution functions. The several electric fields within the system are analyzed. (*PA*, 1962, #4116)

84. **THE ELECTRICAL CONDUCTIVITY OF DRY CYTOCHROME C: EVIDENCE FOR IONIC CONDUCTION [ABSTRACT]**
Taylor, C. P. S.
In "International Biophysics Congress, 1961. Abstracts of Contributed Papers," pp. 214–215
Tryckeri Aktiebolaget Thule, Stockholm, Sweden, 1961

85. **THE SO-CALLED "COMPENSATORY EFFECT" IN ORGANIC SEMICONDUCTORS**
Airapetyants, A. V., Voitenko, R. M., Davydov, B. E. Serebryanikov, V. S.
***Vysokomolekulyarnye Soedineniya*, v. 3, no. 12, p. 1876, 1961**
(Translated from the Russian in *Polymer Science U.S.S.R.*, v. 3, no. 6, pp. 1148–1149, 1962; published May 1963)

The dependence of the energy of activation E on σ_0, as displayed in the diagram, shows that for the materials used energy of activation does not rise with the increase of σ_0, as it did with Talroze and Blyumenfeld, but decreases; i.e., there occurs the same type of dependence of E on σ_0 as is found with normal non-organic semiconductors.

86. **ELECTROCONDUCTIVITY OF POLYMERS—VI. CALCULATION OF SPECIFIC CONDUCTIVITIES IN THE REGION OF DIPOLE-RADICAL POLARIZATION**
Sazhin, B. I., Filippovich, D. S.
***Vysokomolekulyarnye Soedineniya*, v. 5, no. 8, pp. 1207–1212, August 1963**

Formulas have been derived permitting calculation of the dependence of the specific cubical resistance upon the temperature and time of holding the specimen under tension in the region of appearance of dipole-radical polarization. Experimental tests have shown that such calculations can be used for assessing the value of ρ_v at comparatively low temperatures from the dipole-radical polarization data obtained in alternating fields.

87. **STATES WITH CHARGE TRANSFER IN ORGANIC SYSTEMS**
Blyumenfeld, L. A., Benderskii, V. A.
***Zhurnal Strukturnoi Khimii*, v. 4, no. 3, pp. 405–414, 1963**

88. **STATES WITH CHARGE TRANSFER IN ORGANIC SYSTEMS. TRANSFER EXCITONS AND CONDUCTANCE ELECTRONS IN MOLECULAR CRYSTALS**
Benderskii, V. A.
***Zhurnal Strukturnoi Khimii*, v. 4, no. 3, pp. 415–424, 1963**

EXPERIMENT

89. **SEMICONDUCTOR PROPERTIES OF ORGANIC MOLECULAR COMPLEXES**
Labes, M., Sehr, R., Bose, M.
In "Proceedings of the International Conference on Semiconductor Physics, Prague, August 29–September 2, 1960," pp. 850–853
Academic Press, Inc., New York, N.Y., and London, England, 1961

For a large number of solid molecular complexes, resistivities lower than those normally expected for organic materials were observed; for eight representative materials, resistivities and Seebeck coefficients as functions of temperature, and unpaired spin concentrations were measured. The validity of the electrical measurements, performed on compressed microcrystalline material is substantiated by their agreement with values obtained in the first case of single crystal measurements on a molecular complex to be reported. (*PA*, 1962, #23,305)

90. **PHOTOCONDUCTIVITY AND SEMICONDUCTIVITY OF THE KEYNON-BANFIELD RADICAL**
Chojnacki, H.
***Acta Physiologica Polonica*, v. 21, no. 4, pp. 359–363, 1962**
(in English)

The surface conductivity of crystals of the Keynon–Banfield radical was measured in the dark and after UV illumination. Dark conductivity rose exponentially with the temperature, the "activation energy" ranging from 1.0 to 1.7 ev. After illumination, a slow rise in conductivity was observed, probably related to the formation of an unstable intermediate in the course of photooxidation. The absorption spectrum of the

Keynon–Benfield radical in methanol solution is also given. (*PA*, 1962, #14,584)

91. ELECTRICAL CONDUCTIVITY OF CHELATE POLYMERS

Terentev, A. P., Rode, V. V., Rukhadze, E. G.,
Vozzhennikov, V. M., Zvonkova, Z. V., Badzhadze, L. I.
***Akademiya Nauk SSSR, Doklady*, v. 140, no. 5,**
pp. 1093–1095, October 11, 1961

The conductivities and activation energies were obtained for several metal chelate polymers found by treating organics with metal acetates. In all, 48 products were examined. Polychelates of Cu have the highest conductivity and those containing *p*-tolyl or diphenyl groups have higher conductivity than do other analogs in which methylene chains are present. Activation energy rises and conductivity decreases in the series Co, Zn, and Ni. The polymer with Co containing an ethylene bridge shows enhanced conductivity and lowered activation energy of conductivity along with reduced magnetic moment (2.58) owing to the improved coplanarity of the chelate nodes; a compound of this type with Ni has higher conductivity and lower magnetic moment (1.11) than does a similar polymer with a diphenyl grouping (moment of 2.62). Ethylene bridges tend to favor square distribution of metal to S bonds. In products based on Cu, conductivity rises rapidly with temperature. In polychelates with rubeanic structures, the conductivity declines in the series Cu, Ni, Cd. In polychelates with Fe, the conductivity rises when metal to N or O bonds are established.

92. THE INFLUENCE OF THERMAL INTERACTION ON SYSTEMS CONSISTING OF POLYMERS AND DISPERSED METALS

Levina, S. D., Lobanova, K. P., Vannikov, A. V.
***Akademiya Nauk SSSR, Doklady*, v. 141, no. 3, pp. 622–624,**
November 21, 1961

Polymer-iron powder compositions were obtained by the method described by Kargin and Plate. All these compositions possess *p*-type conductivity. Fe-polyisobutylene was chosen for studying the structure of the polymer-layer current conductor, and the system Fe-polyethylene was studied analogously. Samples containing 10, 20, and 30% polymer were studied. By warming a sample with 30% *in vacuo* at 180–200°C, specific resistance of the sample was lowered to 2–4 ohm cm^{-1}, and the conductivity decreased as the temperature decreased. The curve log σ vs. $1/T$ resembles those of mixed semiconductors.

93. ELECTRODE BEHAVIOR OF HEAT-TREATED POLYACRYLONITRILE

Frumkin, A. N., Boguslavskii, L. I., Serebrennikov, V. S.
***Akademiya Nauk SSSR, Doklady*, v. 142, no. 4, pp. 878–880,**
February 1, 1962

The electrochemical behavior of heat-treated polyacrylonitrile, an organic semiconductor, was studied and compared with that of C obtained by carbonization of viscose. Samples under study were strands of several hundred threads 2–3 μ in diameter. The potentials in *N* H_2SO_4, in *N* NaOH, and in air were obtained. The activation energies of conductivity were determined on threads and correlated with the potential. A study of the difference between maxima and minima of the potentials (100 mv, corresponding to three orders of magnitude in terms of catalyzed reaction) may indicate some connection with the specificity of organic catalysts in biochemical systems.

94. THE ELECTRIC CONDUCTIVITY OF A POLYAMIDE MELT

Bushin, V. V., Dumanskii, I. A., Dumanskii, A. V.
***Akademiya Nauk SSSR, Doklady*, v. 143, no. 4, pp. 894–895,**
April 1, 1962

The electric conductivity of polycaprolactam was measured at 230–290°C in the absence of O. The samples, initially heated for 50 min at the given temperature to remove the moisture from the polymer, showed specific electric conductivity increases with temperature from 4 to 15 ohm^{-1} cm^{-1}. Gamma-irradiation of 0.3–1.2 Mrad did not increase the electric conductivity. The activation energy was 0.32–0.40 ev. The specific electric conductivity decreased slightly with time at constant temperature, explained by volatilization of the remaining H_2O as well as other low mol. wt. substances.

95. ELECTRIC CONDUCTIVITY AND ACTIVATION ENERGY OF DITHIO-OXAMIDE, *N*-SUBSTITUTED DITHIOCARBAMATE, AND THIOCYANATE (CU, CO, NI) POLYMERS

Vozzhennikov, V. M., Zvonkova, Z. V., Rukhadze, E. G.,
Zhdanov, G. S., Glushkova, V. P.
***Akademiya Nauk SSSR, Doklady*, v. 143, no. 5,**
pp. 1131–1134, April 11, 1962

The specific electric conductivity, σ, and the respective activation energy, *E*, of Cu, Ni, and Co chelates of dithiooxamide, *N*-substituted dithiocarbamate, and thiocyanate polymers were measured at 17–227°C. Results are presented and interpreted. The presence of π-electrons increases σ and lowers *E*. Values of σ and *E* of Cu SCN are also given.

96. THE SIGNIFICANCE OF CONJUGATION AND ORDERLINESS FOR THE SEMICONDUCTING PROPERTIES OF POLYMERS

Dulov, A. A., Slinkin, A. A., Liogonkii, B. I.,
Rubinshtein, A. M.
***Akademiya Nauk SSSR, Doklady*, v. 143, no. 6,**
pp. 1355–1357, April 21, 1962

Semiconducting properties of polymers of the type $Cl[C_6H_4(CH_2)_xC_6H_4]_m[N{:}NC_6H_4(CH_2)_xC_6H_4]_nCl$, where x is 0, 1, or 2, were investigated. Introduction of CH_2 groups between benzene rings, although the degree of conjugation along the chains is reduced, does not diminish the semiconducting character of polymers, as shown by activation energies of electric conductivity between 120 and 250°C. Methylene bridges, increasing the stiffness of macromolecular chains and contributing to denser packing of macromolecules, facilitate electron interactions between individual chains. With lengthening CH_2 bridges, the degree of crystallinity is increased as shown by irreversible conductivity changes on heating the polymers. Polymers with $x = 0$ have the loosest chain packing and, therefore, the irreversible changes of their conductivity on heating are greatest. All of these polymers show relaxation polarization due to translocation of charged segments of polymer chains in the electrostatic field.

97. ELECTRIC AND PARAMAGNETIC PROPERTIES OF PRODUCTS OF THE RADIATION THERMAL TREATMENT OF POLYETHYLENE

Bakh, N. A., Bityukov, V. D., Vannikov, A. V., Grishina, A. D.
***Akademiya Nauk SSSR, Doklady*, v. 144, no. 1, pp. 135–138,**
May 1, 1962

A study is reported of progressive transformation of a dielectric linear polymer (under radiation-thermal treatment) into semiconductor material. Nonevacuated and evacuated samples of high-pressure polyethylene were irradiated with 7.2×10^{23}, 4.3×10^{23}, and 1.5×10^{24} ev/g at 60°C. Thermal treatment at up to [illegible]°C followed irradiation. The following electro-physical properties of the products were investigated: conductivity (δ) in constant and alternating fields, activation energy (ΔE), thermoelectric power, and structural properties by electron paramagnetic resonance (EPR) spectra. The value of δ increases monotonically from 10^{-16}, for a sample that had not been thermally treated, to 10^{-1} ohm-cm^{-1}, for a sample treated at 800°C. An increased radiation dose yields samples more vulnerable to thermal treatment. Temperature dependence of δ between −25°C and +150°C follows the relation $\delta = \delta_0 \exp(-\Delta E/2KT)$, with constant ΔE for each sample. The value of ΔE changes adiabatically with changes of δ as a function of the temperature of thermal treatment. Thermoelectric power is 250–254 μv/°C for samples thermally treated at 620–930°C with p-type conductivity in all cases. In the presence of O, δ and thermoelectric power are greater and ΔE is smaller than for evacuated samples, these differences exist only below certain temperatures, above which both evacuated and nonevacuated samples are identical. All effects of O are reversible. Structural changes which produce an increase of δ (constant field) by a factor of 10^{15} are shown by changes of specific resistance with frequency. EPR spectra of irradiated, thermally treated and untreated samples consist of a single line, the intensity, width, and form of which [illegible]. The concentration of paramagnetic centers for samples treated at <600°C is the same in the presence and absence of O and increases with the irradiation dose. Below 600°C, 90 and 100% losses occur for samples treated at 720 and 820°C, respectively, in the presence of O. Molecular O increases the line width in EPR spectra without changing the number of paramagnetic centers, affects other factors and blocks paramagnetic centers in treated samples at >600°C. Further studies are necessary to correlate these effects with changes of δ and thermoelectric power due to O.

98. THE TEMPERATURE DEPENDENCE OF THE ELECTRICAL RESISTANCE OF POLYCRYSTALLINE GRAPHITE AT PRESSURES UP TO 250,000 kg/cm^2

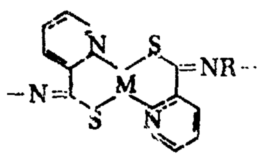
Semerchan, A. A., Kuzin, N. N., Vereshchagin, L. F.
***Akademiya Nauk SSSR, Doklady*, v. 146, no. 4, pp. 803–804,**
October 1, 1962
(Translated from the Russian in *Soviet Physics—Doklady*,
7, no. 10, pp. 901–902, April 1963)

It was of interest to investigate the temperature dependence of the electrical resistance of graphite at high pressures. The investigated material was spectrally pure polycrystalline graphite with a resistivity $\rho = 26 \times 10^{-4}$ ohm-cm. The resistance at temperatures from 20–200°C was measured at pressures of 30,000, 80,000, 140,000, 200,000, and 250,000 kg/cm^2. Resistivity decreased with increased temperature, and the values correlated well with other published data.

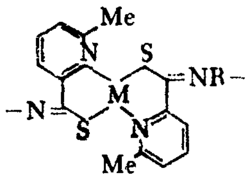
99. ELECTRIC CONDUCTIVITY AND ACTIVATION ENERGY OF CHELATE COMPOUNDS OF DITHIOCARBAMATES AND THIOAMIDES OF PYRIDINE DERIVATIVES

Terentev, A. P., Rukhadze, E. G., Vozzhennikov, V. M., Zvonkova, Z. V., Oboladze, N. S., Mochalina, I. G.
***Akademiya Nauk SSSR, Doklady*, v. 147, no. 5,**
pp. 1094–1097, December 11, 1962

The conductivity of chelated polymers having I, II, and III units, with R = 4,4′-biphenylylene, 3,3′-dimethyl-4,4′-biphenylylene, and 3,3′-dimethoxy-4,4′-biphenylylene groups and M = Cu, Co, or Zn, was determined at 383°K. The values of conductivity were in the range 10^{-10} to 10^{-13} ohm^{-1} cm^{-1}. Temperature coefficients of these polymers with respect to conductivity indicated activation energies of 1.28–5.2 ev. The maximum values were for these substances free of metal atoms. The general level of conductivity depends on M and follows the declining series Cu, Co, Zn.



(I)



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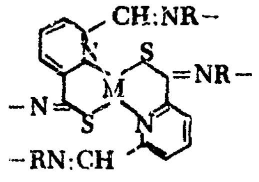


(III)

100. CONDUCTIVITY OF FILMS OF A POLYMERIC COMPLEX FORMED BY TETRACYANOETHYLENE WITH SOME METALS

Boguslavskii, L. I., Stilbans, L. S.
***Akademiya Nauk SSSR, Doklady*, v. 147, no. 5,**
pp. 1114–1117, December 11, 1962

The dependence of the electric resistance of a polymeric film deposited on Fe and Al was studied as a function of the frequency and the established potentials at different temperatures. A mathematic expression is proposed to calculate the variation of the conductivity activation energy. The dependence of the specific resistance of the film on Al as a function of the reciprocal temperature was investigated for the frequency limits 20 to 2×10^7 cps; the activation energy decreases up to 7×10^4 cps. The observed activation energy increase stated for a frequency of 5×10^4 cps is explained. The adopted model departs from an assumption that the film is formed by at least two kinds of polymeric structure.

101. MECHANISM OF CONDUCTIVITY IN ORGANIC SEMICONDUCTOR POLYMERS

Airapetyants, A. V., Voitenko, R. M., Davydov, B. E., Krentsel, B. A.
***Akademiya Nauk SSSR, Doklady*, v. 146, no. 3, pp. 605–608, January 21, 1963**

Graphs are presented showing the conductivity–temperature relation in polyacrylonitrile samples in vacuum and annealed at 580–700°C (with and without heating–cooling cycles), and showing the thermo-EMF produced in polymer fibers with such heat treatment. Preliminary heating to 420°C produced conductance three times as great in the polymer annealed at 730°C and ten times as great in that annealed at 520°C; all specimens, except that annealed at 730°C, showed inversion of sign for thermo-EMF and specimens with hole conductance became electronic conductors. (Another cycle treatment to 420°C again reversed the thermo-EMF sign.) Mobility of current carriers was of the order 1.3×10^{-3} $cm^2/v/sec$; heat treatment variation changed mobility.

102. COMPENSATION EFFECT FOR THE ELECTRICAL CONDUCTIVITY OF CRYSTALLINE DIELECTRIC POLYMERS

Sazhin, B. I., Podosenova, N. G.
***Akademiya Nauk SSSR, Doklady*, v. 148, no. 3, pp. 627–629, January 21, 1963**

The effect of temperature on electrical conductivity (with subsequent determination of σ_0 and change of E) was studied for crystalline poly(ethylene terephthalate), poly(trifluorochloroethylene), and poly[bis(chloromethyl)oxacyclobutane]. Conductivity above T_g increases by a factor of 10–1000 when degree of crystallinity increases from 10 to 50%. The activation energy is shown to be equal to $0.7 \log \sigma_0 - 21$.

103. THE RECTIFYING EFFECT IN ORGANIC SEMICONDUCTORS

Vannikov, A. V.
***Akademiya Nauk SSSR, Doklady*, v. 152, no. 4, pp. 905–907, October 1, 1963**

104. TEMPERATURE DEPENDENCE OF THE X-RAY LUMINESCENCE AND DARK CONDUCTIVITY OF YAKUTSK DIAMONDS

Pogodaev, K. N., Vilutis, E. S.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*,**
v. 25, no. 3, pp. 373–375, 1961
(Paper presented at the Ninth Conference on Luminescence —Entry #498; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 25, no. 3, pp. 364–365, March 1961)

Data are reported for diamond twin crystals from Yakutsk. Measurements are given for the dependence of the electric conductivity on temperature. Both unexcited diamond and diamond irradiated with X-rays were studied in the temperature range 50 to 350°C. Above 220°C, the temperature dependence of the conductivity was exponential. Current carrier activation energies were between 2.05 and 2.82 ev. In X-irradiated diamonds the conductivity increased substantially below 200°C, showing maxima at 180 and 110°C, but annealing to 350°C caused these to vanish. The evidence shows that the low-temperature conductivity is of n-type. The existence of two kinds of trapping level is inferred. (*PA*, 1962, #23,253)

105. ENERGY TRANSFER OF ELECTRON EXCITATION IN STABLE SOLUTIONS OF ORGANIC MATERIALS

Andreeshchev, E. A., Kilin, S. F., Rozman, I. M., Shirokov, V. I.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*,**
v. 27, no. 4, pp. 533–539, 1963

106. EFFECTS OF HIGH PRESSURE ON SOME ORGANIC SEMICONDUCTING POLYMER

Pohl, H. A., Henry, A. W., Rembaum, A.
American Chemical Society, Washington, D.C.
Paper 150, Division of Physical Chemistry, presented at the 141st Meeting, ACS, Chicago, Ill., March 20–29, 1962
(See also Entry #116)

It is shown that certain solid polymers exhibit semiconduction which is sensitive to applied pressure. The effect is rather large and quite reversible. Over a pressure range in which most metals double in conductivity (about 40,000 atm) these solids increase approximately 100-fold in conductivity. Part of the change is due to changes in the activation energy, part to changes in the mobility. A simple theoretical treatment of the effect is presented, based upon pressure effects on the intermolecular overlap of electron orbitals. The equations appear to fit the experimental observations.

107. RESISTIVITY STUDIES ON POLYMER SEMICONDUCTORS

Pohl, H. A., Gogos, C. G., Cappas, C.
American Chemical Society, Washington, D.C.
Paper 52, Division of Physical Chemistry, presented at the 142nd Meeting, ACS, Atlantic City, N.J., September 9–14, 1962
(See also Entry #190)

The class of polymers synthesizable from aromatic hydrocarbons and their derivatives and aromatic acids by polycondensation is outstanding in that the members are semiconducting and contain high concentrations of unpaired spins. The present study is directed at delineating the effects of synthesis variables upon the electronic characteristics. Eighteen polymers of this class were synthesized, varying degree and type of substitution on the monomeric portions, as well as catalyst, time, and temperature. The resistivities of the highly purified polymers were found to be sensitive to the conditions of synthesis and to temperature and pressure during resistance measurement. The thermal energy interval (analogous to the forbidden energy gap in single crystal semiconductors, E_g) ranged from 0.4 to 0.5 ev.

Although the formalism of the simple intrinsic semiconductor band model is not strictly applicable to data on these polymers, especially because of their low mobilities and lack of more than short range (*ca* 200 Å) order, such analysis was found instructive.

108. PIEZO-RESISTIVE CHARACTERISTICS OF SOME SEMICONDUCTING POLYMERS

Henry, A. W., Pohl, H. A.
American Chemical Society, Washington, D.C.
Paper 53, Division of Physical Chemistry, presented at the 142nd Meeting, ACS, Atlantic City, N.J., September 9–14, 1962

The piezo-resistive behavior of a series of highly conjugated polymers and of an elemental polymer (Te) was examined over a range of high pressures. The resistivities of the organic polymers, ranging from 10^2 to 10^{11} ohm-cm at room temperature and at 18,400 atm, decreased 100-, and for some polymers, 1000-fold as the pressure was increased to 35,000 atm. Elimination of voids and particle-to-particle contact problems was obtained by preconditioning at high temperature and pressure, as evidenced by (1) absence of hysteresis in the piezo-resistivity and (2) low measured permeation rate to gas.

A correlation between the extrapolated zero-pressure activation energy for the polyacene quinone radical polymers and the number of fused rings in the aromatic portion of the polymer was obtained, indicating a dependence of the conduction parameters upon molecular structure as predicted.

The elemental semiconductor in polymeric form (*p*-type tellurium) was observed to change from *p*- to *n*-type upon compression. Both the resistivity and thermoelectric power were observed to change markedly with pressure. It appears that the intrinsic energy gap is "compressible" to near zero values, while the impurity level gap remains relatively unaffected by pressure. This interpretation accounts for the observed transition in carrier type, as the mobility of the electrons is greater than that of the holes.

High piezo-resistive changes were also observed in several other types of polymers, namely, a Schiff's base polymer obtained by polycondensation of naphthaquinone and *p*-toluene diisocyanate, a polytetrachlorothiophenol, and an infinite order polymeric complex, prepared from pyrene and I_2. The highly conjugated monomeric material, nickel phthalocyanine, was also observed to show large piezo-resistive changes. The results were considered to show good agreement with the predictions based upon a theory built upon an absolute reaction rate formalism.

109. MOLECULAR STRUCTURE PARAMETERS IN CERTAIN SEMICONDUCTING POLYMERS

Kho, J. H. T., Cappas, C., Pohl, H. A.
American Chemical Society, Washington, D.C.
Paper 54, Division of Physical Chemistry, presented at the 142nd Meeting, ACS, Atlantic City, N.J., September 9–14, 1962

Three series of highly conjugated polyacene quinone radical polymers (PAQR) exhibiting semiconduction were synthesized and their electronic behavior was studied. The effect of the following variables on the electrical properties were examined: (1) hydrocarbon portion of the polymer, (2) acidic portion of the polymer, (3) copolymerization and mole ratio of starting monomers, (4) metallic salt formation, and (5) pressure and temperature.

Correlations between the structural parameters and the macroscopic properties were established. Room temperature resistivities were found to depend inversely on the number of fused aromatic rings of the monomer, on the ionization constant of the acidic monomer, on the square root of the external pressure, and directly on the energy interval (analogous to the conventional forbidden energy gap term) in all the PAQR polymers studied. Furthermore, the pressure coefficient of resistivity, the energy interval, and the resistivity at "infinite" temperature were observed to depend upon the size of the conjugated regions, expressed as the number of fused rings in the monomeric portion. The piezo-resistive coefficient varies directly as the observed energy interval. The concentration of unpaired electrons was observed to vary directly as the carrier concentration, exceeding it by several orders of magnitude. The spin concentration observed was inversely proportional to the resistivity of the PAQR polymers.

For the PAQR polymers studied, room temperature resistivities ranged from 10^2 to 10^{12} ohm-cm. The Seebeck coefficients ranged from 0.05 to 66 μv/°C and the spin concentrations from 10^{17} to 10^{19} cm^{-3}.

110. ELECTRONIC PROPERTIES AND STRUCTURE IN CONJUGATED POLYMERS

Pohl, H. A., Chartoff, R. P., Reinisch, R. F., Cappas, C.
American Chemical Society, Washington, D.C.
Paper 55, Division of Physical Chemistry, presented at the 142nd Meeting, ACS, Atlantic City, N.J., September 9–14, 1962

The relation between chemical structure and electronic properties for three classes of organic polymers containing extensively conjugated double bonds was studied. These included three linear polyalkynes, 11 wholly aromatic polybenzimidazoles, and several dozen polyacene quinone radical (PAQR) polymers.

The polyalkynes studied have high resistivities (*ca* 10^{13} ohm-cm), but relatively low thermal energy intervals (E_g) (*ca* 0.5 to 0.7 ev). The polybenzimidazoles had resistivities ranging from 10^{10} to 10^{16} ohm-cm, E_g's ranging from 1 to 3 ev, and no detectable electron spin resonance. This can be interpreted as due to the large amount of low molecular weight material in the molecular weight distribution curve, diluting the effects of the *eka*-conjugated molecules of higher molecular weight. The PAQR polymers studied here have properties typical of this class, with resistivities ranging from 10^4 to 10^{11} ohm-cm, E_g's ranging from 0.35 to 0.8 ev, sharp electron spin resonance spectra, and high concentrations of unpaired electrons, low carrier mobilities, positive Seebeck coefficients indicating dominance of *p*-type carriers, and high piezoresistive coefficients.

As structure is varied, spin concentration clearly parallels conductivity, although exceeding carrier concentration, usually by order of magnitude. A linear relation between the thermal energy interval, E_g, and the log of the extrapolated resistivity at "infinite" temperature, σ_0, is well obeyed, except for the most conductive polymers.

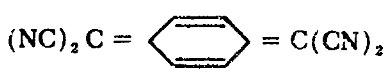
Infrared spectra taken, using a KBr pellet technique, showed one polymer (PAQR) made from phenol and phthalic anhydride to have phthalide groups linked in highly extended conjugation forming the repeating groups. Polymers with similar chemical structure have similar electronic properties.

The wide range of electronic properties observed in these polymers lends support to the view that highly conjugated molecules can exist partially in the form of biradicals and internal ionic states, characteristic of the electronically excited states of *eka*-conjugated molecules, and that the enhanced electronic behavior of these materials is directly related to the observable electron spin resonance.

111 ELECTRONIC CONDUCTION AND EXCHANGE INTERACTION IN A NEW CLASS OF CONDUCTIVE ORGANIC SOLIDS

Kepler, R. G.
American Chemical Society, Washington, D.C.
Paper 26, Division of Polymer Chemistry, presented at the 144th Meeting, ACS, Los Angeles, Calif., March 31–April 5, 1963

Salts of tetracyanoquinodimethane (TCNQ)



are found to exhibit high electronic conductivity. The salts which exhibit the highest conductivity, on the order of 100 $\text{ohm}^{-1}\,\text{cm}^{-1}$, also exhibit a paramagnetic contribution to their magnetic susceptibility which is independent of temperature, whereas the salts with conductivity lower than about 1 $\text{ohm}^{-1}\,\text{cm}^{-1}$ exhibit a paramagnetic contribution to their susceptibility given by

$$\chi_p = (2g^2\beta^2N/3kT)\,[1 + \tfrac{1}{3}\exp(J/kT)]^{-1}.$$

These results are interpreted as meaning that in the higher conductivity materials the electrons of the TCNQ ion radicals form a degenerate system such as that in a metal, while in the less conductive materials these same electrons are paired in quasi-molecular states, each having a triplet state lying an energy J above a singlet ground state. The electronic properties of the higher conductivity materials are consistent with the hypothesis of metallic character. Their conductivity is large and relatively independent of temperature, and they exhibit relatively low thermoelectric powers. In the less conductive salts the conductivity varies exponentially with temperature and the thermoelectric power is large relative to values observed in metals and semi-metals.

112. DONOR-ACCEPTOR COMPLEXING AND CONDUCTIVITY

Labes, M. M.
American Chemical Society, Washington, D.C.
Paper 27, Division of Polymer Chemistry, presented at the 144th Meeting, ACS, Los Angeles, Calif., March 31–April 5, 1963

For a large number of solid organic complexes, conductivities higher than those normally expected for organic materials have been observed. Extensive studies of the conductivity and its activation energy, of the Seebeck coefficient, and of magnetic properties of these interesting solids have been made in the last few years and will be reviewed.

Most of the measurements have been made on compacted microcrystalline material. However, utilizing micromanipulative techniques, measurements have been performed on tiny single crystals, and these results will be compared with previous measurements on compacts. A discussion of this relationship or lack thereof of crystal structure, chemical structure, magnetic properties, and electronic properties will be presented.

When one allows a gas to come in contact with an organic crystal with which it may interact in a donor-acceptor sense, pronounced effects on the bulk conductivity of that crystal occur. Thus, 10^{-1} mm Hg of iodine enhances the dark conductivity of anthracene from 30- to 175-fold, depending on whether the electrodes are attached perpendicular or parallel to the *ab* plane; ammonia and alkylamines increase the bulk dark conductivity of a chloranil single crystal. These effects are rapid and reversible and will be discussed in terms of surface complexing leading to carrier injection into organic crystals.

113. ELECTRONIC CONDUCTIVITY OF COMPLEXES OF POLY-*p*-PHENYLENE

Mainthia, S. B., Kronick, P. L., Ur, H., Chapman, E. F., Labes, M. M.
American Chemical Society, Washington, D.C.
Paper 28, Division of Polymer Chemistry, presented at the 144th Meeting, ACS, Los Angeles, Calif., March 31–April 5, 1963

Poly-*p*-phenylene forms a molecular complex with the electron acceptors iodine and tetracyanoethylene. Polymer-iodine complex samples, prepared both in solution and by exposing solid polymer to iodine vapor, have remarkable stability as compared to aromatic-hydrocarbon-iodine complexes reported earlier. The formula for the weight-average species in the iodine-saturated system is $[(C_6H_4)_4I_2]9\text{-}10$, the resistivity of which is 2.5×10^4 ohm-cm, lower than that of poly-*p*-phenylene by eleven decades and that of iodine by four decades. The activation energy for conduction is 0.87 ev. Poly-*p*-phenylene-iodine is believed to be the first reported example of a conducting complex involving a polymer.

It is likely that charge separation due to the donor-acceptor interaction plays a role in the conductivity, leading to some orbital overlap between molecules containing delocalized electrons.

114. ELECTRONIC CONDUCTIVITY IN ORGANIC MATERIALS

Pope, M.
American Chemical Society, Washington, D.C.
Paper 29, Division of Polymer Chemistry, presented at the 144th Meeting, ACS, Los Angeles, Calif., March 31–April 5, 1963

The prerequisites for conductivity are a supply of carriers and a mechanism for their transport through the given material. Among other ways, the carriers may be supplied by thermal ionization of the host material or they may be injected by the electrode. This work with different electrodes has emphasized the role of charge injection. Using evaporated metal electrodes on an anthracene crystal, saturation photocurrents can be driven through a crystal at sufficiently high fields. Using NaCl electrolyte electrodes, saturation photocurrent can be attained at 1/10 the field strength of the metal electrode configuration. Using iodine electrodes, large conductivity with light to which the crystal is transparent can be obtained; with Ce^{4+} electrodes, saturation currents may be reached in complete darkness. The differences in electrode behavior may be understood in terms of an energetic criterion for charge injection and an image force analysis of the same process.

In the presence of strongly absorbed light, anthracene will demonstrate a photovoltaic effect. If the electrodes are electrolytic, unusual chemical reactions accompany the flow of current.

At sufficiently high fields, both ac and dc, a large dark current can be produced in anthracene, accompanied by the emission of light (electroluminescence). The light is characteristic of the normal fluorescence of anthracene. The voltage dependence of the brightness is typical of an impact excitation mechanism.

The scale and variety of these phenomena warrant the close attention of those concerned with the interaction of organic solids with other substrates in the presence of additional energy such as light, and especially if electric fields are present.

115. ELECTRON-SPIN RESONANCE IN MOLECULAR COMPLEXES. I. ELECTRONIC SPLITTING AND HYPERFINE INTERACTIONS IN THE SOLID STATE

Bose, M., Labes, M. M.
***American Chemical Society, Journal of the*, v. 83, pp. 4505–4508, November 20, 1961**

The resolution of the ESR absorption of several amine-quinone complexes in the solid state establishes the existence of uncoupled spins as a rather general feature of these materials. Hyperfine structure has also been observed. A delineation and discussion of the respects in which amine–quinones differ from the paramagnetic hydrocarbon–halogen complexes is given. The relationship of ESR data to information regarding electronic conduction in the same materials is also discussed.

116. EFFECTS OF HIGH PRESSURE ON SOME ORGANIC SEMICONDUCTING POLYMERS

Pohl, H. A., Rembaum, A., Henry, A.
***American Chemical Society, Journal of the*, v. 84, no. 14, pp. 2699–2704, July 20, 1962**
(See also Entry #106)

Certain organic polymers are shown to possess a very high piezo-resistive coefficient. Compared to metals which change up to two-fold in a given pressure range, these materials change by a factor of 100-fold or more. The results are explained in terms of the easily compressible intermolecular distances and energy barriers for electron transfer. A more quantitative theory in terms of an absolute reaction rate formalism is presented.

117. PREPARATION AND ELECTRICAL CONDUCTIVITY OF COPPER TETRA-2,3-PYRIDINOPORPHYRAZINE AND COPPER TETRA-2,3-PYRAZINOPORPHYRAZINE

Danzig, M. J., Liang, C. Y., Passaglia, E.
***American Chemical Society, Journal of the*, v. 85, no. 6, pp. 668–671, March 20, 1963**

In order to relate semiconduction of organic substances to structure, copper tetra-2,3-porphyrazines were made containing pyridine and pyrazine rings. The measured resistivity of Cu phthalocyanine, Cu tetra-2,3-pyridinoporphyrazine, and Cu tetra-2,3-pyrazinoporphyrazine follows the equation $\rho = \rho_0 \exp(E_d/2kT)$, where ρ_0 is a constant and E_d is an activation energy. Values of E_d for the three substances are 1.3, 1.17, and 0.81 ev, respectively, and ρ_0 is the same for the three substances. It is deduced from these results that the mobility for the materials is an activated process. The photocurrents for these samples are proportional to the applied voltage at various temperatures.

118. EFFECT OF GASES ON THE CONDUCTIVITY OF ORGANIC SOLIDS. I. THE ANTHRACENE–IODINE INTERACTION

Labes, M. M., Rudyj, O. N.
***American Chemical Society, Journal of the*, v. 85, no. 14, pp. 2055–2059, July 20, 1963**

Although gases are generally thought to affect the surface conductivity of organic crystals alone, evidence is presented that the bulk dark conductivity of anthracene is increased in a sensitive, specific, and reversible manner upon exposure to iodine.

119. EFFECT OF GASES ON THE CONDUCTIVITY OF ORGANIC SOLIDS. II. THE *p*-CHLORANIL–AMINE INTERACTION

Reucroft, P. J., Rudyj, O. N., Labes, M. M.
***American Chemical Society, Journal of the*, v. 85, no. 14, pp. 2059–2062, July 20, 1963**

Ammonia and aliphatic amine vapors are shown to increase the bulk dark conductivity of *p*-chloranil single crystals. These data, when viewed in conjunction with previous results on the anthracene–iodine interaction, suggest that a rather general phenomenon exists—bulk conductivity of organic crystals being affected by donor-acceptor interaction at the surface.

120. LOW-RESISTANCE ORGANIC SEMICONDUCTOR

Kommandeur, J., Hall, F. R.
American Physical Society, New York, N.Y.
Paper R2, presented at the Thanksgiving Meeting of the American Physical Society, Case Institute of Technology, Cleveland, Ohio, November 27–28, 1959

Addition of iodine to the aromatic hydrocarbon pyrene results in a material of much lower resistivity than either one of the components by itself. The phase diagram of pyrene and iodine shows the existence of a metastable complex of composition 2 Py I_2, as well as a stable complex of composition Py 2 I_2. The latter material can also be prepared from solutions of the constituent components; pressed pellets have a specific resistivity of 75 ohm-cm at room temperature. From the temperature dependence, the activation energy for conduction is about 0.11 ev. A complex prepared of another aromatic hydrocarbon, perylene, and iodine, with the formula 2 Per 3 I_2 has a specific resistivity of 8 ohm-cm at room temperature with an activation energy of 0.016 ev. Single crystals of this material show the same general behavior as the pressed pellets. Since a Hall effect was not observed in either substance, an upper limit for the mobility of 0.01 $cm^2v^{-1}sec^{-1}$ was inferred. The carrier densities, therefore, must be at least $7 \times 10^{18} cm^{-3}$ and $8 \times 10^{19} cm^{-3}$ for the pyrene and perylene complexes, respectively.

121. ELECTRON SPIN RESONANCE IN SOME ORGANIC SEMICONDUCTORS

Singer, L., Kommandeur, J.
American Physical Society, New York, N.Y.
Paper R3, presented at the Thanksgiving Meeting of the American Physical Society, Case Institute of Technology, Cleveland, Ohio, November 27–28, 1959

Electron spin resonance measurements have been made on organic semiconducting complexes of pyrene and perylene with iodine. At room temperature, the spin concentration in the pyrene–iodine complex is about 10^{19} g^{-1}. The temperature dependence of the spin concentration is exponential with an activation energy close to that found for the electronic conduction. Furthermore, there is no anisotropy of the spin resonance in single crystals, and the spin-lattice relaxation time T_1 approximately equals the inverse line width T_2. These observations suggest that the spin resonance is due to charge carriers. At low temperatures the spin concentration becomes independent of temperature, T_1 becomes much larger than T_2, and the resonance of single crystals becomes anisotropic; these results indicate that some type of trapped spin is present.

122. ELECTRON CURRENT THROUGH THIN POLYMER FILMS

Perry, R. L.
American Physical Society, New York, N.Y.
Paper T3, presented at the Winter Meeting of the American Physical Society, California Institute of Technology, Pasadena, Calif., December 19–21, 1963

The current through films of silicone polymer with thicknesses of 190–425 Å has been measured as a function of voltage and temperature. The polymer films were formed by electron bombardment of a thin layer of silicone oil and the metal electrodes were evaporated silver films on a glass substrate. A dependence of the current on the temperature of the form $I = A \exp BT$ was found. The comparison of the data with theory is discussed.

123. E.S.R. STUDIES ON THE SEMI-CONDUCTOR THEORY OF FREE ELECTRONS IN LARGE ORGANIC MOLECULES

Allen, T., Ingram, D. J. E.
***Archives des Sciences*, v. 13, Special Number, pp. 219–223, 1960 (in English)**
(Paper presented at the Ninth Ampere Colloquium, Pisa, September 12–16, 1960 — Entry #501)

Electron spin resonance spectra of tyrosine, leucine, egg albumin, and mixtures of amino acids and proteins irradiated at 3600 A at 90 and 300°K were studied. In the first two cases there was no signal at 300°K. It appears that loosely bound water must be present for the energy level system of the protein to act as a semiconductor. (*PA*, 1961, #11,115)

124. ELECTRICAL CONDUCTIVITY AND PHOTOCONDUCTIVITY OF THIN ANTHRACENE LAYERS IN VACUUM

Gheorghita-Oancea, C.
***British Journal of Applied Physics*, v. 12, no. 10,**
pp. 579–580(L), October 1961

Electrical conductivity and photoconductivity measurements performed on thin evaporated layers of anthracene are discussed. In order to eliminate as much as possible the surface phenomena produced by air and water vapor adsorption, cells were prepared inside the vacuum system used for the electrical conductivity and photoconductivity measurements. It was found that the dark and photocurrents increase with increase of pressure. (SSA, #12,579)

125. A REVIEW OF RECENT INVESTIGATIONS INTO ELECTRICAL CONDUCTION AND BREAKDOWN OF DIELECTRIC LIQUIDS

Swan, D. W.
***British Journal of Applied Physics*, v. 13, no. 5, pp. 208–218,**
May 1962

Recent work concerning electrical breakdown and conduction in dielectric liquids is reviewed. Particular emphasis is given to liquids of simple molecular structure, although reference is made to some investigations using complex oils where the results obtained are also applicable to other liquids. Conduction measurements have been extended to fields up to 1.3 Mv cm^{-1} using microsecond pulse techniques, and under these conditions very large currents are observed. The evidence concerning a collision ionization process is conflicting. Negative ion mobility measurements have been reported for fields of 500 kv cm^{-1} in *n*-hexane, and both the positive and negative ion mobilities in superfluid liquid helium have been thoroughly investigated. Electrical breakdown of liquid argon has revealed pronounced electrode effects, and the influence of the anode is particularly emphasized. Dissolved oxygen is found to increase the strength of a liquid and to give rise to a number of effects which can be explained by assuming the formation of space charge layers at the electrodes. Recent measurements of formative and statistical time lags in *n*-hexane have shown that previous interpretations were frequently incorrect. 74 references. (*PA*, 1962, #11,383)

126. ELECTRICAL CONDUCTIVITY OF THIN ANTHRACENE FILMS

Gheorghita-Oancea, C., Teodorescu, G.
***Buletinul Institutului Politechnic Bucuresti*, v. 22, no. 3,**
pp. 13–18, July–September 1960 (in French)

The authors studied the electrical conductivity in vacuum of thin anthracene films obtained by thermal evaporation in vacuum. The thin polycrystallite films exhibit polarization which is stronger in air than in vacuum, and also hysteresis. The electrical conductivity is strongly influenced by humidity. (*PA*, 1962, #6424)

127. CRYOSCOPIC AND CONDUCTIMETRIC PROPERTIES OF PHENOL AND OF THE THREE CRESOLS

Perrin, R.
***Bulletin de la Société Chimique de France*, pp. 333–336,**
1963

The melting points of very pure phenol (I) and *o*-, *m*-, and *p*-cresol (II–IV) and their conductivities below melting points were determined. The values for specific conductivities of I–IV were 270 × 10^{-10} (at 50°C), 2.2 × 10^{-10} (at 25°C), 2.9 × 10^{-9} (at 25°C), and 2.3 × 10^{-9} (at 25°C) Ω^{-1} cm^{-1}, respectively. The effect of traces of H_2O or of Na was considered.

128. THE EFFECT OF THE AMBIENT OXYGEN ON THE ELECTRICAL PROPERTIES OF AN EVAPORATED FILM OF PENTACENE

Kuroda, H., Flood, E. A.
***Canadian Journal of Chemistry*, v. 39, no. 10,**
pp. 1981–1988, 1961

The "oxygen-effect" on the dark current as well as that on the photocurrent was investigated using thin evaporated films of pentacene, 1,2-benzpentacene, 1,2,8,9-dibenzpentacene, 6,13-diphenylpentacene, and 5,7,12,14-tetraphenylpentacene. No oxygen effect could be detected in the dark current.

From the photocurrent dependence on oxygen pressure and from the rate of photocurrent decay, it is concluded that additional charge carriers are produced on illumination by photoexcitation of a surface complex.

129. THE ELECTRICAL CONDUCTIVITY OF ORGANIC THIN FILMS: PERYLENE, CORONENE, AND VIOLANTHRENE

Inokuchi, H., Kuroda, H., Akamatu, H.
***Chemical Society of Japan, Bulletin of the*, v. 34, no. 6,**
pp. 749–753, June 1961

A sandwich cell and a surface-type cell were used for specimens in the form of thin film, and a quartz tubing having two electrodes in it was used for a compressed powder (under the pressure of 116 kg/cm^2). The resistivity ρ, given by $\rho = \rho_0 \exp(\Delta\varepsilon/2kT)$, where $\Delta\varepsilon$ is the apparent energy gap, showed values at 15°C as follows: perylene 4 × 10^{15} ohm cm (with $\Delta\varepsilon = 2.0$ ev), ~10^{13} (2.2), and 10^{18} ~ 10^{19} (2.0); coronene 1.7 × 10^{17} (1.7), 10^{12} ~ 10^{13} (1.65), and 10^{17} ~ 10^{18} (1.6); and violanthrene 2.1 × 10^{14} (0.85), ~ 10^{9} (0.9), and ~ 10^{14} (0.9), for the compressed powder, the sandwich cell, and the surface-type cell, respectively. An explanation is offered for the discrepancies among the values, and substantiating evidence is given.

130. ORGANIC SEMICONDUCTORS WITH HIGH CONDUCTIVITY. III. PERYLENE–IODINE COMPLEX

Uchida, T., Akamatu, H.
***Chemical Society of Japan, Bulletin of the*, v. 34. no. 7,**
pp. 1015–1020, July 1961

(For Part I, see Entry #80, AI/LS 341; for Part II, see Entry #42, AI/LS 341.) Preceding papers in the series have presented a preliminary survey of the semiconducting properties of these complexes and the violanthrene-iodine system. In this paper, the preparation, composition, electronic properties, magnetic susceptibility, ESR absorption and structure are discussed for two complexes. Both complexes show resistivity of 9 ~ 10 ohm cm and an energy gap of 0.06 ev

131. SEMICONDUCTIVITY AND ABSORPTION SPECTRUM OF PERYLENE SINGLE CRYSTALS

Sano, M., Akamatu, H.
***Chemical Society of Japan, Bulletin of the*, v. 34, no. 11,**
pp. 1569–1571, November 1961

Synthesis of perylene from naphthalene is described. When the electric resistivity of perylene was measured, no departure from Ohm's law was observed in the voltage region employed up to 1.6×10^3 v/cm. The resistivity decreased with increasing temperature and a good linear relationship was obtained between the log of the resistivity and the reciprocal of the temperature. The absorption spectra of a perylene crystal and its solution in EtOH were obtained with a Cary Model 11 spectrophotometer. Anisotropy was found in regard to the conductivity, but not to the value of the energy gap. It is concluded that the anisotropy arises from the difference in the mobility of free carriers, which is dependent on the direction of drift, but not from the difference in the number of carriers, which are in thermal equilibrium.

132. ELECTRICAL CONDUCTION IN THE VIOLANTHRENE-IODINE SYSTEM

Uchida, T., Akamatu, H.
***Chemical Society of Japan, Bulletin of the*, v. 35, no. 6,**
pp. 981–985, June 1962

Electrical conduction and ESR absorption in the violanthrene iodine system have been investigated, varying the iodine content. Observation of the Hall effect has been attempted, but the Hall voltage was so small that the effect could not be determined. It was pointed out that, concerning conductive behaviors, the violanthrene-iodine system is analogous with the nickel(II) oxide-lithium oxide solid solution, and that the hopping model of electrical conduction can be applied. From such a viewpoint, the correlation between the observed unpaired spins and charge carriers has been estimated.

133. ELECTRIC PROPERTIES OF SINGLE CRYSTALS AND THIN FILMS OF α,α′-DIPHENYL-β-PICRYLHYDRAZYL

Inokuchi, H., Harada, Y., Maruyama, Y.
***Chemical Society of Japan, Bulletin of the*, v. 35, no. 9,**
pp. 1559–1561, September 1962

The electronic conductivity of two forms of α, α′-diphenyl-β-picrylhydrazyl, the single crystal and the thin film, was observed. The resistivity (ρ_{15}) at room temperature along c-axis (1×10^{10} Ω cm) is 10^5 times lower than that perpendicular to the axis (1×10^{15} Ω cm), but its activation energy ($\Delta\varepsilon$) against temperature is in good agreement (1.5 and 1.6 ev). This large anisotropy may be introduced from that of the arrangement of molecules in the crystal. In the case of thin film, the values of ρ_{15} and of $\Delta\varepsilon$ are ~ 10^{10} Ω cm, 1.7 ev for a surface-type cell, and ~ 10^{13} Ω cm, 2.7 ev for a sandwich-type cell, respectively. A great difference on the characteristics of photoconduction and on the current–voltage relation in these two types of cell was found.

134. A NOTE ON THE EXCHANGE INTERACTION BETWEEN DIFFERENT ELECTRON SPINS IN ORGANIC MOLECULAR COMPLEXES

Kinoshita, M.
***Chemical Society of Japan, Bulletin of the*, v. 36, no. 3,**
pp. 307–309, March 1963

An explanation is offered for the three observed g-values of the complex of 2,2′-dinaphthyl disulfide with antimony pentachloride. Experiments are reported which support the theory. The complex p-phenylenediamine with p-chloranil, and the aromatics-iodine system are also considered. The g-values for the iodine complexes and for the monopositive ions are tabulated for pyrene, perylene, pyranthrene, violanthrene, and phenothiazine. Mention is made of the relation of ESR data to electron transfer and electrical conduction.

135. SEMI-CONDUCTIVITÉ ET PROPRIÉTÉS DIÉLECTRIQUES DE LA GUANINE (THE SEMICONDUCTIVITY AND DIELECTRIC PROPERTIES OF GUANINE)

Mesnard, G., Vasilescu, D.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 255, no. 6, pp. 1081–1083, August 6, 1962**

Conductivity and dielectric properties were measured from −120 to +100°C in dry and in slightly humid air. At 10^{-3} mm, $\sigma = \sigma_0 \exp(-E/kT)$; $\sigma_0 \approx 7 \times 10^{-13}$ ohm^{-1} cm^{-1} for pellets compressed at 100 kg/cm^2; σ_0 increases with the pressure up to 2×10^{-12} ohm^{-1} cm^{-1}; $E = 0.14$ ev. At room temperature, $\sigma = 3 \times 10^{-16}$ ohm^{-1} cm^{-1}. Abnormally high resistivity zones appear at −50, −90, and −105°C, but outside these zones the conductivity decreases with the temperature, in dry air. Dielectric measurements are normal for temperatures above room temperature. Below room temperature, the dielectric constant goes through a maximum at −70°C. Large deviations occur in slightly humid air owing to structural evolution and dipolar Debye relaxation. The humidity tends to increase the dielectric constant and tan δ. No ferroelectric effect is obtained.

136. CATALYSE SUR SEMI-CONDUCTEURS ORGANIQUES (CATALYSIS ON ORGANIC SEMICONDUCTORS)

Salle, R., Gallard, J., Traynard, P.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 256, no. 12, pp. 2588–2590, March 18, 1963**

The present study was undertaken to show relation between catalytic properties and electronic characteristics of organic semiconductors. Catalysts studied included phthalocyanines, polybenzimidazole (I), polyacenequinone (pyromellitic anhydride and quinone), condensation polymer of polyisoprene-benzoquinone and polyisoprene-chloranil (II), and polyacrylonitrile (III) pyrolyzed in air or Ar. Catalyst activities were expressed on the basis of unit weight and unit area. Three catalysts (I, II, and III pyrolyzed in Ar) had greater activity for decomposition of N_2O than NiO (green). Other catalytic processes studied were simultaneous dehydrogenation and dehydration of cyclohexanol and iso-PrOH, isomerization of butene, and oxidation of Tetralin. All polymers studied were conjugated structures and produced a signal in electronic paramagnetic resonance, and at least some polymers were semiconductors. The catalytic properties of these organic semiconductors are closely related to their electronic properties.

137. CONDUCTIVITÉ ÉLECTRIQUE DE QUELQUES AMINES ALIPHATIQUES SIMPLES; INFLUENCE DE LA PRÉSENCE DE PETITES QUANTITÉS D'EAU (ELECTRIC CONDUCTIVITY OF SOME SIMPLE ALIPHATIC AMINES; INFLUENCE OF THE PRESENCE OF SMALL AMOUNTS OF WATER)

Pouyet, B.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 256, no. 13, pp. 2834–2836, March 25, 1963**

Measurement of the electric conductivities permits one to put in evidence and to determine the amounts of very small quantities of water in the amines. This sensitive method permits a dosage of water from around 30 mg/l. Conductivity appears in this case superior to cryoscopy, as a criterion of purity. Measurements are reported on *n*-propylamine, *n*-butylamine, and *n*-amylamine. The curves show variation of conductivity of the amine-water mixtures as a function of quantities of water at 25°C.

138. ELECTRICAL PROPERTIES OF THIN ORGANIC FILMS

Bradley, A. Hammes, J. P.
***Electrochemical Society, Journal of the*, v. 110, no. 1, pp. 15–22, January 1963**

Thin organic polymer film specimens were prepared for electrical conductivity measurements by the glow discharge polymerization process. The experimental procedure for film preparation is described in detail. Data on film properties and deposition efficiencies (g/kwhr) are presented for their possible bearing on the polymerization mechanisms. Dark conductivities (σ) were measured over the temperature range 75–275°C. Plots of log σ vs. $1/T_{abs}$ generally gave straight lines above about 125°C with slopes characteristic of the chemical composition of the polymer film. Conductivities at 150°C ranged from 10^{-17} mho/cm (films rich in halogen) to 10^{-13} mho/cm (ferrocene, tetracyanoethylene). A possible relationship between structure and conductivity is discussed.

139. CONDUCTIVITY AND THERMOELECTRIC POTENTIAL MEASUREMENTS ON PERYLENE-METAL HALIDE COMPLEXES

Frant, M. S., Eiss, R.
***Electrochemical Society, Journal of the*, v. 110, no. 7, pp. 769–772, July 1963**

The conductivities and Seebeck coefficients of a series of perylene complexes with metal halides from groups IIB, IIIA, IVA, VA, VB, VIB, VIIA, and VIII of the periodic table have been studied to determine possible dependence of these properties on the nature of the halide. No direct correlation was found between conductivity and position on the periodic table. The complexes having a conductivity of $>10^{-5}$ mho/cm ($InCl_3$, PCl_3, $FeCl_3$, ICl, $SbCl_5$, I_2) were black in color; none of the others were black. Activation energies were measured for materials having a conductivity $>10^{-11}$ mho/cm and were 0.60 ev or lower. There was an approximate straight line relationship between the log conductivity and the activation energy, indicating that conductivity for the series is determined primarily by the number of thermally activated carriers rather than by the reservoir of available carriers in lower energy states. As a rule the most conductive materials had the lowest Seebeck coefficients. It was found that perylene:$FeCl_3$ could be prepared as either *p*- or *n*-type depending on the initial reactant ratio, with the perylene-rich material showing *p*-type properties.

140. SEMICONDUCTIVITY OF ORGANIC SUBSTANCES. PART 6.—A RANGE OF PROTEINS

Eley, D. D., Spivey, D. I.
***Faraday Society, Transactions of the*, v. 56, pt. 10, no. 454, pp. 1432–1442, October 1960**

The variation of dc electrical conductivity with temperature has been investigated in some fourteen proteins and polypeptides in the dry state *in vacuo*. All the substances show a reproducible semiconductivity, with relatively high energy gaps, 2.6 to 3.1 ev, and high mobilities of charge carriers, 10^3 to 10^5 $cm^2\ v^{-1}\ sec^{-1}$ assuming band theory equations and an effective mass equal to the free electron. These results confirm and extend earlier work on hemoglobin, and their outstanding feature is the overall similarity of behavior in so many substances. The results are discussed in terms of a model in which the determining process is the penetration of a potential energy barrier by thermally excited electrons. The basic unit is regarded as the 4 π-electron $>$CO . . HN$<$ unit, excited electrons traveling through a whole chain of these units of length l, with barriers between units (which might be α-keratin spirals). On the whole, the more ordered structures have lower $\Delta\varepsilon$ and higher mobility values, but the changes (e.g., due to denaturation) are small. Ohm's law deviations are also smaller than in other organic semiconductors. Reference is made to the correlation of thermal energy gaps with optical transitions in the solid, and a solid-state spectrum reported for hemoglobin.

141. SEMICONDUCTIVITY OF ORGANIC SUBSTANCES. PART 7.—THE POLYAMIDES

Eley, D. D., Spivey, D. I.
***Faraday Society, Transactions of the,* v. 57, pt. 12, no. 468. pp. 2280–2287, December 1961**

In an earlier paper, Baker and Yager demonstrated dc conductivity in polyamide 66 and 610, and suggested that the amide protons acted as charge carriers. In this paper the dc conductivity for nine polyamides is shown to be (1) 10^3 times that for the electronic semiconductors, proteins and amino acids, (2) markedly time-dependent and non-ohmic, (3) to possess an activation energy of *ca* 1.0 ev at high temperatures changing to one of *ca* 2.5 ev below a transition temperature around 100°C. It is suggested that protonic charge carriers are generated by a self-ionization process, with a heat of formation which gives rise to the high-temperature activation energy. Below the transition temperature, the rate-determining process is one of rotation of chain segments, which is a necessary preliminary to transfer of protons between amide groups on neighboring chains. Since chain rotation is ruled out in proteins, proton conduction cannot occur and the observed conductivity arises from mobility of π-electrons.

142. SEMICONDUCTIVITY OF ORGANIC SUBSTANCES. PART 8.—PORPHYRINS AND DIPYRROMETHENES

Eley, D. D., Spivey, D. I.
***Faraday Society, Transactions of the,* v. 58, pt. 2, no. 470, pp. 405–410, February 1962**

The porphyrins, and the copper and cobalt complexes of 4,4′-diethyl-3,3′,5,5′-tetramethyl dipyrromethene (dipyrromethene I or DI) have energy gaps of 1.8–1.9 ev, and this fact suggests that there is a certain degree of resonance interaction between the two dipyrromethene groups, although for steric reasons they cannot be exactly coplanar.

The complexes of 5-bromo-3,4′-diethyl-4,3′,5′-trimethyldipyrromethene (dipyrromethene II or DII) have an energy gap of 2.2 ev, which corresponds to electronic excitation within a single dipyrromethene molecule. The absence of resonance interaction suggested by this result may arise from the electron-attracting inductive effect of a Br atom tending to favor tetrahedral ionic bonds between metal and N atoms. The zinc complex of mesomethyl 4,4′-di(2-methoxycarbonylethyl)-3,3′,5,5′-tetramethyl dipyrromethene (dipyrromethene Ia or DIa) also has $\Delta\Sigma = 2.2$ ev. Presumably, here the dipyrromethenes have a nonplanar configuration, because the Zn atom is restricted to a tetrahedral sp^3 arrangement of valencies.

143. SEMICONDUCTIVITY OF ORGANIC SUBSTANCES. PART 9.—NUCLEIC ACID IN THE DRY STATE

Eley, D. D., Spivey, D. I.
***Faraday Society, Transactions of the,* v. 58, pt. 2, no. 470, pp. 411–415, February 1962**

The dc conductivity of four samples of DNA and one of RNA in the dry state has been examined. All five specimens show similar behavior, with a specific resistivity of about 5×10^{11} Ω cm at 400°K and an energy gap of 2.42 ± 0.05 ev.

It is probable that the conduction arises from thermally excited electrons on the paired bases traversing the whole length of the axis of the DNA double helix, and tunneling through the barriers between one DNA molecule and its neighbor.

144. ELECTRONIC PROCESSES IN PARAFFINIC HYDROCARBONS. PART 1.—ON THE NATURE OF CARRIER TRAPS

McCubbin, W. L.
***Faraday Society, Transactions of the,* v. 58, pt. 7, no. 475, pp. 2307–2315, July 1962**

Previous work in the field of radiation-induced conductivity in long-chain hydrocarbons has left open several important questions. The question dealt with here is the role which indigenous impurities play in the phenomenon of carrier trapping. The method involves a comparison of certain conductivity parameters of pure octacosane ($C_{28}H_{58}$) with those of commercial polythene, which has already been studied. It is a direct consequence of the different ways in which these substances are prepared that most of the impurities which are probable in the one are lacking in the other.

The important physical quantities which are measured, or deduced from conductivity measurements, include the following: the activation energy of conductivity in the absence of radiation, the total density of traps, the approximate form of the energy distribution of traps, and the free electron-hole recombination coefficient. It is found for octacosane that all values except the trap density lie close to the corresponding values for polythene. This is shown to be inconsistent with the idea that chemical impurities constitute the fundamental traps in these materials and consistent with the theory that long- or short-range ordering of molecules is the source of the trapping phenomenon. (For Part 2, see Entry #44.)

145. CHARGE-TRANSFER COMPLEXES OF LINEAR POLYMERS

Slough, W.
***Faraday Society, Transactions of the,* v. 58, pt. 7, no. 475, pp. 2360–2369, July 1962**

A series of charge-transfer complexes in which the electron donor was one of the polymers—polystyrene, poly-α-vinylnaphthalene, polyacenaphthylene or polyvinyl mesitylene—and the electron acceptor was one of the species—tetracyanoethylene, tetrachloro-*p*-benzoquinone (chloranil), 2,3-

dichloro-5,6-dicyano *p*-benzoquinone, or silver perchlorate—has been prepared and examined in the solid state. For the polyvinylnaphthalene-tetracyanoethylene system the complexes with a stereoregular (isotactic) polymer have also been prepared and examined. All the complexes prepared showed an exponential variation of specific conductivity with temperature in the range 20–75°C. Values of E and $\log_{10} \sigma_0$ calculated from $\sigma = \sigma_0 \exp(-E/2kT)$ were not found to be very sensitive to the proportion of the two components in the complexes. Seebeck coefficients were measured for certain of the materials and showed the majority current carriers to be positively charged. From a combination of the conductance and Seebeck coefficient data the carrier concentration and mobility have been calculated for these materials. In solution, spectra showing charge-transfer absorption bands are recorded for the polymers poly-α-vinyl naphthalene and polyvinylmesitylene behaving as electron donors and tetracyanoethylene, or tetrachlorobenzoquinone (chloranil) behaving as acceptors. The spectrum of one chloranil complex is also recorded in the solid state. Spectra in the solid state are also recorded for complexes in which polyvinyl naphthalene and polystyrene behaved as π-electron donors and silver ion was electron acceptor. In these spectra no new absorption bands appeared, but a slight red shift of the long wavelength edge of the aromatic absorption band occurred, together with a considerable increase in the intensity of absorption in comparison with the parent polymeric molecule.

The structure of the complexes, particularly the effect of the polymeric nature of the donor, is discussed in relation to the observed properties.

146. EFFECT OF OXYGEN ON THE OPTICAL AND ELECTRICAL PROPERTIES OF NUCLEIC ACIDS

Snart, R. S.

***Faraday Society, Transactions of the*, v. 59, pt. 3, no. 483, pp. 754–760, March 1963**

The dc electrical conductance of solid gels of deoxyribonucleic acid, under high vacuum, shows a semiconductive behavior, with an activation energy of 2.44 ev and a σ_0 value of 6.3×10^2 ohm^{-1} cm^{-1}. In an atmosphere of air or oxygen the activation energy is decreased to 1.27 ev and the σ_0 value to 4×10^{-6} ohm^{-1} cm^{-1}. However, after heating at 75°C in oxygen for a period of two days, the activation energy increased to 1.56 ev and the σ_0 value to 2.5×10^{-4} ohm^{-1} cm^{-1}, which were reproducible under oxygen or a high vacuum. The absorption spectrum of the sample that had undergone oxygen treatment showed a higher degree of hypochromicity than native DNA. A difference spectrum between oxygen treated DNA and native DNA shows a peak at 300 mμ which may be due to an increase in the hyperchromicity of the nucleic acid. Experiments have demonstrated a phosphorescence at 470 mμ on illumination of a solid gel of DNA with 300-mμ light, which is possibly the wavelength corresponding to the $n \rightarrow \pi^*$ transition in nucleic acids. Temperature curves have shown that the oxygen-treated sample may be cross-linked.

147. THERMOSTIMULATED E.M.F. APPEARING IN IRRADIATED HYDROCARBONS UNDER A TEMPERATURE GRADIENT

Frankevich, E. L., Talroze, V. L.

***Fizika Tverdogo Tela*, v. 3, no. 1, pp. 180–181, January 1961**
(Translated from the Russian in *Soviet Physics—Solid State*, v. 3, no. 1, pp. 131–132, July 1961)

Paraffin and polyethylene were irradiated with 1.6-Mev electrons at 200°K and allowed to warm up. The EMF was measured for temperature drops across the specimens of less than 20°K. "Bursts" of EMF appear between 250 and 280°K for paraffin and 260–280 and 340–380°K for polyethylene. The maximum voltages were 50–1000 v. There must be current carriers in shallow traps which may be radicals produced by the irradiation. The dependence of the EMF on the temperature gradient is probably due to the nonuniformity of trapped carriers rather than the gradient of carrier concentration produced by the temperature gradient. The equivalent electrical circuit is discussed. (*PA*, 1961, #17,842)

148. THERMAL ACTIVATION ENERGY OF THE DARK CONDUCTIVITY OF ORGANIC COMPOUNDS

Vartanyan, A. T., Rozenshtein, L. D.

***Fizika Tverdogo Tela*, v. 3, no. 3, pp. 713–722, March 1961**
(Translated from the Russian in *Soviet Physics—Solid State*, v. 3, no. 3, pp. 520–526, September 1961)

The activation energy was obtained from the temperature dependence of the dark conductivity of solid layers of a series of organic dyes and uncolored compounds. It was shown that these values agree with the short-wavelength edge of the phosphorescence band at low temperatures and with the long-wavelength drop of the spectral absorption curves of the corresponding substances. The free carriers are thus thought to be created by a singlet-singlet electron transition. (*PA*, 1961, #14,388)

149. THE TEMPERATURE DEPENDENCE OF DARK CURRENTS IN ANTHRACENE

Plotnikov, Yu. I.

***Fizika Tverdogo Tela*, v. 4, no. 11, pp. 3104–3109, November 1962**
(Translated from the Russian in *Soviet Physics—Solid State*, v. 4, no. 11, pp. 2271–2274, May 1963)

Thermal activation energy values are given for dark currents in single-crystal and polycrystalline anthracene specimens prepared by different methods. These values amounted to 1.98 ± 0.04 ev for both bulk and surface currents and no dependence on crystallographic direction was observed.

In the presence of oxygen, the thermal activation energy increased in the initial experiments, but in later experiments decreased to 1.46–1.80 ev in correspondence with the E value of anthraquinone, which is formed as the end product of anthracene oxidation.

150. INVESTIGATION OF ORGANIC SEMICONDUCTORS

Aftergut, S., Brown, G. P.
July 1961
General Electric Co., Schenectady, N. Y.
Report for March 1960–March 1961 on Solid State Research and Properties of Matter, WADC TR 59-469, Pt. II, AF 33(616)-6908
AD-268,

Measurements of specific resistivity vs. temperature were performed on a variety of organic compounds including phenazine and some of its derivatives, solutions of phenazine in naphthalene, hydrogen-bonded compounds such as imidazole, benzimidazole, and 4-hydroxypyridine, pigments of the aniline black type, polymers, and pyrolyzed polymers. Activation energies for semiconduction were computed. The mechanism of semiconduction of organic compounds is discussed in terms of the overlap of molecular orbitals. The recent literature is reviewed.

151. INVESTIGATION OF ORGANIC SEMICONDUCTORS

Aftergut, S., Brown, G. P.
May 1962
General Electric Co., Schenectady, N. Y.
Report for May 15, 1961–April 14, 1962, WADC TR 59-469, Pt. III, AF 33(616)-8293

The temperature dependence of the electrical resistance was obtained on polymers and simple substances including poly(*m*-phenoxylene), poly(*p*-phenylene sulfide), a *p*-dimethylborophane polymer, a polybenzimidazole, acridone, diphenylguanidine, carbanilide, and phenothiazine. The resistance versus temperature of imidazole was measured in a zone-refining tube; the energy gap changed on zone-refining but became constant after 39 passes. New (apparently polymeric) complexes of imidazole and copper, zinc, and cobalt were prepared. The recent literature on organic semiconductors was surveyed.

152. RADIATION-INDUCED CHANGES IN SOME PHYSICAL PROPERTIES OF GRAPHITES OF VARIOUS DEGREES OF GRAPHITIZATION

Aleksenko, Yu. N., Kakushadze, L. E.
International Journal of Applied Radiation and Isotopes,
v. 8, no. 2–3, pp. 131–132, July 1960

Volume increase of graphite after neutron irradiation is assumed to result from decrease in size of the crystallites, i.e., to graphitization. Six samples of graphites of various degrees of graphitization were irradiated by 6.2×10^{20} neutrons cm^{-2} at 350–450°C. The absolute radiation-induced changes in electrical and thermal resistivities are, within accuracy of the measurements, independent of graphitization. The relative changes are smaller for the less graphitized samples. Thermal conductivity versus temperature indicates that the radiation-induced breakdown of the crystal lattice in graphite has the same effect on the propagation of thermal vibrations as the crystallite boundaries or impurities. The mechanism by which radiation affects the electrical conductivity of graphite appears to be that of forming additional traps for the current carriers. Radiation-induced changes in the Hall coefficient were observed previously. Swelling was practically absent in these experiments which suggests that this is due to less stable forms of radiation damage. (*PA*, 1961, #17,586)

153. THE CONDUCTIVITY OF ARTIFICIAL GRAPHITE

Shulepov, S. V., Pashnin, M. I.
Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika,
no. 2, pp. 34–39, 1962

Electrical conductivity, Hall effect, and Nernst-Ettinghausen effect were studied in powder and solid samples of graphite. With increasing temperature of graphitization, electron mobility increases in comparison with holes. The type of conductivity—*n*- or *p*-conductivity—depends on graphitization temperature; above 2600°C *n*-type is present.

154. ELECTRIC CONDUCTIVITY AND DIELECTRIC LOSS IN POLY (VINYL CHLORIDE) PLASTICS

Anikeenko, V. M., Kevroleva, K. M., Kessenikh, R. M., Sotnikov, V. G.
Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika,
no. 5, pp. 75–80, 1962

Electrical conductivity at 500–1500 v/cm at 48–97°C and dielectric losses at 10^4 cps were determined for poly(vinylchloride) plastics of various compositions. The following results were found: specific resistivity was 2×10^{12} to 1×10^{13} ohm/cm; dielectric permittivity varied with the temperature and increased to 9–10 at 97°C; tan δ varied from 0.1 at 40°C to 3–3.5 × 10^{-2} at 90°C.

155. EFFECT OF PRESSURE ON CONDUCTIVITY OF POLYACENEQUINONE RADICAL POLYMERS

Rembaum, A., Moacanin, J., Cuddihy, E.
In "Research Summary, Volume 36–14," pp 152–154
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Calif., May 1, 1962

Conductivity measurements were carried out in an apparatus which consisted of a cell, press, and electrometer. Using this equipment, an evaluation was made of the properties of four polyacenequinone radical PAQR powders. The conductivities, forbidden energy gap E_g, and pre-exponential factors of these materials were studied as functions of both pressure and temperature.

A study was made of the dc conductivities of the four powders at eight pressures from 7,000 to 57,000 atm and temperatures of about 22, 60 and 93°C. For any given polymer at constant temperature, the conductivity increases by about a factor of 100 over the pressure range investigated. At constant pressure, conductivity increases by about a factor of 10 over a 70°C temperature range. Experimental results are graphed.

156. ANIONIC POLYMERIZATION OF 9-VINYLANTHRACENE AND SEMICONDUCTIVITY OF POLY-9-VINYLANTHRACENE-IODINE COMPLEXES

Rembaum, A., Henry, A., Waits, H.
In "Space Programs Summary, 37-19, Volume IV,"
pp. 103–110
Jet Propulsion Laboratory, California Institute of Technology, February 28, 1963

It is concluded that the electrical conductivity of polymers appears to be due mainly to mobile π-electrons, as for example, in molecules containing conjugated double bonds, or to charge transfer complexes such as polycyclic hydrocarbons and halogen addition compounds. Both types of compounds possess a conductivity intermediate between metals and insulators, i.e., in the range of 10^{-3} to 10^{12} ohm^{-1} cm^{-1}. According to this classification dehydrogenated PVA may therefore be classified as a polymeric semiconductor. Conductivity of PVA is considerably enhanced by complexing it with iodine and is probably due to (1) the quinonoid structure, and (2) the substituted anthracene structure.

The average iodine content of the complex was found by elemental analysis to be equal to 32.3%, and on the basis of reaction yields, the average amount was 27.9%. One iodine molecule per three anthracene units would require an iodine content of 29.6%, which is in fair agreement with the experimental results. Monomeric complexes of this kind contain a much larger proportion of halogen and are generally easily dissociated. This limits the temperature range at which electrical measurements may be made and generally makes the determination of resistivity a great deal more difficult. The PVA-iodine complex is stable over a wide temperature range, and furthermore the uncomplexed iodine may be removed by extraction with boiling benzene or similar solvent. This stability may be due to the comparatively high energy gain which, according to Mulliken, constitutes the attractive charge-transfer force. The latter depends on the value of the ionization potential of the donor component. It is likely that the electrical conductivity of charge-transfer complexes may be correlated with this value of energy gain. Studies in this direction may throw some light on the mechanism of electrical conduction in organic solids.

157. ELECTRICAL SURFACE PROPERTIES OF POLYMERS CONTAINING BOUND ANIONIC GROUPS

Holmes, F. H., Perkins, P. G.
***Journal of Applied Chemistry*, v. 12, pp. 150–156, 1962**

Sulfonated sheets of polystyrene cross-linked with divinylbenzene and sheets (with CO_2H groups) of copolymerized styrene, divinylbenzene, and methacrylic acid exhibited surface conductivities which increased with relative humidity. Such increase is consistent with an increase in the dielectric constant of the polymers.

158. CURRENT NOISE IN PYROLYZED POLYACRYLONITRILE

Brophy, J. J.
***Journal of Applied Physics*, v. 33, no. 1, pp. 114–117, January 1962**

Current noise measurements of the organic semiconductor polyacrylonitrile pyrolyzed in nitrogen at temperatures from 550 to 900°C which reveal changes in conductivity similar to those attributed to carrier fluctuations in inorganic semiconductors are reported. The current noise spectra exhibit characteristic time constants of 10^{-2}, 3×10^{-4}, and 5×10^{-5} sec which are independent of pyrolysis temperature and are tentatively associated with the molecular structure leading to conductivity. The observed noise magnitude suggests the existence of a large number of independent sub-volumes which increase in size with treatment temperature. Samples pyrolyzed above 700°C exhibit noise that may be indicative of a different molecular structure.

159. SPACE-CHARGE-LIMITED CURRENTS IN ORGANIC CRYSTALS

Mark, P., Helfrich, W.
***Journal of Applied Physics*, v. 33, no. 1, pp. 205–215, January 1962**

Electrical conductivity measurements performed on thin (50 μ) single crystals of *p*-terphenyl, *p*-quaterphenyl, and anthracene using aqueous electrodes are discussed. The results strongly indicate that the acceptor electrode (an I-I solution) can form ohmic contact for hole injection into these crystals and that space-charge-limited currents can be drawn through them. The crystals were found to contain hole-trapping states; the location-in-energy of these states can be approximated by a decreasing exponential distribution above the valence band. Measurements showed that the hole mobility in *p*-terphenyl is about 3×10^{-2} cm^2/v-sec and is independent of the field up to about 4×10^4 v/cm, and that the hole-trap concentration is at least 10^{13}cm^{-3}. The acceptor electrode used does not form ohmic contact to crystals of naphthalene and diphenyl; an explanation for this is proposed. Some theoretical aspects of ohmic contact formation to organic crystals and space-charge-limited current flow in insulators are also discussed. (SSA, #14,076)

160. PYROLYTIC GRAPHITES: THEIR DESCRIPTION AS SEMIMETALLIC MOLECULAR SOLIDS

Klein, C. A.
***Journal of Applied Physics*, v. 33, no. 11, pp. 3338–3357, November 1962**

An investigation is made of the electrical, the galvanomagnetic, and the thermoelectric properties of pyrolytic graphites whose morphological features are conditioned by the deposition temperature, the heat treatment, and the doping level. (1) Basal-plane magnetoresistance and *c*-direction specific resistance of deposits prepared at temperatures ranging from 1900 to 2500°C point to a remarkable improvement of the crystallites' alignment with rising deposition temperature. In both crystallographic directions the Seebeck coefficient closely follows semi-empirical predictions based on the two-dimensional model of the π-electron bands. The Fermi level of a standard deposit (2100°C) is at 0.025 ev below the valence-band edge and thus indicates that crystal defects trap about 7.5×10^{19} electrons/cm^3 at room temperature; this figure is in accord with a Hall coefficient of 0.33 cm^3/C. The average in-plane mobility (930 cm^2 v^{-1} sec^{-1}) corresponds to a mean free path of the order of the crystallite diameter (250 A). (2) Post-deposition treatment at temperatures above 2500°C results in (a) a rapid drop of the room-temperature basal-plane resistivity down to 50 $\mu\Omega$ cm or less, (b) a Hall effect conversion from *p*- to *n*-type in the early stages of graphitization, and (c) a trend toward negative Seebeck coefficients in the layer planes. In conjunction with low-field magnetoresistance measurements these results can be described in terms of semimetallic concepts, the simultaneous presence of holes and electrons with equal concentrations (6×10^{18} cm^{-3} at room temperature) stemming from a slight band overlap. Average mobilities imply that the carrier behavior approaches single-crystal characteristics ($\approx 10^4$ cm^2 v^1 sec^{-1} at room temperature) after heat treatment above 3000°C. Normal to the layers, the specific resistance always exceeds 0.1 Ω cm, which points to a molecular conduction process in this direction. (3) An incorporation of boron into the carbon-hexagon networks lowers the electrical resistance of graphite particularly in the *c*-direction (twenty-fold decrease at a composition of 0.6 at. % B); concurrently the two temperature coefficients become approximately equal to zero. In the rigid-lattice approximation band-population figures derived from the resistivity temperature-dependence reflect the Hall coefficient behavior, the peak occurring at an equivalent boron content of 0.04%. The ionization efficiency is of the order of 50% with a Fermi level depressed by more than 0.1 ev. Thermoelectric power measurements in the *c*-direction accord with the view that charge transport across the layer planes involves most of the excess holes, and reveal that boron enhances the Seebeck anisotropy of graphite. (*PA*, 1963, #826)

161. ELECTRICAL CONDUCTIVITY OF POLYPROPYLENE

Foss, R. A., Dannhauser, W.
***Journal of Applied Polymer Science*, v. 7, no. 3,**
pp. 1015–1022, May 1963

The steady-state (dc) electrical conductivity of polypropylene has been measured as a function of temperature (25–150°C) and field strength (0–94 kv/cm). The temperature coefficient of the conductivity is 34.6 kcal/mole expressed as an activation energy. This is much larger than the activation energy for diffusion of small molecules in the same polymer. Thus, ionization rather than diffusion appears to be the primary activation process. The conductivity is nonohmic; the conductance quotient is a linear function of field strength but is larger than predicted by Onsager's theory. The ion "jump distance," as evaluated from the isothermal field dependence, is the same order of magnitude as the diffusional mean free path estimated from diffusion studies in other polymers. The conductivity, conduction activation energy, and field dependence appear to be relatively insensitive to polymer crystallinity.

162. ELECTRON SPIN RESONANCE IN COMPLEXES OF AROMATIC HYDROCARBONS WITH IODINE

Singer, L. S., Kommandeur, J.
***Journal of Chemical Physics*, v. 34, no. 1, pp. 133–140,**
January 1961

Accurate measurements of electron spin concentration in semiconducting molecular complexes of perylene and pyrene with iodine have indicated an exponential temperature dependence in excellent agreement with the activation energy for electronic conduction. The agreement of the magnitudes of the spin concentrations with the carrier concentration estimates obtained from electrical measurements further confirms the identification of the unpaired spins as charge carriers. At low temperatures, small temperature-independent concentrations of trapped spins or free radicals are observed. Spin resonance line shapes, relaxation times, and *g*-factor anisotropies also have been determined

163. ELECTRICAL CONDUCTIVITIES OF α- AND β-PHTHALOCYANINE

Wihksne, K., Newkirk, A. E.
***Journal of Chemical Physics*, v. 34, no. 6, pp. 2184–2185,**
June 1961

The two crystal modifications have different conductivities: α-phthalocyanine has a higher conductivity with an activation energy of 0.25 ev, while β-phthalocyanine has a conductivity which is 10^5 times lower and an activation energy of 0.9 ev The irreversible transition from α to β by heating can be followed electrically. (*PA*, 1961, #14,393)

164. PHOTO- AND SEMICONDUCTION IN CRYSTALLINE CHLOROPHYLLS *a* AND *b*

Rosenberg, B., Camiscoli, J. F.
***Journal of Chemical Physics*, v. 35, no. 3, pp. 982–992,**
September 1961

Measurements are reported on some characteristics of photoconduction and semiconduction in pure crystalline chlorophylls *a* and *b*. The semiconduction activation energy is 1.12 ev in chlorophyll *a* and 1.44 ev in chlorophyll *b* ($E/2kT$). The latter value is in excellent agreement with the triplet state energy of 1.43 ev measured by the phosphorescence method in chlorophyll *b*. The former value suggests that a possible cause of the lack of detectable phosphorescence in chlorophyll *a* is that it occurs in the infrared at about 11,000 A. The evidence indicates that the mobility of the predominant charge carriers (positive holes) is the same in both crystals. Photoconduction is easily measured in chlorophyll *b* and less easily in chlorophyll *a*, because of the much larger dark current. The photoconduction activation energy in chlorophyll *b* is 0.36 ev. This supports Rabinowitch's view that photoconduction in chlorophyll is not involved in the primary act of photosynthesis.

The oxygen adsorbed on the surface of the crystals forms an oxygen-chlorophyll complex. This leads to an increase in both the dark current and the photocurrent probably by increasing the mobility of the surface charge carriers. There is no detectable effect of oxygen upon the semiconduction activation energy, since the increase of the magnitude of the current is small (a factor of 4 to 10). The binding energy of the oxygen-chlorophyll *a* complex is about 1.4 ev; that of the oxygen-chlorophyll *b* complex 0.63 ev. There is no detectable activation energy for the formation of the complex. It is not a photo-oxidation process. Some evidence suggests that a more tightly bound oxygen complex exists which has no effect on electronic conductivity. This more stable complex is converted by light into the weakly bound complex described above (probably by photoreduction of chlorophyll in the complex). These results are similar to those of Arnold and Sherwood's work on dried chloroplasts. They favor their alternative explanation—that of an oxygen compound being responsible for thermoluminescence and a thermal spike in conductivity—rather than their first assumption, that of electron trapping and recombination in chlorophyll itself.

165. ORGANIC SEMICONDUCTORS. AROMATIC HYDROCARBON POSITIVE IONS IN SOLIDS

Blomgren, C. E., Kommandeur, J.
Journal of Chemical Physics, v. 35, no. 5, pp. 1636–1639, November 1961

Mixtures of aromatic hydrocarbons with antimony pentachloride in carbon tetrachloride have been studied by the methods of electron spin resonance and visible spectroscopy. The observation of a Tyndall effect and the spectroscopic properties show that the mixtures are colloidal suspensions. The visible spectra are characteristic of aromatic ions, and a comparison of ion concentrations measured by visible spectroscopy and spin concentrations measured by spin resonance indicates that the aromatic ions in the solids are the only paramagnetic species present. The solids were found to exhibit high electronic conductivity.

166. ORGANIC SEMICONDUCTORS COMPARISON OF MEASUREMENTS ON SINGLE-CRYSTAL AND COMPRESSED MICROCRYSTALLINE MOLECULAR COMPLEXES

Kronick, P. L., Labes, M. M.
Journal of Chemical Physics, v. 35, no. 6, pp. 2016–2019, December 1961

Measurements of conductivity, activation energy of conduction, and Seebeck coefficient performed on charge-transfer complex single crystals are reported. Very small single crystals were grown using slow cooling or evaporative techniques. They were large enough to be handled by specialized manipulative methods, which are described to some detail. Measurements on single crystals of three diamine-quinone complexes are reported and discussed in relationship to measurements on the compressed materials. Detailed interpretation of the data given must await crystallographic analyses, since it is not known what kind of molecular stacking occurs in X, Y, and Z directions. (*SSA*, #13,104)

167. ON THE NATURE OF THE ELECTRODE EFFECTS IN THE CONDUCTIVITY OF ANTHRACENE MONOCRYSTALS

Reucroft, P. J.
Journal of Chemical Physics, v. 36, no. 4, pp. 1114–1116, February 15, 1962

Dark conductivity measurements indicate that the electrode barrier is independent of the work function of the metal of the electrode. Non-ohmic behavior was observed with electrodes of aquadag and copper iodide prepared by two methods. A copper iodide electrode on one face is positive, at zero current, with respect to a metallic electrode on the opposite face; the potential difference correlates with the work function of the metal. (*PA*, 1962, #8295)

168. SEMICONDUCTIVITY OF NAPHTHALENE

Bornmann, J. A.
Journal of Chemical Physics, v. 36, no. 6, pp. 1691–1692, March 15, 1962

Measurements on both high-purity and further zone refined material showed an extremely sharp 1000-fold drop in the intrinsic resistance on melting of very pure naphthalene. $E = 0.73$ ev ($\zeta = \zeta_0 \exp E/kT$) for the solid and the resistance charge was found to be independent of the direction of temperature change. (*PA*, 1962, #8369)

169. ELECTRONIC PROPERTIES OF POLYSULFUR NITRIDE

Kronick, P. L., Kaye, H., Chapman, E. F., Mainthia, S. B., Labes, M. M
Journal of Chemical Physics, v. 36, no. 8, pp. 2235–2237, April 15, 1962

This linear polymer of alternating sulfur and nitrogen atoms with conjugated double bonds is of interest in connection with studies of the electronic properties of conjugated organic polymers. The value of 0.013 ohm cm at 25°C for the electrical resistivity of a compressed sample extrapolated to infinite pressure, the lowest that has been observed in any alternant polymer chain, suggests that there may be unique structural features in $(SN)_x$ influencing its electrical properties. The material was synthesized by the method of Goehring from tetrasulfur tetranitride.

The Seebeck coefficient (S) was measured on pressed pellets 15 mm in diameter and 4 mm thick in an evacuated die at various pressures.

The resistivity as a function of temperature was measured *in vacuo* on a Kelvin double bridge, using platinum probes and a thermocouple embedded in a sample compressed in a special die at 5000 atm.

For organic conjugated polymers it is calculated that chain-chain interaction and the extent of delocalization of π-electrons within the individual chains are small. For $(SN)_x$ the individual chains represent a conjugated system with resonance forms involving the alternation of positive and negative sulfur atoms, which is believed to lead to a high intrachain conductivity. In addition, the expansion of the sulfur valence shell gives more opportunity for interaction involving the $d\pi$-orbitals. The extra electrons on the negatively charged sulfur, situated in such an expanded orbital, might be expected then to facilitate charge transport between chains.

170. ELECTRICAL PROPERTIES OF CHLORPROMAZINE

Gutmann, F., Netschey, A.
***Journal of Chemical Physics*, v. 36, no. 9, pp. 2355–2360,**
May 1, 1962

Chlorpromazine (10-dimethylaminopropyl phenothiazine) in the form of slabs cast from the melt is a semiconductor. The activation energy of conductivity has an average value of $E = 2.1$ ev, referring to the equation $\sigma = \sigma_0 \exp(-E/2kT)$, above a transition temperature of 32°C. There is no significant change of E upon fusion, its value remaining constant up to 80°C. The transition has been confirmed by thermal analysis, dielectric measurements, and by infrared spectroscopy. The spectra indicate that the side chain as well as the ring system is affected by the transition, which is believed to be due to an unfolding of the side chain above a critical temperature, this causing a change in the micellar association of the substance. Values are reported, as functions of temperature, for the refractive index, the permittivity at 1 Mc and at 1592 cps, the parallel ac conductivity and the loss tangent at the latter, lower, frequency. The substance is diamagnetic.

171. CHARGE INJECTION INTO ORGANIC CRYSTALS: INFLUENCE OF ELECTRODES ON DARK- AND PHOTOCONDUCTIVITY

Pope, M., Kallmann, H. P., Chen, A., Gordon, P.
***Journal of Chemical Physics*, v. 36, no. 9, pp. 2486–2492,**
May 1, 1962

Studies have been made of dark and photoconductivity in thin anthracene single crystals using a Ce^{4+} solution as one electrode and a $1M$NaCl solution as the other electrode. It was found that the Ce^{4+} electrode was capable of injecting holes into anthracene in the dark, the saturation current at 15,000 v/cm being about 1 μa/cm^2. This current was observed when the Ce^{4+} electrode was at a positive potential. With the same polarity, it was found that there was practically no increase in the saturation current upon illumination of the crystal with 3650- or 4300-Å light. At low voltages there was a distinct photoeffect which was attributed to the emptying of polarization producing traps, thus increasing the internal field. The saturation current was proportional to the six-tenths power of the Ce^{4+} concentration. At low voltages, the current was very small until a certain voltage, referred to as the onset voltage, was reached, after which the current increased rapidly. The onset voltage was larger for the dark current than for the photocurrent. The efficiency of carrier production by the Ce^{4+} ion was about 10^{-10} based on a simple collision hypothesis. Possible explanations for this low efficiency were advanced but no definite mechanism was chosen. The use of Ce^{3+} ion was without effect in increasing either the dark or photocurrent.

Using a positive electrode of I_2 in glacial acetic acid, it was found that there was practically no hole injection, in contrast with the marked hole injecting characteristics of the aqueous $I_2 - I^-$ electrode. Furthermore, the Ce^{4+} and $I_2 - I^-$ electrodes were ineffective with naphthalene. These results are explained by reference to a criterion for hole injection $I_A - W_E - E_x < 0$, where W_E is the work function of the electrode, I_A is the ionization energy of anthracene in the solid, and E_x is the externally supplied energy (optical, thermal, electric field).

172. EFFECT OF PRESSURE ON THE RESISTANCE OF PYROLYTIC GRAPHITE

Samara, G. A., Drickamer, H. G.
***Journal of Chemical Physics*, v. 37, no. 3, pp. 471–474,**
August 1, 1962

The effect of pressure to several hundred kilobars was measured on samples of pyrolytic graphite of density 2.18 and 2.20. Measurements along the c-axis show a relatively high resistance which decreases with increasing pressure and levels at high pressure, apparently due to strongly decreasing compressibility. Along the a-axis the resistance is low, but increases at higher pressures, apparently due to recrystallization. (*PA*, 1962, #18,633)

173. EFFECT OF PRESSURE ON THE RESISTANCE OF FUSED-RING AROMATIC COMPOUNDS

Samara, G. A., Drickamer, H. G.
***Journal of Chemical Physics*, v. 37, no. 3, pp. 474–479,**
August 1, 1962

The effect of pressure to several hundred kilobars was measured on the resistance of seven fused ring aromatic compounds, including two polyacenes and five quinones. In general, there is a rapid drop in resistance at lower pressures, followed by a marked leveling at above 200–250 kilobars. The leveling is apparently associated with the rapid decrease in compressibility at high pressure observed by Bridgman. The resistance at high pressure varied by several orders of magnitude among the compounds. It seems to be closely associated with the amount of overlap between adjacent molecules in the unit cell. The temperature coefficient of resistance at high pressure was obtained for three compounds. They all remained semiconductors at the highest pressure studied, but the activation energy was about one-sixth of the atmospheric pressure value. (*PA*, 1962, #18,701)

174. ELECTRONIC TRANSPORT IN CRYSTALLINE AND LIQUID PYRENE

LeBlanc, O. H., Jr.
***Journal of Chemical Physics*, v. 37, no. 4, pp. 916–917, August 15, 1962**

Electronic mobilities were measured in several organic solids and liquids and the results suggest that the mechanism of transport is different in the two phases. In the experiment reported here, it was found that the hole mobility in pyrene decreases abruptly by three orders of magnitude at the melting point; thus the transport mechanism is clearly different in the solid and liquid phases. A possible transport mechanism is suggested for the liquid phase. (*PA*, 1962, #23,256)

175. ELECTRIC CONDUCTION IN LIQUID HYDROCARBONS. I. BENZENE

Forster, E. O.
***Journal of Chemical Physics*, v. 37, no. 5, pp. 1021–1028, September 1, 1962**

A technique has been developed which allows the determination of specific conductance in the bulk of a liquid, independent of electrode materials or electrode separation. By this method, the specific conductance of benzene saturated with air was determined to be $1.1 \pm 0.1 \times 10^{-14}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for fields between 50 and 400 v/cm. Measurements of the potential gradients between electrodes show them to be strongly asymmetric. The temperature dependence of the dark current conduction of benzene was shown to follow the typical relation normally associated with semiconductance. The value of E was determined to be 0.42 ± 0.4 ev for both liquid and solid benzene. The photoconductance of benzene was bound to follow closely its spectroscopic behavior. The experimental results are interpreted to suggest that conduction in both liquid and solid benzene is based on an electron transfer mechanism. The temperature dependence of this mechanism is shown to be independent of impurities and to be a property only of the bulk of the liquid. (*PA*, 1962, #21,922)

176. EFFECT OF HALOGENS ON THE RESISTANCE OF SINGLE CRYSTALS OF COPPER PHTHALOCYANINE

Curry, J., Cassidy, E. P.
***Journal of Chemical Physics*, v. 37, no. 9, pp. 2154–2155, November 1, 1962**

The resistances of single crystals of semiconducting copper phthalocyanine were determined in a vacuum and in the presence of gaseous iodine, bromine and chlorine. The presence of halogens reduced the resistances by eight to ten orders of magnitude. (*PA*, 1963, #6593)

177. ELECTRICAL MEASUREMENTS ON POLYVINYLENE AND POLYPHENYLENE

Mainthia, S. B., Kronick, P. L., Labes, M. M.
***Journal of Chemical Physics*, v. 37, no. 10, pp. 2509–2510, November 15, 1962**

The resistivity of polymer samples depends markedly on the presence of water. Different drying techniques led to variations of 10^4 ohm cm. (*PA*, 1963, #4936)

178. INVESTIGATION OF BULK CURRENTS IN METAL-FREE PHTHALOCYANINE CRYSTALS

Heilmeier, G. H., Warfield, G.
***Journal of Chemical Physics*, v. 38, no. 1, pp. 163–168, January 1, 1963**

The bulk current in many single crystals of metal-free phthalocyanine was found to exhibit ohmic behavior up to fields of 10^4 v/cm and square-law dependence on voltage for higher fields. Photocurrents in these crystals were ohmic over the entire range. If one interprets these results as space-charge-limited currents, trap densities of 10^{12} to $10^{14}/\mathrm{cm}^3$ are found from the temperature behavior of the I-V characteristic. From the transition between ohmic and square-law regions, the concentration of free carriers was calculated to be approximately 10^6 to $10^7/\mathrm{cm}^3$, in fairly good agreement with that found from Hall measurements. Samples were measured which had both dark and photocurrents which varied as V at low fields, but as $V^{1.5-1.7}$ at higher fields. These observations are interpreted qualitatively in terms of a model in which a layer of higher resistivity than the bulk extends from the contact into the bulk.

179. DIELECTRIC PROPERTIES OF SOME POWDERED ORGANIC SEMICONDUCTORS

Huggins, C. M., Sharbaugh, A. H.
***Journal of Chemical Physics*, v. 38, no. 2, pp. 393–397, January 15, 1963**

The use of electrical conductivity measurements to characterize the charge density and/or mobility parameters of a material is discussed. The common practice of using simple, pressed electrodes with dc measurements is felt to be grossly inferior to four-probe techniques. Even this refinement, however, is subject to considerable error for powdered samples. Many workers have used fairly simple ac techniques to eliminate interparticle contact resistances in organic semiconductors; this approach is shown to have been misapplied. It is possible, however, to measure what appears to be a specific conductivity (independent of packing pressure or filling factor) by more elaborate ac analysis. Measurements of the effective parallel resistance and capacitance are given for anthracene (powder and single-crystal), metal-free β-phthalocyanine, and a β-carotene tri-iodide complex for a frequency range of 0.05 cps to 300 Mc (*PA*, 1963, #8557)

180. CONDUCTION IN HEXAMETHYLBENZENE THROUGH THE CRYSTALLINE TRANSITION

Kronick, P. L., Labes, M. M.
***Journal of Chemical Physics*, v. 38, no. 3, pp. 776–777,**
February 1, 1963

Hexamethylbenzene has been shown to undergo a reversible transition from a triclinic crystal lattice below 109°C to an orthorhombic lattice, stable above this temperature. The log of the resistance varies linearly with $1/T$, with an apparent activation energy of 0.89 ev. There seems to be no discontinuity and no slope change at the 109°C transition point.

181. EFFECT OF PURIFICATION ON THE SEMICONDUCTION OF IMIDAZOLE

Brown, G. P., Aftergut, S.
***Journal of Chemical Physics*, v. 38, no. 6, pp. 1356–1359,**
March 15, 1963

The technique of measuring the temperature dependence of the electrical resistance of organic compounds directly in a zone-refining tube has been explored with imidazole. The temperature dependence, determined as a function of the number of zone-refining passes, became constant after 39 passes. The results were compared with those of imidazole purified by successive sublimations. The contribution of hydrogen bonding to the semiconduction of imidazole is discussed. (*PA*, 1963, #10,826)

182. RECTIFICATION PHENOMENA IN POLYCRYSTALLINE PHTHALOCYANINES

Haak, F. A., Nolta, J. F.
***Journal of Chemical Physics*, v. 38, no. 11, pp. 2648–2651,**
June 1, 1963

Rectification was observed on polycrystalline samples of metal-free, copper, nickel, and molybdenum phthalocyanines when these materials were sandwiched between different metal electrodes. The presence of a small amount of a liquid polar impurity proved essential for rectification, and it is suggested that the observed rectification is caused by the formation of an ionic space-charge barrier in the vicinity of the least noble electrode. The highest rectification ratio observed was 500 and was obtained with copper phthalocyanine between a platinum and a silver electrode and also between a silver and an aluminum electrode. The effects of temperature, electrode material, and electrode size on the rectification ratio are given.

183. ON THE VARIATION OF ELECTRICAL RESISTANCE OF A POLYMER AS A FUNCTION OF THE EXTENT AND NATURE OF SORBED WATER

Kawasaki, K.
***Journal of Colloid Science*, v. 16, no. 4, pp. 405–410,**
August 1961

Results are given for polymethylmethacrylate, polyvinyl alcohol and gel cellophane. (*PA*, 1962, #6429)

184. SYNTHESIS AND CHARACTERIZATION OF SOME HIGHLY CONJUGATED SEMICONDUCTING POLYMERS

Pohl, H. A., Engelhardt, E. H.
***Journal of Physical Chemistry*, v. 66, no 11, pp. 2085–2095,**
November 1962

Conductivity, energy interval (corresponding to the energy gap in single-crystal semiconductors) thermoelectric power, Hall coefficient, ohmic behavior, spin concentration, photoconductivity, and photovoltage were studied, using a series of synthetic organic polymer semiconductors. These included the polyacene quinone radical polymers, polyquinazones, a polyacene, and aniline black. Conduction was shown to be electronic, not ionic, and, in a homologous series, to depend upon the chemical structure. The conductivity-thermoelectric power data are best fitted by a two-carrier model. A slight field dependence of conductivity is observable. A common feature of high conjugation appears in these semiconductors. High spin concentration (ESR) parallels high conductivity, but spin concentrations greatly exceed the apparent carrier concentrations. (*PA*, 1963, #10,837)

185. THE NATURE OF SEMICONDUCTION IN SOME ACENE QUINONE RADICAL POLYMERS

Pohl, H. A., Opp, D. A.
***Journal of Physical Chemistry*, v. 66, no. 11, pp. 2121–2126,**
November 1962

Semiconduction ranges from 10^{-5} to 10^{-12} mho/cm in 51 examples of organic polymers prepared by condensing aromatic hydrocarbon derivatives with acids. Conduction is electronic, not ionic or electrolytic. It depends strongly on the chemical nature of the monomeric units, mildly on the field strength. The concentration of unpaired spins (*ca* 10^{19} cm^{-3}) is roughly 100-fold larger than the apparent carrier concentration. Certain of these substances are highly piezo-conductive, reflecting sensitivity of orbital overlap to intermolecular distance in these *eka*-conjugated structures.

186. SEMICONDUCTIVITY AND PHOTOCONDUCTIVITY OF PURINES AND PYRIMIDINES

Basu, S., Moore, W. J.
***Journal of Physical Chemistry*, v. 67, no. 7, pp. 1563–1564,**
July 1963

High quantum yields in macromolecules suggest that an exciton may travel freely through the molecule until it is trapped at a site at which the elementary reaction of deactivation can occur. Such exciton mechanisms are closely related to the phenomenon of photoconductivity. If, during the course of its motion, the exciton encounters a strong donor or acceptor entity (i.e., a trapping center), then either the positive hole or the negative electron will be trapped, leaving its counterpart mobile. The trapping effect, therefore, leads to the generation of charge carriers which can carry electric current through a conduction band. In order to obtain further information on such transfer processes in nucleic acids, the conductivity and the photoconductivity of their constituent purines and pyrimidines were measured on thin films of the powdered samples in air and *in vacuo*. The dark conduction was the same in air and *in vacuo*, but the photocurrent was markedly higher in air. In air the photocurrent was higher when the sample was illuminated through the positive electrode than when it was illuminated through the negative electrode, which is in accord with a mechanism in which the predominant current carriers are positive holes. *In vacuo* the photocurrent was independent of the direction of illumination. The activation energies for the semiconduction were calculated.

187. CONDUCTANCE IN DIMETHYLSULFOLANE

Eliassaf, J., Fuoss, R. M., Lind, J. E.
***Journal of Physical Chemistry*, v. 67, no. 8, pp. 1724–1725, August 1963**

The compound 2,4-dimethylsulfolane was distilled at 100°C and about 1 mm, from sodium hydroxide, using nitrogen to sweep air out of the system; the solvent conductance was 2–4 × 10^{-8}. The viscosity at 25°C is 0.0904. The dielectric constant is 29.5 and the density is 1.1314. Tetraphenylarsonium iodide was prepared as described by Lyon and Mann and recrystallized twice from water. Trimethylphenylammonium iodide (Eastman) and potassium thiocyanate were recrystallized from ethanol. Conductances were measured at 25°C in a cell with constant equal to 0.1245.

188. THE TEMPERATURE DEPENDENCE OF THE CONDUCTIVITY OF DRY CELLULOSE

Murphy, E. J.
***Journal of Physics and Chemistry of Solids*, v. 15, no. 1-2, pp. 66–71, August 1960**

An experimental investigation of the electrical conductivity is described. It leads to the following expression for the conductivity:

$$\sigma = 4.50 \times 10^{2} \exp(-30.7 \times 10^{3})/RT + 3.55 \times 10^{-10}$$
$$\exp(-10.6 \times 10^{3})/RT$$

where σ is the conductivity in $(\Omega\ \mathrm{cm})^{-1}$. R the gas constant, and T the absolute temperature. This has the form usual in the theory of ionic conduction in crystals. From the coefficient of the first term, the lattice constant for conduction can be calculated: the value obtained is 5.4 A. The observed energy in the Boltzmann factor for the first term can be regarded as splitting into the sum of two terms: a dissociation energy of 40.2 kcal/mole and an activation energy for mobility of 10.6 kcal/mole; this gives (40.2/2) + 10.6 = 30.7, the observed value. The second term, which is due to impurity conduction of some kind, has an activation energy for mobility of 10.6 kcal/mole. This agrees approximately with the activation energy for conduction in ice; consequently, the second term is regarded as due to conduction in adsorbed water. The first term is regarded as representing volume conduction in which dissociation requires 40.2 kcal/mole, but mobility is governed by the breaking of two hydrogen bonds. The ratio 3.55 × 10^{-10}/4.50 × 10^{2} (= 0.79 × 10^{-12}) is proportional to the concentration of "impurities." It is unusually small. A possible significance of this is discussed. (*PA*, 1961, #17,632)

189. STRUCTURAL DEPENDENCE OF THE ELECTRICAL CONDUCTIVITY OF POLYETHYLENE TEREPHTHALATE

Amborski, L. E.
***Journal of Polymer Science*, v. 62, no. 174, pp. 331–346, December 1962**

The dc conductivity of three different forms of polyethylene terephthalate was studied over a wide temperature and voltage range to determine the structural dependence of the conduction process. From the films in the amorphous, crystallized, and oriented and crystallized forms, it was determined that crystallization reduces the conductivity by more than one order of magnitude. Orientation results in a six-fold decrease in conductivity. The conductivity does not change over a wide range of molecular weight or carboxyl end group concentration. As shown from model polymers and copolymers, disruption of chain symmetry and molecular packing, introduction of side chains, or any other modification which reduces the crystallinity and order, result in greater conductivity. The structural dependence of conductivity, the temperature dependence, and the current–voltage relationships of polyethylene terephthalate are consistent with a proposed ionic mechanism for the conduction process.

190. RESISTIVITY STUDIES ON POLYMER SEMICONDUCTORS

Pohl, H. A., Gogos, C. G., Cappas, C.
***Journal of Polymer Science, Part A: General Papers*, v. 1, no. 6, pp. 2207–2212, June 1963**
(See also Entry #107)

Eighteen polyacene polymers were synthesized, and their resistivities were found to be of the order of 10^{4}–10^{5} ohm-cm. The resistivity of these polymer semiconductors was found to be sensitive to changes in the conditions of synthesis, changes in the structure of the polymers, and variations of pressure and temperature during experimentation. The forbidden energy gap for these polymers was about 0.5 ev. Although the formalism of the simple intrinsic semiconductor band model was not strictly applicable to the data on these polymers, such a treatment was found instructive.

191. RELATIONSHIP BETWEEN LUMINESCENCE AND SEMICONDUCTING PROPERTIES OF SOME SYNTHETIC POLYMERS

Kryszewski, M., Kurczewska, H., Szymanski, A.

Preprint 77, presented at the International Symposium on Macromolecular Chemistry, Paris, France, July 1–6, 1963, sponsored by the International Union of Pure and Applied Chemistry, under the patronage of Monsieur le Ministre d'État chargé de la Recherche Scientifique, under the auspices of the Délégation Générale à la Recherche Scientifique et Technique, and the National Committee for Chemistry
(To be published in *Journal of Polymer Science, Part C: Polymer Symposia*)

The luminescence (fluorescence and phosphorescence) and electrical resistance of polyamides and copolymers of vinylidene chloride with vinyl chloride, as well as the influence of ultraviolet irradiation on both phenomena occurring in these polymers, were investigated. It was found that ultraviolet irradiation influences in different ways the luminescence and resistance of both kinds of polymers. In polyamides, ultraviolet irradiation results in the decrease of duration of phosphorescence and resistance. The first phenomenon is due to the formation of radicals and their subsequent oxidation; the second is due to the breaking of intramolecular hydrogen bonds in the amorphous part of polymer, which enhances chain mobility and proton transfer by appropriate orientation of segments in electric field. The ultraviolet irradiation of vinyl polymers containing chlorine atoms causes formation of vinylene chains and results in greater luminescence ability and resistance decrease. The radicals being formed are more easily oxidized without change of vinylene sequences so the luminescence is not destroyed by the oxidation of radicals.

192. ÉTUDE DE LA CONDUCTIBILITÉ ÉLECTRIQUE DE FILMS D'ACIDE DÉSOXYRIBONUCLÉIQUE (STUDY OF THE ELECTRICAL CONDUCTIVITY OF FILMS OF DEOXYRIBONUCLEIC ACID)

Hanss, M., Douzou, P., Sadron, C.
Preprint 78, presented at the International Symposium on Macromolecular Chemistry, Paris, France, July 1–6, 1963, sponsored by the International Union of Pure and Applied Chemistry, under the patronage of Monsieur le Ministre d'État chargé de la Recherche Scientifique, under the auspices of the Délégation Générale à la Recherche Scientifique et Technique, and the National Committee for Chemistry
(To be published in *Journal of Polymer Science, Part C: Polymer Symposia*)

The study of electrical conductivity of dehydrated films of DNA as a function of temperature presents a number of difficulties, especially those of establishing good electrical contacts and of measuring currents of very low intensity. Despite this it is possible to present some results of experiments actually realized. (1) After the first cycle of heating, one observes an important lessening of conductivity. (2) Within the limits of experiment (20–100°C), one is able to represent the variations of conductivity σ by a law of the form: $\sigma = \sigma_0 C^{-E/nT}$, where $E = 0.86 \pm 0.1$ ev. (3) At 90°C, the resistivity of the samples is of the order of 10^{13} ohm-cm. When the films of DNA are prepared by dialysis of a solution, the resistivity is not measurable above 10^{16} ohm-cm. This result tends to show that the conductivity is of an ionic nature.

193. ON ELECTRICAL ASYMMETRY AT THE JUNCTION OF CATIONIC AND ANIONIC PERMSELECTIVE MEMBRANES

Friedlander, H. Z.
Preprint 80, presented at the International Symposium on Macromolecular Chemistry, Paris, France, July 1–6, 1963, sponsored by the International Union of Pure and Applied Chemistry, under the patronage of Monsieur le Ministre d'État chargé de la Recherche Scientifique, under the auspices of the Délégation Générale à la Recherche Scientifique et Technique, and the National Committee for Chemistry
(To be published in *Journal of Polymer Science, Part C: Polymer Symposia*)

Previously electrical asymmetries and amplification of signals have been reported for arrays of separate ion-exchange membranes, ion-exchange membranes in conjunction with insulation layers, and ion-exchange membranes mixed with metallic depolarizers. This communication describes the preparation of integral bipolar ion-exchange membranes, which are electrolytic analogues of *p–n* junctions, from thermoplastic sheets by compression molding. By use of this new, simplified junction, the question of asymmetrical, electrolytic resistance is examined for direct current, alternating current, and square waves, and comparisons are made among junctions, arrays of dissimilar membranes, and individual pieces for the case of highly washed samples free from electrolyte. The salinization–desalinization mechanism generally advanced for explaining asymmetry is analyzed with relation to these data. A new method for the measurement of electrical resistivity of ion-exchange membranes, namely, that of the equiconductive electrolyte, is described. This new method compares the resistivity of the ion-exchange membrane to that of a known electrolyte without the necessity of measuring the dimensions of the membrane or the variabilities associated with pressuring probes.

194. ELECTRICAL CONDUCTIVITY OF MOLTEN POLYCAPROLACTAM

Bushin, V. V., Dumanskii, I. A.
***Khimicheskie Volokna*, no. 1, pp. 23–25, 1963**

The specific electrical conductivity of molten polycaprolactam changes with time and temperature, the latter dependence analogous to that of polymer semiconductors. Gamma irradiation has no significant effect.

195. INFLUENCE OF ADSORBED GASES ON ELECTROPHYSICAL PROPERTIES OF PYROLYZED POLYACRYLONITRILE FIBERS

Kustanovich, I. M., Patalakh, I. I., Polak, L. S.
***Kinetika i Kataliz*, v. 4, no. 1, p. 167, 1963**

Pyrolyzed polyacrylonitrile fibers with semiconductive properties were subjected to desorption of pyrolysis products in air for three hours at 200°C and 10^{-4} mm pressure, with an increase in conductivity from 10^{-6} to between 10^{-3} and 10^{-2} ohm^{-1} cm^{-1}. The conductivity was independent of temperature between −78 and +200°C. Electron conduction was indicated, and the EPR signal intensity increased. A *p–n* junction was prepared.

196. ELECTROCONDUCTIVE SILICONE RUBBER. I. CARBON BLACK-COMPOUNDED ELECTROCONDUCTIVE SILICONE RUBBER

Manami, H., Nishizaki, S.
***Kogyo Kagaku Zasshi*, v. 62, pp. 884–887, 1959**

The compounding, curing, and testing of electroconductive silicone rubber are reported. The rubber was tested for electrical and other properties, and the effects of manufacturing variables were investigated. Resistivity less than 10 ohm-cm was exhibited.

197. ELECTROCONDUCTIVE SILICONE RUBBER. II. HEAT DEGRADATION AND RESISTIVITY OF ELECTRO-CONDUCTIVE SILICONE RUBBER

Manami, H., Nishizaki, S.
***Kogyo Kagaku Zasshi*, v. 62, pp. 887–890, 1959**

The effect of temperature on resistivity from 25 to 150°C is noted, and the change in resistivity by blending is discussed.

198. DIE BEEINFLUSSUNG DER ELEKTRISCHEN LEITFÄHIGKEIT DURCH HOCH POLYMERE. KONZENTRATIONS-DP-EFFEKT (INFLUENCE OF ELECTRICAL CONDUCTIVITY THROUGH HIGH POLYMERS. CONCENTRATION AND DEGREE OF POLYMERIZATION EFFECT)

Kolos, F., Treiber, E.
***Kolloid-Zeitschrift*, v. 180, no. 1, pp. 1–11, January 1962**

199. ANOMALOUS ANISOTROPIC ELECTRICAL CONDUCTIVITY OF TRIGLYCINE FLUOROBERYLLATE NEAR THE PHASE-TRANSITION POINT

Gurevich, V. M., Zheludev, I. S.
***Kristallografiya*, v. 6, no. 5, pp. 778–779,**
September–October 1961
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 6, no. 5, pp. 624–625(L),
March–April 1962)

Measurements of the electrical conductivity of triglycine fluoroberyllate in the temperature range 20–95°C are reported. The results show that the temperature dependence of conductivity is exponential, but with an anomaly near the phase transition point. The nature of the transition, i.e., first order or second order, is still uncertain. (*SSA*, #15,960)

200. SEMICONDUCTIVITY IN ORGANIC MOLECULAR COMPLEXES

van der Hoek, J. A., Lupinski, J. H., Oösterhoff, L. J.
***Molecular Physics*, v. 3, no. 3, pp. 299–300, May 1960**

Complexes of benzidine or tetramethylbenzidine with iodine, bromine, or tetranitromethane were prepared and the electrical conductivities measured at 27°C. The measurements were made on compressed powders by a dc method. The accuracies were not good and the complexes were not stoichiometric. The electrical conductivities of the complexes ranged from 10^{-3} ohm^{-1} cm^{-1} for benzidine:I_2 to 10^{-10} ohm^{-1} cm^{-1} for benzidine:Br_2 and tetramethylbenzidine:I_2. (*PA*, 1961, #17,718)

201. STRUCTURAL DEPENDENCE OF THE ELECTRICAL CONDUCTIVITY OF POLY(ETHYLENE TEREPHTHALATE)

Amborski, L. E.
1961
National Academy of Sciences, National Research Council, Washington, D. C.
Publication 973, pp. 11–13

Substantiation of an ionic mechanism for dc conductivity is given by the following observations: the log of the conductivity decreases linearly with polymer density, which is proportional to the degree of crystallinity; the conductivity of the crystalline forms is one to two orders of magnitude less than for the amorphous film; the temperature dependence of conductivity is also less, and evidently the number of current carriers or mobility, or both, is reduced; film orientation produces a six-fold decrease in conductivity, because of decreased segmental mobility and mobility of the current carriers. Replacing the terephthalate with isophthalate results in increased conductivity by three to four orders of magnitude because loss of symmetry disrupts packing and introduces greater segmental mobility. Lowered internal viscosity, with resultant increased conductivity and lowered activation energy, is produced when 25% of the terephthalate is replaced by aliphatic sebacate, and the use of glycols with > 2 C atoms or with lateral groups enhances these effects

202. RESISTIVITY MEASUREMENTS AND ANALYSIS BY AC AND DC TECHNIQUES [ABSTRACT]

Huggins, C. M.
In "Program and Abstracts. Organic Crystal Symposium, October 10–12, 1962," pp. 68–74
National Research Council, Ottawa, Canada, 1962

The usual measuring technique consists of applying a known voltage (*E*) across a sample of known dimensions and measuring the induced current (*I*) in the external circuit. Two major difficulties can arise immediately from the electrode-sample contacts: the contact at the electrode-sample interface may be of such high resistance as to effect a significant voltage drop at the electrode rather than across the sample, and/or the electrode system may in some way serve to change the nature of the sample itself. Measurements give a value of the resistance, R, of the system, including sample, electrodes, and measuring devices. This number can, and does, have practical significance in many instances.

For the determination of the specific conductivity, the electrode-sample contact difficulty can be eliminated or minimized by the use of a four-probe technique. In this method, four probes (or contacts) are arranged in-line so that the outer pair supply the current and the inner pair measure the voltage gradient in the sample. Providing the inner pair are sufficiently removed from the outer pair, the nature of all these contacts is unimportant insofar as their resistance is concerned. The conductivity as determined above is often the most refined measurement that can be made. However, extreme caution should be exercised in making theoretical interpretations of even this measurement. A variety of pitfalls have been shown to be present. The electrical conductivity of most materials is an extreme function of many, otherwise minor, perturbations such as impurity content, degree of crystalline perfection, surface effects, and perhaps cosmic-ray activity.

It is universally agreed that, where possible, conductivity should be determined using large, perfect crystals. For many materials, this concept has not been realized. Polymers simply do not form large. single crystals; other materials resist the formation of large crystals to a prohibitive limit. To obviate this difficulty, three approaches have been used: simple dc measurements on compressed powder, four-probe dc measurements on mechanically fused samples, and ac methods on powders. Each of these has its appealing features. Alternating current methods of resistance measurements have been used by many workers. The usual measurements consist of determining the net effective resistance of a sample at audio or radio frequencies by bridge or Q-meter techniques. The assumption is made that at sufficiently high frequencies the high-resistance contact is electrically shorted by its own capacitance, the remaining resistance then being ascribed to the bulk resistivity of the particles themselves. As it is shown, this assumption may prove valid.

Where single-crystal measurements have been made, most valence semiconductors and molecular semiconductors show marked crystalline orientation dependence of conductivity. For example, one TCNQ compound exhibits conductivities of 4.0, 0.05, and 0.001 mho cm^{-1} along the three principal crystal directions. Since the relative magnitudes of these principal conductivities are intimately associated with the proposed mechanism of conduction in TCNQ compounds, it was essential to have them determined for single crystals. No such information can possibly be obtained from dc measurements on powders.

Another technique, developed by Bean, De Blois, and Nesbitt, utilizes the rate of decay of induced, diamagnetic flux in a conductor as a measure of the specific conductivity. For metals, this method is quite successful particularly since effects of sample geometry, electrodes and macroscopic inhomogeneities are either removed or reduced. For organic semiconductors with their large displacement currents and non-degenerate carriers, it is not certain at this time whether the method would be applicable. Some workers have used square-wave, dc pulses in conductivity measurements. This method is mainly used to avoid ohmic heating in high-current measurements on good conductors. The wave-form analysis of square-wave pulsing can also be used to study frequency-dependent effects such as discussed in relation to ac methods, but the interpretation of results is severely complicated.

It is concluded that, because of the many pitfalls discussed here, credible determinations of specific conductivities of a crystalline material can only be made from dc measurements on single crystals. The ac methods as previously used are not satisfactory; some improvements have been achieved. The interpretation of mechanism for organic semiconduction is now most severely limited by the lack of single-crystal measurements, including direct determinations of anisotropic contributions.

203. THE SEMICONDUCTION OF IMIDAZOLE AS A FUNCTION OF PURIFICATION [ABSTRACT]

Brown, G. P., Aftergut, S.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," p. 80
National Research Council, Ottawa, Canada, 1962

Elimination of the effect of impurities by successive purifications, until constant electrical properties are attained, has been attempted. The temperature dependence of the resistance of imidazole was measured on five samples which had been sublimed up to five times, but the results did not converge to a constant value. In addition, imidazole which had been purified by recrystallization and sublimation was subjected to zone-refining in a sealed glass tube which was equipped with platinum electrodes for making electrical measurements. It was found that a constant temperature dependence was obtained only after 39 zone-refining passes.

204. ON THE INTRINSIC CONDUCTIVITY OF ANTHRACENE [ABSTRACT]

Helfrich, W., Riehl, N.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 94–98
National Research Council, Ottawa, Canada, 1962

The conductivity of anthracene has been studied by many workers. It is, however, not understood why the results differ widely as to magnitude and temperature dependence. Agreement exists only about the form of temperature dependence of the conductivity σ, which is always found to be

$$\sigma = \sigma_0 \exp(-E/2kt)$$

where E = activation energy of conductivity. In this investigation, single crystals of 10 to 100μ thickness were used which had been prepared from the vapor phase under reduced pressure ($\leqq 10^{-8}$ Torr). They showed violet fluorescence. The crystals were clamped between polystyrol plates having 4-mm-D holes serving as electrodes when filled with liquid. Distilled water was usually chosen, on the assumption that it would not inject excess holes or electrons and that it forms no complex with anthracene. A constant voltage source connected to the sample produces a time variable current. An initial current transient which is due, at least in part, to the properties of the measuring circuit has decayed after less than one minute. Yet, the current does not become stationary but continues to decrease. Even after 30 min no stationary value is reached. A plot of current vs. time usually shows two portions of reduced slope occurring after a few minutes. The current at these particular sections is proportional to the field strength up to the rather high value of 25,000 v cm^{-1}, the limit of this investigation. The logarithm of current for a fixed value of field strength was plotted against the inverse temperature. The current was measured near the end of the sections of reduced slope. The experimental points are compatible with two straight lines having a slope corresponding to the activation energy of 1.65 ev reported by Mette and Pick. It is assumed that these two straight lines indicate the temperature dependence of two separate conduction mechanisms. For the lower line a value of $\sigma_0 = 3.10^{-3}$ ohm^{-1} cm^{-1} is found; the upper line leads to about twice that value. Equal results were obtained with two different crystals, one of which was 18μ the other 52μ thick. According to Mette and Pick, $2.5 \times 10^{-3} < \sigma_0 < 5 \times 10^{-3}$ ohm^{-1} cm^{-1} is to be expected for currents which flow, like these, perpendicular to the *ab* plane. Thus, an extrapolation of the temperature dependence of conductivity reported by Mette and Pick agrees with the present results at much lower temperatures of 20 to 50°C.

A model is proposed which may be able to account for the existence of two apparently separate conduction mechanisms. The familiar pair of excess carrier bands are called "dissociation bands." These dissociation bands can be populated as well by thermally dissociated carriers as by injected carriers. In addition, the existence is postulated of another pair of conducting bands which are populated when electron wave functions belonging to a molecular ground state are replaced by those of an excited state. These two additional bands are called "excitation bands." While thinking of a molecular state of excitation, one would have to consider the exciton as being smeared out over the entire extent of the lattice. Recombination of the wave functions representing holes and electrons in these excitation bands should occur bimolecularly so that E in the equation is indeed the activation energy of the molecule. In the case of anthracene it is suspected that the excited state may be the first triplet state. Thermal excitation alone determines the population of the excitation bands which thus always contain equal numbers of holes and electrons. Carriers in the excitation bands are not localized; each molecule remains electrically neutral and excess carriers are not allowed to exist. Charge transport, i.e., current, through the excitation bands requires not only a driving field but also the existence of sources and sinks for the charges. Thus, the excitation bands may be compared to water-filled pipes. The water cannot flow through such a pipe even if the pipe is tilted, as long as at least one end of it is closed. Objections to the model are presented.

205. THE MEASUREMENT OF DARK CONDUCTIVITY OF ANTHRACENE BY THE USE OF PULSE TECHNIQUES [ABSTRACT]

Feilchenfeld, H., Many, A.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 99–101
National Research Council, Ottawa, Canada, 1962

In the present work, advantage is taken of the characteristics of blocking contacts to measure the bulk conductivity of single crystals of anthracene, and the transient rather than the dc response is studied. A voltage pulse is applied across the sample in series with a resistor (10^9 or 10^{10} ohm), which serves as the grid resistor of a low input-capacitance high-gain amplifier driving a CRO. To eliminate the large capacitative surge at the onset of the voltage pulse, a relay is employed which short-circuits the grid resistor until a short time (1 msec) after the pulse onset. With this arrangement a response time of about 5 msec is obtained for currents above 10^{-12} amp. All samples are provided with a guard ring to eliminate surface currents. The sample is enclosed in a cryostat whose temperature may be continuously varied between room temperature and 200°C.

A detailed study of the transient characteristics can afford useful information regarding both metal-insulator contacts and trapping effects. In this paper, however, the emphasis is on the bulk conductivity and its temperature dependence, and so only the initial peak of the current is of interest. Measurements of peak current have been carried out along the principal crystallographic orientations. Semilog plots of the conductivity vs. $1/T$ are presented. All plots yield a value of 0.5 ev for the activation energy. For comparison purposes the "conductivity" plots derived from the steady-state current are also included. For most contacts these plots exhibit an activation energy of 0.8 to 1 ev, which is within the range of values quoted for anthracene by dc measurements. An exception to this behavior is an evaporated silver contact, where the steady-state activation energy approaches that derived from the peak current (0.5 ev).

In conclusion, it is seen that contact effects may play a dominant role in dc conductivity measurements and may well lead to erroneous interpretation of the experimental data. Transient measurements, on the other hand, seem to be a promising tool for the study of high resistivity materials. It is interesting to note that blocking contacts and large trap densities, which in many cases are undesirable, are here the factors which make the measurements possible.

206. THE HALL EFFECT AND BAND MODEL IN METAL FREE PHTHALOCYANINE SINGLE CRYSTALS [ABSTRACT]

Heilmeier, G. H., Warfield, G., Harrison, S. E., Assour, J. M.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 133–138
National Research Council, Ottawa, Canada, 1962

The conductivity of the crystals was measured along the *b*- and *c'*-axes of the crystal using ohmic contacts of silver paste over the temperature range from 26 to 350°C. The plot of conductivity vs. the reciprocal of the absolute temperature yielded a straight line over the entire temperature range from which an activation energy of 1.66 ev was obtained. This value was found to be independent of crystalline orientation. However, the conductivity along the *b*-axis was ten times greater than that along the *c'*-axis. This indicates that the mobility is anisotropic which is accounted for by the difference in the π-orbital overlap in the two directions. A striking equality was found between the thermal activation energy for conductivity and the onset of strong optical absorption. The optical absorption of the crystal which is similar to the shifted molecular spectrum was obtained using an 80-hr exposure on a Jarrel-Ash grating spectrometer. This was necessary due to the opacity of the crystals in their strong absorption region. The measurements of conductivity were repeated on four different crystals and reproduced on each. It is felt that this evidence speaks strongly for a conduction process which involves the excitation of an electron from the highest filled level to a conducting state deriving from the molecular singlet state.

Previous attempts at Hall measurements on organic semiconductor crystal and films have succeeded only in establishing an upper limit for carrier concentration and mobility. The experimental apparatus used here consisted of a Cary vibrating reed electrometer whose output can be displayed on a recorder, a reversible balancing supply to remove spurious voltages due to any asymmetry in the positioning of the Hall probes which was introduced into the feedback loop of the electrometer to preserve its input impedance, a main voltage supply for the sample current, and a Varian magnet. The measurement technique consisted of recording the output of the Hall probes with the electrometer as a function of time with the magnetic field on, off and reversed. A typical result with field in a specific direction is shown. The data were then integrated using a planimeter to eliminate the effects of noise on the Hall voltage. The results of these measurements on several samples are tabulated, assuming that in the calculation of the Hall coefficient, mobility, and carrier concentration only one type of carrier is mobile, a band model is applicable, and the conductivity is isotropic. The assumption of an isotropic conductivity is probably not completely valid, as the separation of the molecules in the lattice is a function of crystallographic direction, as is undoubtedly the case for the overlap of the molecular wave functions. Thus, the assumption is only a crude first approximation to the true solution which is much more complex. Results are compared with previous experiment and with theory.

207. OBSERVATION OF HALL EFFECT IN COPPER-PHTHALOCYANINE [ABSTRACT]

Delacote, G., Schott, M.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 143–147
National Research Council, Ottawa, Canada, 1962

Hall mobilities have been measured in two monocrystals of copper phthalocyanine, in the range 400–620°K. As this work is already in progress and extended toward lower temperatures and to other ambients, and as a detailed account of the most important results of the first part of the work is to be published, only a brief report is given.

The Hall mobility is close to the microscopic mobility, which in Cu-phthalocyanine is definitely greater than the macroscopic mobility already measured in anthracene; this means that the theory of high mobility semiconductors may perhaps be applied here, and supports the idea that a model of conduction through free carriers frequently trapped in shallow levels can be more useful than the model of hopping processes. The discrepancy between the results of LeBlanc and Kepler, and those presented here, can be explained by (1) intrinsic difference in the materials, (2) the existence of shallow levels, and (3) a very field-dependent mobility, but a value of $<\tau^2>/<\tau>^2$ so different from unity is not probable.

208. INVESTIGATION OF BULK CURRENTS IN METAL-FREE PHTHALOCYANINE SINGLE CRYSTALS [ABSTRACT]

Heilmeier, G. H., Warfield, G., Harrison, S. E.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 148–152
National Research Council, Ottawa, Canada, 1962

Direct-current measurements of the current–voltage characteristics of metal-free phthalocyanine single crystals with ohmic guard ring electrodes have been made. Phthalocyanine is a molecular crystal having semiconductor properties. The dark current at room temperature is characterized by an ohmic dependence on voltage up to fields of 10^4 v/cm. A square law behavior is obtained beyond this field strength. Photocurrents were ohmic over the entire range of measurement, indicating that the mobility was not field dependent. Data are presented and the results are interpreted.

209. STUDIES OF THE CARBAZOLE-CHLORANIL CHARGE TRANSFER COMPLEX BY ELECTRON SPIN RESONANCE [ABSTRACT]

Kohin, R. P., Müller, K. A., Hoegl, H.
In "Program and Abstracts· Organic Crystal Symposuim, October 10–12, 1962," pp. 170–174
National Research Council, Ottawa, Canada, 1962

The ESR measurements on carbazole-chloranil samples were made with an X-band superheterodyne spectrometer using low-frequency (73 cycle) magnetic field modulation. For the equi-molar sample mainly studied, the resonance consisted of a single Lorentzian-shaped line having a g-factor of 2.0038 and a width of 4.4 gauss. Other equi-molar samples prepared at different temperatures and pressures had in general different line widths and in some cases the line shape was more closely gaussian. All measurements were made at reduced power levels (less than 25 μw) since the signal from the complex was found to saturate for power levels greater than approximately 300 μw when using a cavity having a Q of 2500. At room temperature, the intensity of the signal from a certain equi-molar sample corresponded to 7 × 10^{17} unpaired spins/g, or approximately one unpaired electron for every 2000 donor or acceptor molecules.

As the temperature was lowered the intensity of the signal was found to decrease and could be fitted by the equation $I \propto T^{-1} \exp(-E/kT)$ where the activation energy, E, had a value of approximately 0.014 ev. Measurements were made in the temperature range from 150 to 300°K. During intense illumination of a thin powdered sample by visible light from a filtered 200-w high pressure mercury arc lamp, the signal was found to increase in intensity by approximately 40% of that obtained from the sample in the dark. Variations in the concentrations of the two components produced variations in the concentration of unpaired electrons in the sample.

Since no spin resonance signal has been observed from the complex in solution, it is assumed the paramagnetism is not associated with the donor-acceptor pair itself but must be related to properties of the solid. The behavior of the spin resonance signal from the carbazole-chloranil mixture is, to a certain extent, similar to that reported for the perylene-iodine and some similar complexes, which shows an intensity temperature dependence characteristic of a low thermal activation energy. These complexes exhibit a spin resonance due to thermal excitation of unpaired conduction electrons or holes, as is supported by their large conductivity and the equivalence between the thermal activation energies for both the conduction and the unpaired carrier concentration. On the other hand, the complex studied at present has a relatively low conductivity (less than 10^{-9} ohm^{-1} cm^{-1}).

210. ELECTRON SPIN RESONANCE AND THE CONDUCTIVITY OF COPPER AND METAL-FREE PHTHALOCYANINE [ABSTRACT]

Harrison, S. E. Assour, J. M
In "Program and Abstracts: Organic Crystal Symposium,
October 10–12, 1962," pp. [illegible]5–180
National Research Council, Ottawa, Canada, 1962

The electrical conductivity of metal-free and copper phthalocyanines has been measured over a 300°C range (50–350°C). The ln σ vs. $1/T$ plots reveal straight lines over the entire temperature range. Measurements on the same compound show the respective slopes to be reproducible with less than 5% deviation. This is believed to be evidence in favor of intrinsic conduction. The results indicate higher room temperature conductivity by three orders of magnitude for the copper derivative. The activation energy ($\sigma = \sigma_0 e^{-E/2kT}$) for the copper compound is 1.35 vs. 1.65 ev for the metal-free compound. One possible source of this difference in conductivity can be found in an analysis of the electron spin resonance of copper phthalocyanine diluted in metal-free phthalocyanine. This analysis predicts a greater overlap of π-electrons in the copper compound.

The important qualitative feature to be noted is that there must be considerable out-of-plane π-bonding. The situation is further complexed by the fact that from the phthalocyanine orbital calculation the π-electron density is determined to be 20% higher on the ligating nitrogens than on the other atoms of the phthalocyanine ring.

The increase in conductivity of copper phthalocyanine over metal-free phthalocyanine can be explained in terms of the increased π-electron flow through the center of the phthalocyanine molecule through positions of maximum overlap between parallel molecules.

211. EFFECTS OF BULK AND SURFACE CHARGE-TRANSFER COMPLEXING ON THE CONDUCTIVITIES OF ORGANIC CRYSTALS [ABSTRACT]

Labes, M. M.
In "Program and Abstracts: Organic Crystal Symposium,
October 10–12, 1962," pp. 190–194
National Research Council, Ottawa, Canada, 1962

The effect of exposure to iodine, water, sulfur dioxide, oxygen, hydrogen chloride and nitrogen dioxide on the bulk dark conductivity of anthracene was examined. To establish the generality of the gas–solid interaction observed, the case of an electron-acceptor crystal interacting with an electron-donor gas was investigated, using a single crystal of chloranil in amine vapors. Results of the experiments are reported. A four-probe technique for resistivity measurement is described.

212. ELECTRONIC PROPERTIES OF TCNQ ANION RADICAL SALTS [ABSTRACT]

Siemons, W. J.
In "Program and Abstracts: Organic Crystal Symposium,
October 10–12, 1962," pp. 195–197
National Research Council, Ottawa, Canada, 1962

Thermal-EMF and electrical resistivity measurements were made as a function of temperature on a large number of organic salts formed from the radical of tetracyanoquinodimethane (TCNQ) and various cations. In general, the activation energy of conductivity, thermal EMF and electrical resistivity show the same order of increasing magnitude in the various compounds. They can be classified roughly into three groups. The first group has electrical conductivity high (> 10^{-2} ohm^{-1}cm^{-1}), thermal EMF low (< 100 μv/°C), and activation energy of conductivity low (< 0.1 ev). The compounds in this group have temperature independent paramagnetism. The second has electrical conductivity medium ($10^{-3 \text{ to } -1}$ ohm^{-1} cm^{-1}), thermal EMF variable (0–1250 μv/°C), and activation energy of conductivity medium (0.1–0.3 ev). The compounds in this group have paramagnetism as a result of a low-lying triplet state. The third group has electrical conductivity medium to low ($< 10^{-2}$ ohm^{-1}cm^{-1}), thermal EMF medium to high (> 200 μv/°C), and activation energy of conductivity medium to high (> 0.2 ev). The compounds in this group are diamagnetic or have only a small amount of paramagnetism.

Most of the samples were compacted powders. Single crystal measurements were only made on $[(C_2H_5)_3NH]$ $(TCNQ)_2$. $[(C_6H_5)_3As(CH_3)]$ $(TCNQ)_2$ and $Cs_2(TCNQ)_3$, all belonging to the second group. The effects of compacting and of impurities were investigated.

It was concluded that both holes and electrons acted as carriers.

213. CONDUCTIVITY AND THERMOELECTRICAL POTENTIAL MEASUREMENTS ON PERYLENE: METAL-HALIDE COMPLEXES [ABSTRACT]

Frant, M. S., Eiss, R.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," p. 198
National Research Council, Ottawa, Canada, 1962

The effect on the conductivity and Seebeck coefficients of changing the nature of the metal halide acceptor has been studied in a series using perylene as the donor. Complexes have been formed with acceptors from groups IIB, IIIA, IVA, VA, VB, VIB, VIIA, and VIII of the Periodic Table. In a more detailed study of a single compound, it was found that perylene·$FeCl_3$ could be prepared as either *n*- or *p*-type depending on the initial reactant ratio, with the perylene-rich material showing *p*-type properties.

214. CONDUCTION IN NUCLEIC ACID COMPONENTS [ABSTRACT]

Eley, D. D., Leslie, R. B.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 199–202
National Research Council, Ottawa, Canada, 1962

In order to gain further insight into the conduction mechanism, the authors have investigated the units used in building up the nucleic acids, namely, (1) the nucleotides—base-ribose-phosphate units which are the "monomers" of the molecular chains; (2) the nucleosides—base-ribose (or base-desoxyribose) units; and (3) the bases—adenine, thymine, guanine, cytosine and uracil.

All five bases gave difficulties due to sublimation, which still occurred even in a nitrogen atmosphere, and all that can be stated is that their specific resistivities were all around 10^{15} Ω cm at 400°K. Thermal decomposition effects were also difficult to avoid, but the observed resistivity is consistent with a predicted value of $\Delta\epsilon = 3$ ev for this group.

The nucleosides were found to have resistivities in the range 10^{12}–10^{13} Ω cm at 400°K, and to have high-energy gaps of 4.5–5.0 ev, but good results were obtained by using specially slow rates of cooling. The nucleotides, with resistivities generally in the range 10^{7}–10^{12} Ω cm (riboflavin had nearly 10^{14} Ω cm) and $\Delta\epsilon$ values of 2 ev, gave no experimental difficulties. The only exception to this grouping is guanosine, a nucleoside, with $\Delta\epsilon = 2.1$ ev. The results are tabulated. Theoretical explanation is offered.

215. THE ELECTRICAL CONDUCTIVITY AND THE HALL COEFFICIENT OF GRAPHITE

Sugihara, K., Sato, H.
***National Technical Report,* Matsushita Electric Industrial Co., Osaka, v. 7, pp. 254–257, 1961**

The electrical resistivity of graphite increases with temperature approximately proportional to $T^{1.2}$ up to liquid-N temperature. The Hall coefficient is strongly field-dependent. Theoretical explanation is offered. The lattice vibrations of graphite are divided into two modes, one on the layer plane and one parallel to the *c*-axis. The relation process is determined predominantly by the interaction of electrons with the former mode, and the coupling constant is five times as large as that of the latter mode.

216. BULK CONDUCTIVITY IN ORGANIC CRYSTALS

Kallmann, H. P., Pope, M.
***Nature,* v. 186, no. 4718, pp. 31–33, April 2, 1960**

In former experiments an anthracene crystal was provided with electrolyte electrodes. One electrode compartment was filled with 1 *M* sodium iodide solution saturated with iodine, while the other electrode compartment was filled with 1 *M* sodium iodide solution without iodine. The dark current which flowed when the iodine compartment was made electrically positive was 22 times that when the iodine compartment was negative and 80 times the dark current when neither compartment had any iodine. These results were explained by assuming that the iodine extracted an electron from the adjacent anthracene crystal, becoming an I^- ion, thereby injecting a positive hole into the anthracene

The energy balance is shown to be favorable for the extraction of an electron from the anthracene, and the injection of a positive hole into the anthracene. At the opposite electrode, the process is the discharge of the positive hole, similar to the discharge of an ion at a metal electrode, probably producing free iodine. The magnitude of the current ($i-$) which flows when the illuminated side of the crystal is at a negative potential is markedly affected by the nature of the electrode distant from the light, and in the same way that the positive current is affected; the $i-$ has almost the same dependence on the exciting light intensity as the positive current: both negative and positive currents are saturated at about the same voltage although at greatly different currents Most dark currents differ in behavior from the conductivity described in this communication.

217. ENHANCED SEMICONDUCTIVITY IN PROTEIN COMPLEXES

Davis, K. M. C., Eley, D. D., Snart, R. S.
***Nature*, v. 188, no. 4752, pp. 724–725, November 26, 1960**

An aqueous solution of bovine plasma albumin was shaken with *p*-chloranil, the excess *p*-chloranil filtered off, and the solution evaporated to form a bovine plasma albumin-chloranil complex film. Such a film contained a very small amount of chloranil, approximately 0.5%, corresponding to 3 chloranil molecules to 1 molecule of bovine plasma albumin. This plasma–chloranil film in the dry state had a room temperature resistivity of $3 \times 10^{12} \Omega$ cm and an energy gap of 1.06 ev, compared with values for a control dry film of bovine plasma albumin of $8 \times 10^{17} \Omega$ cm (extrapolated) and 2.80 ev. Thus, the chloranil has raised the specific conductivity of the protein by a factor 3×10^5. The bovine plasma albumin-chloranil complex showed a weak but definite electron resonance signal, with a g-value of 1.998 and a line-width of 6 gauss. There was no optical absorption or photoconductivity at a wavelength corresponding to the energy gap of 1.06 ev. Bromanil and iodanil complexes gave very similar results. Admission of water vapor at a vapor pressure chosen to give approximately a Brunauer–Emmett–Teller monolayer over the (relatively small) available surface of the bovine plasma albumin–chloranil complex gave a twelve-fold increase in resistivity. This is in marked contrast to the effect of water vapor in decreasing the resistivity of pure dry proteins, including bovine plasma albumin. These results may be explained on lines well known for inorganic semiconductors.

218. SEMICONDUCTIVITY IN HYDRATED HAEMOGLOBIN

Eley, D. D., Spivey, D. I.
***Nature*, v. 188, no. 4752, p. 725, November 26, 1960**

Hemoglobin is regarded as a model for a large class of oxidation enzymes where electron mobility may be of biological significance. In the dry state its very low specific conductivity, about $10^{-18} \Omega^{-1}$ cm^{-1} at 30°C, is attributed to electron and hole mobility in the CO. . . .HN bridge system. Water is adsorbed on natural, or methanol-denatured, hemoglobin, corresponding to a Brunauer–Emmett–Teller "*BET* monolayer volume" V_m of 319 moles/10^5 g protein, whereas a close-packed monolayer of water molecules over all the molecular surfaces throughout the crystal would involve 1,160 moles/10^5 g protein. The molecular dimensions for the latter calculation are taken from X-ray data which also show that water molecules do not penetrate within the actual molecules, but only over the molecular surfaces. A study has been made of the effect of adsorbed water on the semiconductivity of a solid specimen of methanol-denatured hemoglobin, allowing three days for equilibrium for each point. The result shows that there is a large increase in conductivity which reaches a constant value at about V_m. Thereafter, there is little change until a relative vapor pressure of about 0.9, corresponding to 4 V_m, when the conductivity increases sharply to about $10^{-8} \Omega^{-1}$ cm^{-1} at 30°C.

It is suggested that initially water molecules are held on special sites and donate electrons into the conductivity band of the protein molecule giving an *n*-type (negative) protein, where a high mobility is expected throughout the crystal. This view differs from that of Baxter, who suggested that electrons tunneled from one adsorbed water molecule to the next. It may be that the relatively marked effect of water on the conductivity of some polymers points to the operation of yet a third effect due to adsorbed water on flexible chain molecules containing CONH groups, that is, the plasticizing effect of water molecules on chain movement, facilitating transfer of protons between NH and CO groups in different chains, first described by Baker and Yager.

219. ELECTRONIC PROPERTIES OF IMIDAZOLE

Aftergut, S., Brown, G. P.
***Nature*, v. 191, no. 4786, pp. 379–380, July 22, 1961**

If the overlapping of molecular orbitals gives rise to semiconduction, then any other factors which contribute to such overlapping should also encourage semiconduction, even if only few π-electrons are present in the individual molecule. Since intermolecular hydrogen bonds may provide such overlap, it might be expected that activation energies in the hydrogen-bonded compounds should be lower than anticipated solely on the basis of the number of π-electrons.

Supporting evidence for this view has now been found in a study of the resistivity of imidazole. Imidazole is extensively hydrogen-bonded as adduced from its relatively high melting and boiling points and from its spectra. In the present work, imidazole was purified by several recrystallizations, distillation at reduced pressure, and zone-refining. The resistivity was measured as a function of temperature on a compacted polycrystalline sample, and the results are graphed. The energy gap computed from the equation $\rho = \rho_0 \exp(E/2kT)$ was 2.6 ev in the temperature range of 28–66°C. Slightly higher resistivities were obtained at a higher potential stress; it is not known whether this is a significant effect. Energy gaps ranging between 2.8 and 3.0 ev were obtained on several other samples which had not been as rigorously purified.

220. SEMICONDUCTIVITY OF CHLORPROMAZINE

Gutmann, F., Netschey, A.
***Nature*, v. 191, no. 4796, pp. 1390–1391, September 30, 1961**

Fifteen runs of heating and cooling cycles on four different samples gave a plot of log R vs. $1/T$ which shows five parts. From 34 to 80°C (m.p. 56–85°C) a continuous curve was obtained, corresponding to an activation energy of 2.1 ev. The discontinuity at 32°C, where the temperature coefficient of resistance reverses sign, is associated with a crystallographic change. (*PA*, 1961, #19,875)

221. ELECTRICAL PROPERTIES OF PHENOTHIAZINE

Brown, G. P., Aftergut, S.
***Nature*, v. 193, no. 4813, pp. 361–362, January 27, 1962**

As part of an investigation on the mechanism of conduction of organic substances, the dependence on temperature of the electrical resistivity of phenothiazine has now been investigated. Resistivity measurements have been carried out on a number of specimens of the same substance in various stages of purification. These measurements were made on disks of polycrystalline materials which had been compacted under pressure prior to the measurements.

In the present work, phenothiazine was purified by chromatography, multiple vacuum sublimations and zone-refining. Results obtained at potential stresses of 76 and 760 v/cm on a sample of phenothiazine which had been chromatographed, sublimed, zone-refined and resublimed are presented in a graph, as are the results for a sample purified by chromatography and one sublimation. Using the equation $\rho = \rho_0 \exp(E \; 2kT)$, where ρ is the specific resistivity at absolute temperature T, the energy gap E was computed as 1.6 ev over the temperature range of 50–150°C. The values for resistivity were reproducible and followed Ohm's law.

Failure of the sublimed samples to show ohmic resistivity is tentatively attributed to impurities, and on this basis the value of the energy gap, 1.6 ev, of the zone-refined material would appear to be the more reliable one. Work is continuing in order to confirm this value and to clarify the nature of the possible impurities involved in the behavior of the sublimed samples; details of this work will appear elsewhere.

222. ELECTRICAL CONDUCTIVITY OF PROTEINS

Rosenberg, B.
***Nature*, v. 193, no. 4813, pp. 364–365, January 27, 1962**

A 1.0 mg sample of powdered crystalline bovine hemoglobin (salt-free) was placed between electrodes in a specially prepared and dried conductivity cell. The thickness of the pressed sample was 75 μ, and 45 v dc was applied while the temperature was kept constant (±0.1°C) at 6.5°C. After an initial fall in the current, a steady state was obtained and thereafter the current remained constant, showing that the process of conduction is almost purely electronic. If ionic conduction played any appreciable part, water would have been electrolyzed and the current would have fallen as the time increased. (*PA*, 1962, #8301)

223. MOBILITY OF IONS IN LIQUID DIELECTRICS

Czowski, O.
***Nature*, v. 194, no. 4824, p. 173, April 14, 1962**

Measurements of the mobility of negative and positive ions produced by means of X-rays in *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, and mixtures of *n*-octane–*n*-hexane and *n*-decane–*n*-hexane in the temperature range 8–50°C were made by the layer method. All the liquids investigated had a residual conductivity $k \leq 10^{-19}\ \Omega^{-1}\ \text{cm}^{-1}$. The viscosity ($\eta$) was measured using Hoeppler and Arrhenius viscosimeters. The mobility of negative ions in all the above liquids is greater than that of the positive ions. The transit time of the front edge of the negative ion layer is sharply defined, indicating the existence of ions with small diffusion velocity. The diffuse velocity spectrum for positive ions showed that several kinds of ions were present. The negative ion mobility (u) is expressed by $u = \beta\eta^{-1}$ in agreement with Stokes's law, and that of the positive ion by $u = A\eta^{-3/2}$, where $A = 1.2 \times 10^{-7}$ cm^2/v sec poise $^{2/3}$. (*PA*, 1962, #15,612)

224. ELECTRON-DONATING PROPERTIES OF CENTRAL SYMPATHETIC SUPPRESSANTS

Lyons, L. E., Mackie, J. C.
***Nature*, v. 197, no. 4867, p. 589, February 9, 1963**

Electron-transfer reactions between organic substances have often been implicated in various biological processes. Recently, Karreman, Isenberg, and Szent-Györgi have suggested that certain central sympathetic suppressants act by donating electrons on the inside of the electric double layer of the central nervous system. A consequence of this hypothesis would be that pharmacologically active substances should possess relatively low ionization potentials. Though the direct measurement of ionization potential is quite difficult, it is nevertheless possible to derive values of this quantity from photoelectric measurements on the solid.

The following table presents I_C and I_G (threshold energy) for several central sympathetic suppressants and for one pharmacologically inactive substance:

	I_C(ev)	I_G(ev)
Phenothiazine[a]	5.14 ± 0.05	6.7
Promazine	5.16 ± 0.05	6.8
Promazine hydrochloride	5.46 ± 0.05	7.1
Chlorpromazine	5.08 ± 0.05	6.7
Chlorpromazine hydrochloride	5.22 ± 0.05	6.8
Trifluoperazine dihydrochloride	5.68 ± 0.10	7.3
Prochlorperazine	5.45 ± 0.10	7.1
Reserpine	5.40 ± 0.05	7.0

[a] Inactive pharmacologically

The measurements indicate that these substances have striking electron-donating properties.

225. DIE ELEKTRISCHEN UND THERMOELEKTRISCHEN EIGENSCHAFTEN VON PHTHALOCYANINEN (ELECTRICAL AND THERMOELECTRIC PROPERTIES OF PHTHALOCYANINES)

Hamann, C., Storbeck, I.
***Naturwissenschaften*, v. 50, p. 327, 1963**

Phthalocyanines were prepared, pressed at 4000 atm, and contacted with Cu or Ag powder.

The following data came from measurements in N:

	Form	Resistivity (ohm-cm)	Activation energy (ev)	Thermo-electric power μv/°C	Type of conduction
$H_2C_{32}H_{16}N_8$	α-	790×10^7	0.71	1250	p-type
	β-	42×10^{12}	0.87	670	p-type
$CuC_{32}H_{15}ClN_8$	α-	1×10^7	0.30	910	p-type
	β-	2×10^{13}	0.78	1170	p-type
$NiC_{32}H_{16}N_8$	α-	14×10^7	0.60	970	p-type
	β-	40×10^{13}	1.14	1280	p-type
$ZnC_{32}H_{16}N_8$	α-	4.7×10^7	0.43	960	p-type
	β-	0.043×10^{13}	0.72	1750	p-type
$InClC_{32}H_{15}ClN_8$	β-	3.8×10^{12}	0.82	1610	n-type

Resistivity and activation energy of p-conductors were sensitive to C partial pressure. Activation energies of α-forms changed at 100-150°C.

226. ELECTRON SPIN RESONANCE OF TWO BENZIDINE COMPLEXES IN WEAK FIELDS

Roest, R., Poulis, N. J., Horsman, G.
***Physica*, v. 28, no. 1, pp. 15–20, 1962 (in English)**

Measurements were carried out on the electronic spin concentration in two molecular complexes of benzidine, both of which have semiconducting properties. The widths of the absorption curves increase rapidly with decreasing temperature. Activation energy for conversion of conducting to nonconducting states are 0.08 and 0.23 ev for the two complexes.

227. ELEKTRISCHEN EIGENSCHAFTEN DÜNNER BENZOLPOLYMERISAT- UND KOHLEAUFDAMPF-SCHICHTEN (ELECTRICAL PROPERTIES OF THIN BENZENE POLYMER AND CARBON EVAPORATION LAYERS)

Pagnia, H.
***Physica Status Solidi*, v. 1, pp. 499–511, 1961**

In order to learn the conducting mechanisms of the higher conductivity shown by these organic films when coked, thin carbon layers, varying in composition from H-free benzene polymers to practically pure C, were prepared by three processes: (1) by glow discharge in a benzene atmosphere, yielding layers with specific electrical resistances of 10^{10}–10^{-2} ohm-cm depending on the hydrocarbon used; (2) by evaporation of C by the Bradley process in which layers were condensed on various hot bases, giving specific resistances of 1–10^{-2} ohm-cm; and (3) by pyrolytic decomposition of gasoline in a tube furnace at 1300°K with resultant specific resistance of 2×10^{-3} ohm cm. All samples showed increasing electrical conductivity with increasing temperature. Activation energies of 1–0.02 ev were calculated for benzene polymer and carbon vaporization deposit layers; as the activation energy increased, the conductivity decreased. The thermal power and the Hall coefficients were also measured. The pyrolytic C layer had a negative Hall constant. Not all observations could be explained quantitatively with a simple model of homogeneous semiconductor. 25 references.

228. EFFET HALL ET MOBILITÉ DES PORTEURS DE CHARGE DANS UN CRISTAL MOLÉCULAIRE (PHTALOCYANINE DE CUIVRE) (HALL EFFECT AND MOBILITY OF CHARGE CARRIERS IN A MOLECULAR CRYSTAL, COPPER PHTHALOCYANINE)

Delacote, G., Schott, M.
***Physica Status Solidi*, v. 2, no. 11, pp. 1460–1465, 1962**

The Hall effect was measured in a molecular crystal, in the temperature range 400–600°K. The Hall mobility is of the order of 100 cm²/v sec. The charge carriers are holes. This result shows that the usual model of free carriers in energy bands can be applied to some molecular crystals. (*PA*, 1963, #2911)

229. CARRIER DENSITIES AND MOBILITIES IN PYROLYTIC GRAPHITE

Klein, C. A., Straub, W. D.
***Physical Review*, v. 123, no. 5, pp. 1581–1583, September 1, 1961**

Based on conductivity, Hall effect, and magnetoresistance measurements, an attempt is made to describe the behavior of current carriers in the layer planes of well-ordered pyrolytic graphite. The total carrier concentration decreases from approximately 11×10^{18} cm^{-3} at room temperature to less than 4×10^{18} cm^{-3} at very low temperatures, in good agreement with single-crystal results. The average mobility, which is strongly dependent upon the crystallite size, was found to exceed 3000 cm² v^{-1} sec^{-1} at liquid nitrogen temperature in specimens deposited at 2500°C; the mobility ratio (μ_e/μ_h) appears to remain temperature independent and equal to 1.08 ± 0.01. (*PA*, 1961, #12,447)

230. EVIDENCE OF SINGLE-CRYSTAL CHARACTERISTICS IN HIGHLY ANNEALED PYROLYTIC GRAPHITE

Klein, C. A., Straub, W. D., Diefendorf, R. J.
***Physical Review*, v. 125, no. 2, pp. 468–470, January 15, 1962**

It is demonstrated that massive specimens of pyrolytic graphite heat-treated at 3600°C may exhibit electrical characteristics comparable to those of the best single crystals presently available. Low-field magnetoresistance data taken perpendicularly to the c-direction of these specimens yield average carrier mobilities (1.3×10^4 cm²/v sec at 300°K; up to 8×10^5 cm²/v sec at 4.2°K) in substantial agreement with Soule's and McClure's results for the layer planes of highly purified natural graphite. In conjunction with temperature dependence studies of the zero-field resistivity, it is found that the carrier density reproduces the theoretically predicted behavior down to 77°K, but departs at lower temperatures. Plausible interpretations of this discrepancy and of the "knee" in the resistivity curve are briefly discussed. (*PA*, 1962, #4035)

231. MEASUREMENT OF THE HALL EFFECT IN METAL-FREE PHTHALOCYANINE CRYSTALS

Heilmeier, G. H., Warfield, G., Harrison, S. E.
***Physical Review Letters*, v. 8, no. 8, pp. 309–311,**
April 15, 1962

Experimental techniques for the measurement of the Hall coefficient of organic semiconductors of very low electrical conductivity are described and the results of measurements on single crystals of metal-free phthalocyanine are reported. The results are interpreted on the assumptions that only one type of carrier is mobile, the band model is applicable, and the conductivity is isotropic. A table is given showing the values of the measured and the corrected Hall voltages, Hall coefficient, carrier concentration, Hall mobility and the sign of the carriers. The sign of the Hall voltage is explained using the molecular model of the crystal. (*PA*, 1962, #16,730)

232. ELECTRONIC CONDUCTION OF POLYMER SINGLE CRYSTALS

Van Roggen, A.
***Physical Review Letters*, v. 9, no. 9, pp. 368–370,**
November 1, 1962

The current–voltage characteristics of microcrystals of polyethylene were measured. Electrical contact with the crystals was made by means of a metallic support and a cat's whisker. The characteristics show rectification and negative resistance regions, dependent on the composition of the metallic contacts and the structure of the polyethylene crystals. (*PA*, 1963, #8558)

233. RADIATION DAMAGE IN WELL ORIENTED PYROLYTIC GRAPHITES

Blackman, L. C. F., Saunders, G., Ubbelohde, A. R.
***Physical Society, Proceedings of the*, London, v. 78, pt. 5 (ii),**
pp. 1048–1055, November 15, 1961

Graphite formed by cracking methane under various conditions was exposed to neutron irradiation. Changes in electronic properties were measured: (1) after radiation damage by neutron doses of the order 10^{17} neutrons/cm^2; (2) after "mild" annealing around 470°C; and (3) after "strong" annealing at 2200°C and above. Effects of radiation damage are proportionately greatest in specimens whose properties are initially nearest to those of ideal graphite. Some discrimination can be made between the types of disorder originally present, and the disorder added by irradiation. Changes of thermoelectric power of graphite in the direction of the c-axis show "latent" increases attributed to disorder frozen in until after mild annealing. (*PA*, 1962, #614)

234. ELECTRIC ZERO-INDICATOR APPARATUS FOR THE MEASUREMENT OF ELECTRICAL CONDUCTIVITY OF POLYMERS (POLYELECTROLYTES)

Batyuk, V. P., Rybalka, K. F., Gordienko, S. A.
***Plasticheskie Massy*, no. 4, pp. 61–64, April 1962**
(Translated from the Russian in *Soviet Plastics*, no. 4,
pp. 55–58, April 1962)

The present article describes work on measuring the resistivity of a solution of polyelectrolytes (polymers) by an "alternating-current bridge," providing separate measurement of the active and reactive parts of a complex resistance. In developing measuring apparatus, attention was paid mainly to ensuring maximum sensitivity and the requisite accuracy. Simplified bridge circuits with no balancing of the reactive components are too crude, and the requisite sensitivity and accuracy can be obtained only by a carefully constructed "ac bridge," i.e., a bridge circuit with separate adjustment of the active and reactive components. Furthermore, to obtain high sensitivity the selection of a null-indicator, i.e., a device indicating the degree of out-of-balance of the bridge, is important. The best results are considered to be given by frequency-sensitive null-indicators which eliminate various sources of interference and the effect of harmonics in the output signal of the bridge circuit. Such a null-indicator was used to improve the sensitivity of the bridge and increase the accuracy of the apparatus. Such an indicator is also essential because, to give the requisite sensitivity, an amplifier with a sufficiently high amplification must be incorporated in its circuit. The null-indicator with the apparatus for determining conductivity can be used to characterize the aggregate composition of soil and determine its connection with the mobility of nutrients in a soil solution. Other applications are mentioned.

235. SEMICONDUCTION IN PHTHALOCYANINE: A STUDY IN ORGANIC SEMICONDUCTION

Heilmeier, G. H.
1962
Princeton University, N. J.
Thesis
(Microfilm available as Mic 63-526, University Microfilms,
Ann Arbor, Mich.)

This work is a study of the semiconduction properties of the organic molecular crystal, phthalocyanine. The band model is shown to be applicable to this material, and the conduction band is found from optical absorption data to consist of a series of bands of width 0.56 kT (0.014 ev) separated by 0.049 and 0.12 ev. The optical absorption spectrum of the crystals retains much of the characteristic spectrum of the isolated molecule due to the relatively weak intermolecular binding forces. The importance of the first excited singlet state in the conduction process is emphasized by the equality of the edge for optical absorption and photoconductivity and the thermal activation energy for dark conductivity.

The spectral response for photoconductivity is found to be the same as the optical absorption spectrum. Further evidence is presented for the production of carriers by incident radiation in a direct process rather than through the intermediate formation of excitons. The photocurrent as a function of extinction coefficient is calculated for the case of non-zero surface recombination velocity. Application of this relationship together with the effective carrier lifetime determined from photoconductivity shows that the carriers are created more than a diffusion length from the surface. Hence the measured lifetime should be characteristic of the bulk. This lifetime is shown to be of the same order as the lifetime of the carriers in the first excited singlet state, thus further emphasizing the role of this level in the conduction process.

From theoretical considerations of the conductivity and Hall effect in narrow band semiconductors, the mobility is expressed as a function of the width of the band and of the lattice spacing. The Hall effect was measured by integrating out the effects of noise, and a carrier density of $2\text{–}12 \times 10^6/\text{cm}^3$ and a mobility of $0.1\text{–}0.4 \text{ cm}^2/\text{v sec}$ were found.

Bulk currents were measured in single crystals using guard ring electrodes. The I-V characteristic is linear up to fields of 10^4 v/cm, and then becomes square law. If this behavior is attributed to space-charge-limited currents, the temperature dependence indicates the presence of traps of depth 0.8 ev and of concentration $10^{14}/\text{cm}^3$. This interpretation predicts a room temperature free carrier density of $8 \times 10^6/\text{cm}^3$ from the transition voltage between ohmic and square law behavior. This density is in agreement with that found from the Hall effect measurements. (*DA*, 1962)

236. HIGH POLYMER RESEARCH
Rahm, L. F.
August 1, 1959
Princeton University, Plastics Lab., N.J.
Quarterly Status Report 54 for May 1–July 31, 1959,
DA 36-039-sc-78105
AD-266,372

Doped polymer carbon semiconductors are included as a part of one section of the report.

237. HIGH POLYMER RESEARCH
Rahm, L. F.
November 1, 1959
Princeton University, Plastics Lab., N.J.
Quarterly Status Report 55 for August 1–October 31, 1959,
DA 36-039-sc-78105
AD-230,916

Aluminum doping in high polymers was found to decrease conductivity.

238. HIGH POLYMER RESEARCH
Rahm, L. F.
February 1, 1960
Princeton University, Plastics Lab., N.J.
Quarterly Status Report 56 for November 1, 1959–
January 31, 1960, Report 5, DA 36-039-sc-78105
AD-234,610

Semiconduction in high polymers is included as one section of the report.

239. HIGH POLYMER RESEARCH
Rahm, L. F.
May 1, 1960
Princeton University, Plastics Lab., N.J.
Quarterly Status Report 57 for February 1–April 30, 1960,
Report 6, DA 36-039-sc-78105
AD-239,173

This report deals in part with both semiconduction and dielectric behavior of high polymers.

240. HIGH POLYMER RESEARCH
Rahm, L. F.
August 1, 1960
Princeton University, Plastics Lab., N.J.
Quarterly Status Report 58 for May 1–July 31, 1960,
Report 7, DA 36-039-sc-78105
AD-243,943

Polymers as semiconductors and dielectrics are included.

241. HIGH POLYMER RESEARCH
Rahm, L. F.
November 1, 1960
Princeton University, Plastics Lab., N.J.
Quarterly Status Report 59 for August 1–October 31, 1960,
Report 8, DA 36-039-sc-78105
AD-248,981

Semiconduction and dielectric behavior of polymers are included among the topics discussed.

242. HIGH POLYMER RESEARCH
Rahm, L. F.
February 1, 1961
Princeton University, Plastics Lab., N.J.
Quarterly Status Report 60 for November 1, 1960–
February 1, 1961, Report 9, DA 36-039-sc-78105
AD-253,073

The chemical section contains information on Ziegler polymerization of nonconjugated double bond systems, directional hydrogen bonding–property relationships in polyamides, ferrocene chemistry, and intramolecular π-hydrogen bonding. In the dielectrics section semiconduction in high polymers, melt behavior of sheared high polymers, and stereoregularity and dielectric behavior of high polymers are discussed. Mechanical properties are also considered in a third section.

243. HIGH POLYMER RESEARCH
Rahm, L. F.
June 1, 1961
Princeton University, Plastics Lab., N. J.
Quarterly Status Report 61 for February 1–June 1, 1961,
Report 10, DA 36-039-sc-78105
AD-260,185
(Also available through U.S. Dept. of Commerce, Office of Technical Services, Washington, D.C.)

The topics considered are: polymerization of nonconjugated double bond systems, directional hydrogen bonding–property relationships in polyamides, and ferrocene chemistry; semiconduction in high polymers, and melt behavior of sheared high polymers; dynamic mechanical properties of polyolefins, polymer melt elasticity, and low temperature properties of polypropylene.

244. HIGH POLYMER RESEARCH
Rahm, L. F.
December 1, 1961
Princeton University, Plastics Lab., N.J.
Quarterly Status Report 63 for September 1–November 30, 1961, Report 1, DA 36-039-sc-89143
AD-270-961
(Also available through U.S. Dept. of Commerce, Office of Technical Services, Washington, D.C.)

Polyacene quinone radical polymers exhibited changes in conductivity and thermal activation energy upon application of the pressure ranges used by Bridgman for metals. There was a 100-fold change in conduction.

245. HIGH POLYMER RESEARCH
Rahm, L. F.
July 16, 1962
Princeton University, Plastics Lab., N.J.
Final Report for March 1–July 15, 1962, Report 65, DA 36-039-sc-89143
AD-284,382
(Also available through U.S. Dept. of Commerce, Office of Technical Services, Washington, D.C.)

Semiconduction in high polymers is included in the report.

246. FURTHER STUDIES OF SOME SEMICONDUCTING POLYMERS
Bornmann, J. A., Pohl, H. A.
September 10, 1961
Princeton University, Plastics Lab., N.J.
Technical Report 63A, DA 36-039-sc-78105
AD-264,772
(Also available through U.S. Dept. of Commerce, Office of Technical Services, Washington, D.C.)

The structure of certain semiconducting polymers was studied by means of conductivity and infrared measurements. The polymers are formed by the reaction of aromatic hydrocarbons with acids or acid anhydrides. The conductivities of various alternate polymers indicate that it can be concluded that the polymers prepared using phthalic anhydride are not poly(aromatic) ketones, but possibly quinoid or lactone structures. A variety of new polymers showing electronic semiconduction was prepared using either phenanthrene or anthracene and various organic acidic compounds such as acids, acid anhydrides, acid chlorides, and imides.

247. RESISTIVITY STUDIES ON POLYMER SEMICONDUCTORS
Gogos, C. G., Pohl, H. A.
November 1, 1961
Princeton University, Plastics Lab., N. J.
Technical Report 63B, DA 36-039-sc-89143, DA 36-039-sc-78105
AD-266,707
(Also available through U.S. Dept. of Commerce, Office of Technical Services, Washington, D.C.)

Eighteen polyacene polymers were synthesized and their resistivities were found to be of the order of 10^4 to 10^5 ohm-cm. Resistivity of these polymer semiconductors was found sensitive to changes in synthesis conditions, changes in the structure of the polymers, and variations of pressure and temperature during experimentation. The forbidden energy gaps for these polymers was about 0.5 ev. 17 references.

248. SYNTHESIS AND CHARACTERIZATION OF SOME HIGHLY CONJUGATED SEMICONDUCTING POLYMERS
Engelhardt, E. H., Pohl, H. A.
January 1, 1962
Princeton University, Plastics Lab., N.J.
Technical Report 64A, DA 36-039-sc-89143, DA 36-039-sc-78105
AD-273,723
(Also available through U.S. Dept. of Commerce, Office of Technical Services, Washington, D. C.)

A series of highly conjugated, semiconducting polymers was synthesized and electronically characterized. The conductivities of polymers produced ranged from approximately 10^{-3}–10^{11} mho cm at room temperature. A correlation between conductivity in PAQR polymers and the size of the aromatic hydrocarbon monomer was established. Thermoelectric power measurements and a Hall determination generally indicated *p*-type conductivity in the polymers. Additional electrical determinations included: thermal activation energy of conduction, ohmic behavior, carrier species, electron spin density, thermal and chemical stability, and photo-electrical effects. The electronic nature of conduction in the polyacene quinone radical polymers was proven by observing a large (positive) Hall coefficient, and the stability of conduction to large charge passage. Non-ohmic behavior was observed at low electric field strengths. 54 references.

249. SEMICONDUCTION IN METAL-DOPED PYRO-POLYMERS
Rosen, S. L., Pohl, H. A.
January 15, 1962
Princeton University, Plastics Lab., N. J.
Technical Report 64B, DA 36-039-sc-89143, DA 36-039-sc-78105
AD-273,724
(Also available through U.S. Dept. of Commerce, Office of Technical Services, Washington, D.C.)

The electronic properties of pyrolysis products of Na-, Ca- and Th-doped ion-exchange resins were investigated. The resulting pyro-polymers were degenerate semiconductors whose resistivities decreased from approximately 0.1 to 0.01 ohm-cm as the pyrolysis temperature increased from 800 to 1200°C. Resistivities were altered roughly by a factor of 2 with appropriate doping. The materials exhibit the negative resistivity-temperature behavior common to semiconductors, and have small (0.005 to 0.05 ev) energy gaps. Small, negative (0 to -0.05 cc/coulomb) Hall coefficients were observed. Carrier concentrations were estimated at approximately $1\text{–}3\times10^{20}$/cc, with mobilities of 1–4 cm^2/v sec. 27 references.

250. ELECTRONIC PROPERTIES AND STRUCTURE IN CONJUGATED POLYMERIC SYSTEMS

Chartoff, R. P., Cappas, C.
February 15, 1963
Princeton University, Plastics Lab., N.J.
Technical Report 66D, DA 31-124-ARO (D)-21

The relation between chemical structure and electronic properties for three classes of organic polymers with systems of conjugated double bonds was studied. The three classes include linear polyalkynes, wholly aromatic polybenzimidazoles, and highly cross-linked polyacene quinone radical (PAQR) polymers.

The wide range of electronic properties observed for these polymers lends support to the view that (1) highly conjugated polymer molecules exist in the form of stable biradicals, and (2) the enhanced electronic behavior of these materials is directly related to the biradical population which may be observed by electron spin resonance spectroscopy.

Infrared absorption spectra were obtained for several PAQR polymers by the KBr pressed disk technique, and a structure consistent with spectroscopic and chemical evidence has been proposed for phenolphthalein PAQR polymers.

251. PIEZO-RESISTIVE CHARACTERISTICS OF SOME ORGANIC SEMICONDUCTING POLYMERS

Henry, A. W., Cappas, C.
April 15, 1963
Princeton University, Plastics Lab., N.J.
Technical Report 67A, DA-31-124-ARO (D)-21

A series of highly conjugated polymers with semiconducting characteristics was examined to determine the piezoresistive behavior. The resistivities, ranging from 10^2 to 10^{11} ohm-cm at room temperature and 1840 atm. pressure, decreased 100-fold (and for some polymers, 1000-fold) as the pressure was increased to 35,000 atm.

Elimination of voids and particle-to-particle contact problems was obtained by the extreme pressures used, as evidenced by: (1) absence of hysteresis in the piezo-resistivity, and (2) low measured permeation rate to air.

A correlation between the extrapolated activation energy for the PAQR polymers and the number of fused rings in the aromatic portion of the polymer was obtained.

An elemental polymeric semiconductor with high conductivity (i.e., *p*-type tellurium) was also observed to have a decreasing thermoelectric power with increased pressure and a relatively constant activation energy, both due to the *p*-type TeO_2 impurity.

252. MOLECULAR STRUCTURE PARAMETERS IN CERTAIN SEMICONDUCTING POLYMERS

Kho, J. H. T., Cappas, C.
June 15, 1963
Princeton University, Plastics Lab., N.J.
Technical Report 67B, DA-31-124-ARO (D)-21

Three series of highly conjugated PAQR semiconducting polymers were synthesized and their electronic behavior studied. The effects of the following variables on the electrical properties of the PAQR polymers were examined: (1) hydrocarbon portion of the polymers, (2) acidic portion of the polymers, (3) copolymerization and mole ratio of starting monomers, (4) metallic salt formation, and (5) pressure and temperature.

Correlations between structural parameters and macroscopic properties were established. Room temperature resistivity was found to be indirectly dependent on the number of fused rings of monomer, ionization constant of acidic monomer, square root of pressure applied, and directly on the energy interval of all the PAQR polymers studied. Relations between number of fused rings of monomer and the following properties were also found: pressure coefficient of resistivity, energy interval, and resistivity at infinite temperature. Pressure coefficient of resistivity was found to be a direct function of the energy interval of the polymers. Spin concentration varies directly with carrier concentration and indirectly with room temperature resistivity of the PAQR polymers.

For the PAQR polymers studied, room temperature resistivities range from 10^2 to 10^{12} ohm-cm. Seebeck coefficients range from 0.05 to 66.1 μv/°C, and spin concentrations range from 10^{17} to 10^{19} spins/g.

253. ELECTRONIC CONDUCTION IN SOME POLYMERIC SYSTEMS

Krebs, J. A., Cappas, C.
June 30, 1963
Princeton University, Plastics Lab., N. J.
Technical Report 67C, DA-31-124-ARO (D)-21

The main features of electronic conduction in organic substances have been reviewed. Experiments were made to characterize semiconductivity in powdered polyacenes and in amorphous polyphenylacetylene. The influence of various factors such as the number of fused rings per monomeric unit, the introduction of monomers with carbonyl groups, and the introduction of heteroaromatic monomers has been studied. Spin concentration and mobilities of some typical samples were measured. The classical band theory was reviewed to determine its applicability to organic polymers. Some new ideas on the theory of polymer conduction were developed.

254. ELECTRICAL CONDUCTIVITY OF SOLID ORGANIC COMPOUNDS

Htoo, M. S.
1961
Rensselaer Polytechnic Institute, Troy, N.Y.
Thesis
(Microfilm available as Mic 61-3945, University Microfilms, Ann Arbor, Mich.)

The history of electrical conductivity measurements on solid organic compounds such as proteins, dyes, polymers, organic fibers, organic crystals, and organic molecular complexes was reviewed. On the basis of this information, it was decided to limit the investigation to white or colorless organic powders since very little data have been reported in this area.

A special three-electrode assembly for measuring electrical conductivity of organic powders was designed and constructed. The design was a modification of the method developed by Amey for plastic materials. By using this method, it was possible to measure both volume and surface resistivity values on the same sample.

More than 100 organic powders, including saturated aliphatic compounds, unsaturated aliphatic compounds, mononuclear cyclic compounds, polynuclear cyclic compounds, heterocyclic compounds, monomers (for polyelectrolytes), and organometallic compounds, were used for initial conductivity measurements. The purpose was to screen out compounds of very high electrical resistivity and to select low resistivity compounds for further study.

The effects of relative humidity, temperature, applied voltage, and chemical structure on the electrical conductivity of the selected organic compounds were investigated.

There was a correlation between the mechanism of conduction of the material and its electrical conductivity change with relative humidity. Electrical conductivity of compounds possessing ionic conductivity changed with relative humidity. On the other hand, organic compounds reported to be electronic conductors had constant electrical conductivity regardless of relative humidity conditions.

There was no consistent correlation between the electrical conductivity and chemical structure of organic compounds. Impurities appeared to cause greater changes than chemical structure in electrical conductivity.

Four new organic semiconductors ($< 10^{10}$ ohm cm in volume resistivity) were discovered. They were *p*-bromobenzophenone, *p*-chlorobenzophenone, 2,4′-dichlorobenzophenone, and *p*-bromoacetophenone. All of these except *p*-bromobenzophenone were white; *p*-bromobenzophenone was tan. These compounds lost their electrical conductivity on recrystallization, indicating that they were impurity or extrinsic semiconductors.

The thermal activation energy of conduction for the four new semiconductors ranged from 0.38 ev for *p*-bromoacetophenone to 1.06 ev for *p*-bromobenzophenone. This was in good agreement with values reported in literature for other organic semiconductors.

Electrical conductivity measurements made at varying applied voltage levels indicated that Ohm's law was valid within the voltage range of approximately 30 to 1600 v cm^{-1}. (*DA*, 1961)

255. TEMPERATURE DEPENDENCE OF THE ELECTRIC CONDUCTION OF NYLON 6

Nakajima, T., Torii, K.
***Reports on Progress in Polymer Physics in Japan*, v. 5, pp. 209–210, 1962 (in English)**
(Available through Kobayasi Institute of Physical Research, Kokubunji, Tokyo, Japan)

Among a number of crystalline high polymeric substances, nylon 6 (polycaproamide) containing hydrogen bonds between amide groups is, from the electric point of view, the most interesting material. In order to obtain some information about the molecular processes which are responsible for the electrical conduction, a preliminary investigation of conduction was carried out.

Measurements were made in the 0 to 130°C temperature range as temperature increased at the rate of about 0.2 to 0.5°C/min, and at constant electric field of about 10^4 v/cm. The logarithm of current at constant field vs. $1/T$ is shown. The sample was used at 24-hr intervals *in vacuo*. It was found that the current decreases slowly at constant temperature. Logarithm of current vs. $1/T$ curves satisfy a relation $\sigma = \sigma_0 \exp(-E/kT)$.

The effect of water content is noted, and the activation energy E evaluated in the three temperature regions. Two types of conduction mechanisms are suggested. Photoconductive phenomena in nylon 6 will be reported elsewhere.

256. SEMICONDUCTIVITY OF POLYACETYLENE

Hatano, M., Sera, N., Kambara, S., Okamoto, S.
***Reports on Progress in Polymer Physics in Japan*, v. 5, pp. 211–214, 1962 (in English)**
(Available through Kobayasi Institute of Physical Research, Kokubunji, Tokyo, Japan)

High-molecular-weight crystalline or amorphous polyacetylenes have been obtained from acetylene by the use of various catalyst systems of the Ziegler-Natta and other types. It was supposed that the resultant polyacetylene had a stereoregular structure of substantially transconjugated C–C double bonds. Since it was expected that these polymers having long conjugated systems might behave as a semiconductor, the electrical conductivity and its temperature dependency for these polymers were measured. Measurements were made in nitrogen to avoid oxidation and resultant rise in resistance.

The electrical resistance was measured by the direct current produced by a known applied potential. By using a lever system, the specimen was compressed between two metal electrodes under a pressure of up to 160 kg/cm^2. The dimensions of the specimen were between 0.1 and 0.3 cm in height and 0.503 cm^2 in cross section. The cell, together with a thermometer, was placed in a thermostat which was heated at the rate of approximately 0.5°C/min.

The relation between electrical resistivity ρ and applied pressure p can be written as

$$\rho = a + b/\sqrt{p}$$

and the formula is analogous to that for carbon black. The resistivity was approximately constant above 140 kg/cm^2, and values measured at 160 kg/cm^2 were tabulated. The temperature coefficient of the electrical resistance was negative in every case, with a linear relation between log ρ and $1/T$ corresponding to $\rho = \rho_0 \exp(E/kT)$, where E is the activation energy. The expression for resistivity can also be written in a form analogous to that for intrinsic conductivity. All of the observations seem to show the conduction is electronic. The polyacetylenes can be assumed to be so-called intrinsic semiconductors because of the semiconducting behaviors. A tentative explanation is offered for the phenomena observed.

257. ELECTRON SPIN RESONANCE OF POLYACETYLENE

Hatano, M., Kambara, S.
***Reports on Progress in Polymer Physics in Japan*, v. 5,**
pp. 215–218, 1962 (in English)
(Available through Kobayasi Institute of Physical Research,
Kokubunji, Tokyo, Japan)

In the preceding paper, the semiconductivity of these polymers is described briefly.

The polyacetylene having the semiconducting properties had a stereoregular structure of substantially trans-conjugated double bonds, a fact which was supported by various further experimental results. Since it was expected that the polymers containing long chains of conjugated double bonds might have stable free radicals, which arose from lattice defects or conduction electrons, paramagnetic properties of the polymers were measured.

An appreciable concentration of unpaired electrons has been found in all of the polyacetylenes through the application of electron spin resonance spectroscopy. The figure, in spin/g, for crystalline polyacetylene is 10^{19}, for amorphous polyacetylene is 10^{18}, and for oxidized polyacetylene is 10^{17}. The following data for these polyacetylenes are given: conditions of preparation; paramagnetic and electric properties; and chemical analyses of polyacetylenes. A typical recorded curve of the electron spin resonance spectrum of polyacetylene is shown. Some explanation of the observed line shapes is offered.

258. ELECTRIC CONDUCTION OF NYLON 6 (II)

Nakajima, T., Matsumoto, Y.
***Reports on Progress in Polymer Physics in Japan*, v. 6,**
pp. 241–244, 1963 (in English)
(Available through Kobayasi Institute of Physical Research,
Kokubunji, Tokyo, Japan)

The electric surface conduction of the crystalline high polymer nylon 6 was reported in a previous paper. This paper relates to the previous experiment. After being dried sufficiently at room temperature in a vacuum cell which contained P_2O_5 powder and which was packed with a silicone grease, each of the specimens was placed between two quartz plates and was heated at 220°C; after melting, it was suddenly cooled to about 50–190°C. The measuring cell consists of copper electrodes with very pure nickel plates stuck on their surfaces, an electric furnace surrounding the electrodes, a dummy electrode for the purpose of measuring the temperature of the specimen which has the same heat capacity as the electrodes, and the thermocouple which is inserted in a vacuum vessel. In addition, a device was used to prevent induction noise and leak currents. After a specimen was placed between the electrodes, a force of about 1 kg weight was applied by a double spring system.

Measurements of the dark current were made when the specimen nearly reached thermal equilibrium, with the cell maintained at 10^{-3} mm Hg (at least) under vacuum. It was recognized that the contact between the specimen and electrode was ohmic, and the dark current–voltage characteristic, after the absorption current was decayed enough, almost followed Ohm's law in the range of applied potential gradient from 10^3 to 10^4 v/cm.

259. ELECTRICAL PROPERTIES OF PYROLYTIC GRAPHITES

Klein, C. A.
***Reveiws of Modern Physics*, v. 34, no. 1, pp. 56–79,**
January 1962

Pyrolytic graphite can be prepared by deposition from methane over the temperature range 1700 to 2100°C. The degree of preferred orientation and the galvanomagnetic properties of this material are found to be strongly dependent on its temperature of formation. Measurements of the Hall coefficient and magneto-resistance over the temperature range 30 to 1300°K for various samples are compared with X-ray measurements of their degree of orientation. A qualitative comparison is made between the experimental results and the band model for graphite, together with its modification as the crystallite size decreases. (*PA*, 1962, #12,494)

260. ELECTRIC CONDUCTIVITY OF POLYCRYSTALLINE β-NAPHTHOL

Wolter, M., Zyezkowska, T.
***Roczniki Chemii*, v. 36, pp. 137–140, 1962 (in English)**

The specific conductivity σ of crystalline β-naphthol at 60–110°C in air or N was examined. No electrical conductivity was indicated. The results conform to the equation $\sigma = \sigma_0 \exp(-E/2kT)$, where the activation energy E is 2.35 in air and 2.37 ± 0.05 kcal/mole in N, and σ_0 is 2×10^5 in N. This value of E corresponds to the visible region of the optical spectrum, where β-naphthol solutions do not absorb light. The behavior of this material thus differs from that of other simple aromatic molecules.

261. ELECTRICAL PROPERTIES OF CRYSTAL COMPOUNDS OF GRAPHITE. I. CONDUCTANCE OF GRAPHITE/BROMINE

Blackman, L. C. F., Mathews, J. F., Ubbelohde, A. R.
***Royal Society of London, Proceedings of the, Series A—Mathematical and Physical Sciences,* v. 256, no. 1284, pp. 15–27. May 31, 1960**

Measurements are reported of the electrical resistance of graphite/bromine of various compositions. Some of the experiments refer to natural graphite, but the majority deal with specimens of pyrolytic graphite which show good orientation with respect to both a- and c-axes. Changes of resistance in these two directions have been measured as a function of bromine uptake to limiting concentrations; cyclic sorption–desorption studies have been included where appropriate.

Results are discussed in the light of current theories about the electron band structure in graphite and in relation to the nature of the bonding between bromine and graphite.

262. ELECTRICAL PROPERTIES OF CRYSTAL COMPOUNDS OF GRAPHITE. II. ACID SALTS OF GRAPHITE

Blackman, L. C. F., Mathews, J. F., Ubbelohde, A. R.
***Royal Society of London, Proceedings of the, Series A—Mathematical and Physical Sciences,* v. 258, no. 1294, pp. 329–338, October 25, 1960**

Experiments are described on the formation of crystal compounds of various compositions by anodic oxidation of well-oriented pyrolytic graphite. Concentrated sulphuric acid was used in most cases; other acids have also been examined. Changes in the electrical resistance are discussed in relation to use of two- and three-dimensional electron energy band structure models.

263. ELECTRICAL PROPERTIES OF CRYSTAL COMPOUNDS OF GRAPHITE. III. THE ROLE OF ELECTRON DONORS

Blackman, L. C. F., Mathews, J. F., Ubbelohde, A. R.
***Royal Society of London, Proceedings of the, Series A—Mathematical and Physical Sciences,* v. 258, no. 1294, pp. 339–349, October 25, 1960**

Crystal compounds between potassium and well-oriented pyrolytic graphite have been prepared with a range of compositions up to saturation. Measurements have been made of changes of electrical resistance and of thermoelectric power as a function of composition in both a- and c-axis directions. Anisotropy of electrical resistance becomes smaller, and of thermoelectric power sinks to practically zero, on compound formation. Compounds between graphite and rubidium or cesium have been studied more briefly under conditions approximating to saturation.

In the direction of the a-axis, the large decreases of electrical resistance observed can be interpreted on the basis that the alkali metal atoms inject electrons into the upper π-band of graphite. This is confirmed by the observed changes of thermoelectric power. Changes resemble but do not completely mirror those observed with electron acceptor compounds; the fractional transfer of electrons appears to be less complete with the electron donors.

In the direction of the c-axis, intercalation of the electron donor alkali metal atoms leads to a much more striking decrease of electrical resistance than is observed with various electron acceptor groups. To supplement results previously published, brief studies are reported on crystal compounds between graphite and aluminum chloride, and graphite and iodine monochloride.

Possible band models for graphite compounds with both electron donor and acceptor atoms are discussed in the light of the experimental findings.

264. DEFECT STRUCTURE AND PROPERTIES OF PYROLYTIC CARBONS

Blackman, L. C., Saunders, G., Ubbelohde, A. R.
***Royal Society of London, Proceedings of the, Series A—Mathematical and Physical Sciences,* v. 264, pp. 19–40, October 24, 1961**

Defects were studied systematically in graphites prepared by the pyrolysis of methane at temperatures in the range 1600 to 2200°C. Physical methods used included measurements of the bulk density and studies of X-ray diffraction photographs. Electronic properties examined were the electrical resistivity and its degree of anisotropy, the magnetoresistance, the Hall effect, and the thermoelectric power. The uptake of bromine to saturation at room temperature was used to characterize the structural disorder by chemical means. One main conclusion is that a striking change occurs in pyrolytic carbons as their deposition temperature passes through a critical region, around 1900°C. Specimens prepared below this temperature have low bulk densities, show only a comparatively small degree of preferred orientation, and contain appreciable concentrations of residual hydrogen. Specimens deposited above this temperature have bulk densities and other properties which tend toward those of perfect graphite. The crystal orientation improves progressively in specimens deposited up to 2200°C and can be brought still closer to ideal graphite by subsequent recrystallization at around 2700°C. A second main finding is that the a-axis thermoelectric power, whose values at room temperature lead to the same general conclusions about crystal defects as the other methods used, shows remarkable anomalies as the temperature is lowered to values of reduced temperature T/θ around 0.03. A preliminary examination was made of changes in the anomalies resulting from crystal compound formation and from neutron bombardment. Tentative attribution of these anomalies can be made to the interaction of charge carriers with lattice vibrations. (*PA*, 1961, #17,525)

265. ELECTRICAL CONDUCTION AND BREAKDOWN IN LIQUID DIELECTRICS

Chong, P., Kawarabayashi, T., Inuishi, Y.
***Technology Reports of the Osaka University*, v. 10,**
pp. 25–30, January 1960

The electrical conduction and breakdown phenomena in *n*-hexane and nitrobenzene are investigated with the application of dc and rectangular pulse voltages. For the dc experiments a thyratron diverter circuit was used in parallel with the test gap, which enabled more reproducible results up to the breakdown field strength. Experiments with pulse voltages were carried out for information about the dynamical properties of conduction processes. The following relations were obtained between the current i and E. At low field strength in *n*-hexane containing several percent of ethyl alcohol, log i varies in proportion to $\sqrt{E}$ rather than to E. But at higher field strengths, especially just below breakdown, it increases very abruptly, and some electronic processes leading to breakdown appear. Direct-current breakdown strength of *n*-hexane is about 0.7 Mv/cm. (*PA*, 1962, #11,384)

266. CONDUCTIVITY INDUCED BY INJECTED ELECTRONS IN LIQUID DIELECTRICS

Chong, P., Inuishi, Y.
***Technology Reports of the Osaka University*, v. 10,**
pp. 545–551, October 1960

Conductivity induced by injected electrons in *n*-hexane and benzene was investigated. The drift mobilities μ of the injected electrons in *n*-hexane and benzene were found to be 1.0×10^{-3} and 0.45×10^{-3} cm^2 v^{-1} at 20°C, being almost independent of the applied field strengths up to 0.5 Mv cm^{-1}. This small value of the drift mobility shows that the injected electrons do not behave as free electrons such as in gases. From the temperature dependence, assuming $\mu = \mu_0 \exp(-\Delta\epsilon_\mu/kT)$, the activation energy of the drift mobility can be estimated as 0.16 ev both in *n*-hexane and in benzene. This activation energy does not coincide with that of the viscosity. Possible mechanisms for these small drift mobilities are discussed. The magnitudes of induced charges were greatly affected by the conditioning of the electrodes, which may be due to the ionization of absorbed gases on the electrode surface. Electron multiplication due to collision ionization in the liquid itself was not observed below field strengths of 0.5 Mv cm^{-1} (*PA*, 1962, #9288)

267. ELECTRIC CONDUCTIVITY OF SYNTHETIC CERESIN IN THE MELTING RANGE

Bondarenko, A. V., Nikitenko, V. I.
Trudy Novocherkasskogo Politekhnicheskogo Instituta
***Raboty Kafedry Fizicheskogo*, v. 73, pp. 43–46, 1959**
(See also *Referativnyi Zhurnal, Khimiya*, 1961, # 2N356)

Dependence on temperature of the electrical conductivity of synthetic ceresin was studied. Measurements were taken at intervals of 2–5°C, with the rate of heating (or cooling) 1°C for each 2–10 min. In heating up to 57°C (the melting point of low-molecular-weight component paraffins), one constant was maintained in rate of change of log ρ_v (specific volume resistance), while above 57°C this rate of change had another, larger constant. In the melted state the structural orientation seemed to be varied by the electrical field and as a result the cooling curve deviated from the heating curve, crossing it at the middle of the melt region.

268. TRANSMISSION OF ENERGY IN ANTHRACENE CRYSTALS DOPED WITH PHENAZINE AND ACRIDINE

Korsunskii, V. M., Faidish, O. M.
***Ukrains'kii Fizichnii Zhurnal*, v. 8, pp. 683–688, 1963**

269. TEMPERATURE DEPENDENCE OF THE ELECTRICAL CONDUCTIVITY OF SOME MELTS OF POLYMORPHIC SUBSTANCES

Urazovskii, S. S., Kanevskaya, Z. M.
***Ukrains'kii Khimicheskii Zhurnal*, v. 27, pp. 296–302, 1961**

Discussion, graphed data, and explanation are offered for the temperature dependence of the electrical conductivity of monochloroacetic acid, benzophenone, salol, menthol, and acetophenone in liquid and supercooled-liquid state. Transition points show as breaks in the curves.

270. NEW METHOD OF STUDYING CONFIGURATIONAL CHANGES OF POLYMERS

Urazovskii, S. S., Ezhik, I. I.
***Ukrains'kii Khimicheskii Zhurnal*, v. 28, pp. 329–332, 1962**
(in Russian)

The change in phase angle of high-frequency electric currents produced by solutions of high polymers in organic solvents is plotted against temperature. Measurements were made by a Q-meter. Line breaks occur near temperatures at which conformational changes of the polymers take place.

271. THE THERMAL CONDUCTIVITY OF ARTIFICIAL GRAPHITES AND ITS RELATIONSHIP TO ELECTRICAL RESISTIVITY

Mason, I. B., Knibbs, R. H.
March 1962
United Kingdom Atomic Energy Authority, Research
Group, Atomic Energy Research Establishment,
Harwell, Berks, England
AERE-R-3973

Measurements of thermal conductivity at room temperature covering a wide range of commercial and experimental graphites are presented. In addition, some graphites of interest in the nuclear field were examined up to 600°C. It is demonstrated that for a given material thermal resistivity (inverse conductivity) varies linearly with electrical resistivity when either the orientation or the crystallinity varies. Expressions correlating these two quantities are given. It is also found that one such expression fits the data for over 40 different graphites, and enables the thermal resistivity to be estimated from electrical measurements to within ±15%. A fairly simple theoretical analysis of the data suggests that the temperature variation of thermal conductivity of most graphites can be represented by a single family of curves. On this basis it is indicated how values of thermal conductivity at elevated temperatures may be estimated from room temperature data. (*PA*, 1962, #23,093)

272. A STUDY OF THE KINETICS OF INTERFACIAL POLYCONDENSATION BY THE MEASUREMENT OF ELECTRICAL CONDUCTIVITY

Fainberg, E. Z., Mikhailov, N. V.

***Vysokomolekulyarnye Soedineniya*, v. 2, no. 7, pp. 1039–1044, July 1960**

(Translated from the Russian in *Polymer Science U.S.S.R.*, v. 3. no. 2, pp. 222–228, 1962; published August 1962)

A method has been developed for the study of the kinetics of polycondensation at an interfacial boundary, based on the measurement of the electrical conductivity of the aqueous phase (diamine solution). The study of the reaction was carried out on systems consisting of benzene solutions of adipyl and sebacyl chlorides and aqueous solutions of hexamethylenediamine. A quaternary ammonium base of the type of triethylbenzylammonium hydroxide was used as detergent. As has already been noted, for the purpose of the investigation it is sufficient to know the change in concentration of the diamine; hence, platinum electrodes, sealed into the vessel, were immersed in the aqueous phase and consequently disturbance of the organic-solvent phase, the upper layer, was avoided. This enabled the experimental error to be reduced considerably because agitation of the upper phase makes possible the transfer of substances to the aqueous phase which would alter its electrical conductivity and falsify the value of the diamine concentration determined from the electrical conductivity. Moreover, it seems that even under static conditions with no disturbance of the upper phase (organic solvent) some distortion of the value of the electrical conductivity of the aqueous phase (diamine solution) is possible, caused by penetration of reaction products into this phase.

For a stringent, quantitative study of the reaction kinetics this factor should be taken into account and, if necessary, a correction applied. This method seems quite satisfactory for a comparative study. In the first stages of the experiment the measurement was made by means of a valve millivoltmeter. The results obtained in this work indicate that this method can be used for the study of the kinetics of polycondensation reactions in various systems

273. ON THE SO-CALLED "COMPENSATION EFFECT" IN ORGANIC SEMICONDUCTOR MATERIALS

Airapetyants, A. V., Voitenko, R. M., Davydov, B. E., Serebryanikov, V. S.

***Vysokomolekulyarnye Soedineniya*, v. 3, no. 12, p. 1876, December 1961**

It has been shown that semiconductors obtained on the basis of polyacrylonitrile with electroconductivity 2×10^{-7} to 20 ohm^{-1}cm^{-1} at room temperature display a fall in the activation energy of conductivity (E) with increase in value of the pre-exponential factors of the expression $\sigma_0 \exp(E/2kT)$; i.e., the same relation between E and σ_0 holds in the case of ordinary semiconductors.

274. THE SYNTHESIS AND SOME PHYSICAL PROPERTIES OF POLY-*p*-DIETHYNYLBENZENE

Kotlyarevskii, I. L., Fisher, L. B., Dulov, A. A., Slinkin, A. A., Rubinshtein, A. M.

***Vysokomolekulyarnye Soedineniya*, v. 4, no. 2, pp. 174–181, February 1962**

(Translated from the Russian in *Polymer Science U.S.S.R.*, v. 4, no. 1, pp. 58–68, 1963)

Many papers have been published recently on the synthesis and physical properties of polymers containing systems of conjugated bonds. It has been found that such compounds possess special electrical and magnetic properties reminiscent of the properties of inorganic semiconductors and paramagnetic materials. In this field poly-*p*-diethynylbenzene, a polymer in which triple bonds are conjugated with benzene rings, has been synthesized and some physical properties have been examined.

The electrical conductivity was measured at constant current *in vacuo* (5×10^{-3} mm), using tablets of the oligomer compressed at 5000 atm. Specimens of polymer were prepared by heating the tablets at different temperatures for 20 hr in a current of nitrogen. The temperature dependence of the specific conductivity followed the usual experimental law $\sigma = \sigma_0 e^{-E/kT}$. The results showed good reproducibility when the temperature of measurement was repeatedly raised and lowered, the relative error being not more than ±15%.

The conductivity of the oligomer at room temperature before heat treatment was less than 10^{-14} ohm^{-1}cm^{-1} and at 120°C $\sigma = 5 \times 10^{-11}$ ohm^{-1}cm^{-1}. The energy of activation for conductivity, E, in the temperature interval 120–200°C was 0.86 ev.

The conductivities of specimens heated at 220–600°C are given. With increase in the temperature of previous heat treatment the electrical resistance falls and the energy of activation for conductivity decreases. There is a point of inflection in the plots of log σ against $1/T$, and the temperature corresponding to this point increases as the heat-treatment temperature increases.

When specimens previously heated at 220°C are irradiated with ultraviolet light the conductivity increases instantaneously by several orders of magnitude. When the irradiation is stopped the conductivity reverts to the previous value almost instantaneously. When the specimens are heated at 400°C the effect is very much weaker, and with specimens heat-treated at 500 and 600°C, irradiation has no effect on the resistance.

Determination of the sign of the thermal EMF of a specimen heat-treated at 600°C and also the reversible decrease in resistance on absorption of oxygen indicate the "hole" nature of the conductivity.

Magnetic susceptibility was also measured and ESR spectra plotted.

Results confirm that the electrical and magnetic properties are dependent on the crystallinity of the polymer. In fact, specimens heated at the lower temperatures (up to 220°C) are amorphous and give a narrow ESR signal, the intensity of which increases with increasing heat-treatment temperature. The value of χ for the uncompressed specimen in this lower interval of temperature is the same as that of the original polymer. The electrical resistance and energy of activation for conductivity are very high, and the conductivity increases markedly under the action of ultraviolet radiation. Consequently, these specimens still do not have a crystalline structure but consist of weakly associated conjugated segments; hence their electrical and magnetic properties are determined by the behavior of the individual, weakly interacting, unpaired electrons within a given segment and by the energy barriers between the segments. Consequently, it would be expected that in this region of heat-treatment temperatures the number of unpaired electrons calculated from the ESR data would coincide with the number obtained from the magnetic susceptibility.

Since the intensity of the ESR signal varies in the same manner as the electrical conductivity, it may be considered that in polymers heat-treated at lower temperatures the unpaired electrons detected by the ESR and static magnetic susceptibility methods take part in the process of conductivity. The high activation energies are due to the potential barriers at the boundaries of the conjugated segments.

In the general case, a correlation between changes in conductivity and the number of unpaired electrons calculated from the narrow ESR signals should not be expected. Consequently, the identification of unpaired electrons with conductivity electrons in complexes with a "transfer of charge" suggested by Eley is scarcely justifiable, particularly since the changes in conductivity that he obtained do not correspond to the changes in intensity of the ESR signal in these complexes. There is also little basis for the attempt to explain the increase in conductivity of polymers on heating by an increase in the content of biradical structures because, as was shown above, heating at high temperatures leads to the disappearance of the narrow ESR signal with a simultaneous increase in conductivity.

275. STUDIES IN THE ELECTROCONDUCTIVITY OF POLYMERS. V. POLYCARBONATE, POLYETHYLENETEREPHTHALATE, MIXED POLYESTER AND POLYOXYMETHYLENE

Sazhin, B. I., Eidelnant, M. P.
***Vysokomolekulyarnye Soedineniya*, v. 4, no. 4,**
pp. 583–590, April 1962

The results are described of the experimental determination of the resistivity of polycarbonate, polyethyleneterephthalate, mixed polyester of terephthalic and sebacic acids with ethylene glycol, and polyoxymethylene, depending upon the temperature (−180 to 200°C) and the duration of loading of the specimen (0.01 to 1200 sec). It has been shown that for $T < T_g$ the value of ρ_v is greatly dependent upon the establishment of dipole radical polarization. The crystallization of the first two named polymers is accompanied by a considerable increase in ρ_v. (For Part VI, see Entry #86)

276. SOME PROPERTIES OF POLYMERIC SEMICONDUCTORS

Davydov, B. E., Raskina, E. M., Krentsel, B. A.
***Vysokomolekulyarnye Soedineniya*, v. 4, no. 10,**
pp. 1604–1605, October 1962

A study was made of the temperature dependence of the thermal electromotive force of semiconductor polymers; it was shown that they may be classified as semiconductors, semimetals, and metals. It has been found that at elevated temperatures a number of polymers change the sign of the thermal EMF and hence the sign of the current carriers (determined by the sign of the EMF).

277. EIN NACHWEIS DER RAUMLADUNG BEI RAUMLADUNGSBESCHRÄNKTEN DEFEKTELEKTRONENSTRÖMEN IN ANTHRAZEN (DETECTION OF THE SPACE CHARGE IN SPACE-CHARGE-LIMITED DEFECT ELECTRON CURRENTS IN ANTHRACENE)

Helfrich, W., Mark, P.
***Zeitschrift für Physik*, v. 168, no. 5, pp. 495–503,**
July 25, 1962

A method is described with which the space charge of the excess hole current in anthracene, flowing under space-charge limitation, can be detected in spite of the short persistance of this charge in the crystal. One injecting (ohmic) and one non-injecting (blocking) electrode are used. After space-charge-limited current flow is established, a reverse voltage is suddenly applied which causes the excess space charge in the crystal to flow out through the ohmic electrode without additional carriers entering through the blocking electrode. The magnitude of the space charge so measured agrees with that expected from the capacitance of the crystal. (*PA*, 1962, #16,715)

278. EINE BESTIMMUNG DER EFFEKTIVEN ZUSTANDSDICHTE DES BANDES FÜR ÜBERSCHÜSSIGE DEFEKTELEKTRONEN IN ANTHRAZEN (DETERMINATION OF THE EFFECTIVE DENSITY OF STATES OF THE BAND FOR EXCESS DEFECT ELECTRONS IN ANTHRACENE)

Helfrich, W., Mark, P.
***Zeitschrift für Physik*, v. 171, no. 3, pp. 527–536,**
December 28, 1963

Steady-state space-charge-limited current measurements were used to obtain the effective density of states in the band appropriate to excess hole motion in anthracene. Since the energetic trap density decreases exponentially with the energy distance from the band, the traps are filled by the space charge up to a certain quasi-Fermi level. The thermal activation energy of the current should be a kind of spatial average of this level. This energy was measured and used to calculate the effective density of states. The result, 4×10^{21} cm^{-3}, is close to the double molecular density which is 8.4×10^{21} cm^{-3}. A discussion on traps is given in an appendix. (*PA*, 1963, #4844)

279. THE ELECTRICAL CONDUCTIVITY OF SEVERAL AMINATES OF TRIVALENT THALLIUM IN NITROBENZENE SOLUTIONS

Kulba, F. Y., Mironov, V. E., Tszin-Yan, T.,
Filippova, Z. G.
***Zhurnal Neorganicheskoi Khimii*, v. 8, no. 3,**
pp. 672–675, 1963

SYNTHESIS

280. ELECTROPHYSICAL PROPERTIES OF POLYMERIC COMPLEXES FORMED BY TETRACYANOETHYLENE WITH METALS

Berlin, A. A., Boguslavskii, L. I., Burshtein, R. Kh.,
Matveeva, N. G., Sherle, A. I., Shurmovskaya, N. A.
***Akademiya Nauk SSSR, Doklady*, v. 136, no. 5,**
pp. 1127–1129, February 11, 1961

Polymeric chelate coatings were formed by treating etched surfaces of Cu, Fe, Ni particles with vapors of tetracyanoethylene at 150–400°C from 5 to 20 hr at 10^{-5} mm Hg (of thickness 5×10^{-6} to 3×10^{-5} cm). With an ac bridge, the capacity and resistance of films were measured *in vacuo* as a function of temperature. The specific conductance, σ, fluctuated with polymerization temperature, depending on the time of heating and the pretreatment of the metal surface. A thin film formed on Fe chips by reaction at 250°C for 3 hr showed σ of 3×10^{-9} ohm^{-1} cm^{-1}, and the effective dielectric constant ε of 7 at 3000 cps. Heating samples an additional 3 hr caused σ to become 3×10^{-8} ohm^{-1} cm^{-1} and ε 36. Increasing the reaction temperature from 250 to 400°C and heating for 10 hr gave σ equal to 5×10^{-6} ohm^{-1} cm^{-1}, and ε 70. The thermoelectric power is based on *p*-type conduction.

281. SYNTHESIS AND SOME PROPERTIES OF POLY-(TETRACYANOETHYLENE)

Berlin, A. A., Matveeva, N. G.
***Akademiya Nauk SSSR, Doklady*, v. 140, no. 2,**
pp. 368–370, September 11, 1961

Tetracyanoethylene was polymerized in the presence of reagents capable of opening the CN group, alcohols, phenols, amines, and amides, at 200°C. Of various reagents tried, EtOH was most effective with 43.7% polymer formed. The polymer was stable up to 300°C, but suffered some weight loss at 350°C; this became greater at higher temperature, with complete destruction at 500°C. The polymers had a conductivity of about 10^{-7}–10^{-9} ohm^{-1} cm^{-1} and an activation energy of 7–13 kcal/mole. Temperature dependence of conductivity was shown graphically. The polymers gave a narrow electron paramagnetic resonance signal with spacing of 4–6 oersteds between peaks and g-factor = 2; the concentration of paramagnetic particles was 10^{20}–10^{21}/g.

282. SYNTHESIS OF POLYMERS WITH CHARGED HETERO-ATOMS IN THE CHAINS OF THE MACROMOLECULES. ONIUM POLYMERIZATION

Berlin, A. A., Razvodovskii, E. F.
***Akademiya Nauk SSSR, Doklady*, v. 140, no. 3,**
pp. 598–600, September 21, 1961

Heating pure 4-chloropyridine at 50–60°C, or maintaining it at 20°C, yields a yellow-brown polymer consisting of a para-connected chain of pyridine rings with pyridinium chloride units at the N-junctions; the polymer contains some 90% titratable Cl and the chain length is 8–14. The rate of reaction is greatly increased by addition of 0.5–2% compounds with reactive Cl [chloranil or already prepared poly(pyridine chloride)]. The presence of pyridine stops chain formation. The polymer decomposes at 160–165°C and shows a narrow band, electron paramagnetic resonance (EPR), spectrum with 6 oersted bandwidth and g-factor 2; the content of paramagnetic units in the polymer is 3.8×10^{18}/g. This may be explained by facilitated unpairing of the π-electrons and their delocalization along the chain. Copolymers were obtained between chloranil and γ,γ'-bipyridine in a melt at 130°C or in toluene solution. The polymer gives a symmetric EPR signal corresponding to 5×10^{18}/g paramagnetic units; g-factor 2.0 and bandwidth 8 oersted are reported. 4-Pyridylpyridinium chloride-HCl has conductivity δ_0 3×10^{11} and δ_{300} 3×10^{-15} with E = 35.8 kcal/mole; poly(chloropyridine) gives respective values: 10^5, 10^{-7}, 18.2; copolymer bipyridine and chloranil give respective values: 10^6, 10^{-9}, 21.7. These results indicate a sharp rise of conductivity with elevation of the temperature in these polymers.

283. OXIDATION PRODUCTS OF HIGH-MOLECULAR-WEIGHT CONJUGATED POLYENES

Berlin, A. A., Aseevs, R. M., Kalyaev, G. I., Frankevich, E. L.
***Akademiya Nauk SSSR, Doklady*, v. 144, no. 5,**
pp. 1042–1045, June 11, 1962

Polymeric polyenes were formed by dehydrochlorination of poly(vinyl chloride) (I) or chlorinated I resin by NaOAm and subjected to mild oxidation at 20°C They gave a narrow electron paramagnetic resonance (EPR) signal corresponding to 10^{18} paramagnetic particles per gram. The signal from the product derived from I was the wider of the two, indicating lesser exchange interactions between the unpaired electrons. The oxidation with O was followed kinetically in ultraviolet light or visible light. The polymers changed color, and the EPR signal disappeared. The polyene from I reacted the more rapidly of the two. The final oxidation product contained 32.5% bound O and appeared to contain peroxide units, possibly as O bridges across C atoms adjacent to residual double bonds. If the oxidation products are heated to 150–200°C without access of air, the color deepens and the EPR signal appears again. The conductivity rises simultaneously. This product contains but 15% bound O and appears to have an aromatic type of conjugation. A brown polymer formed after the loss of some 50% of initially contained O gives a narrow EPR signal with 10^{17}/g unpaired electrons. The peroxides shown above can convert tetrahydronaphthalene into $C_{10}H_8$. Heating the peroxides of polyenes from chlorinated I in air does not result in the breakdown of the former, and the products actually become more and more stable as heating proceeds. Heating and pressing result in strong plastics with good heat resistance. The dielectric properties of various polymers are improved by incorporation of the polyene peroxides described above.

284. SYNTHESIS AND CHARACTERIZATION OF SOME HIGHLY CONJUGATED SEMICONDUCTING POLYMERS

Pohl, H. A., Englehardt, E. H.
American Chemical Society, Washington, D.C.
Paper 22, Division of Polymer Chemistry, presented at the 140th Meeting, ACS, Chicago, Ill., September 3–8, 1961

Highly conjugated semiconducting polymers are produced by the condensation of an acene with aromatic acid anhydrides, in the presence of zinc chloride, at temperatures of about 200 to 400°C. Specific conductivities ranging from 10^{-2} to 10^{-10} mho cm^{-1} were observed by varying the type and concentration of aromatic hydrocarbon in the polymer. Activation energies of the conduction process in these polyacene quinone radical (PAQR) polymers are observed to range 0.1 to 0.5 ev, and are closely related to the room temperature resistivity as quoted above.

The series of PAQR polymers prepared here exhibit a range of Seebeck coefficients (thermoelectric power) of from −19 to +345 μv/°C. As the temperature increases, the Seebeck coefficient becomes more and more negative, hence also the carrier type. Said in another way, the materials range from *p*-type to *n*-type.

The conduction mechanism in the PAQR polymers is electronic, as evidenced by unchanging resistivity during prolonged electrolysis experiments, and by the existence of a relatively large Hall coefficient. Non-ohmic behavior has been established by comparison of the polymers with ohmic resistors in a Wheatstone bridge.

A semiquantitative relationship between electron spin density and conduction has been established in the PAQR polymers. This indicates that the conduction in polymers in this series is related more by the number of carriers than by the carrier mobility, though not entirely. A high density of electron spins with narrow peak half-widths is observable (10^{18} to $10^{20} cm^{-3}$); hence these polymers are polyradicals.

The PAQR polymers have a dissimilar structure and mode of electronic conduction from that of pyropolymers.

285. REACTIONS OF METAL HALIDES WITH AROMATIC COMPOUNDS

Kovacic, P.
American Chemical Society, Washington, D.C.
Paper 42, Division of Petroleum Chemistry, presented at the 142nd Meeting, ACS, Atlantic City, N.J.,
September 9–14, 1962

A variety of reactions, including halogenation, side-chain attack, nuclear coupling, and polymerization, can occur with aromatic compounds and the Lewis acid metal halides, ferric chloride, antimony pentachloride, or cupric chloride.

Ferric chloride and antimony pentachloride are known to effect nuclear chlorination with halobenzenes, alkylbenzenes, and polynuclear hydrocarbons. The cupric halides are less active halogenating agents. Side-chain involvement, observed with alkylated benzenes, produced di-, tri-, and tetraarylmethanes, disproportionation, and probably polymerization. With *m*-xylene and mesitylene, nuclear coupling and chlorination resulted from the ferric chloride reaction. Benzene can be polymerized in the system, cupric chloride-aluminum chloride-water, under remarkably mild conditions to a solid possessing the properties of *p*-polyphenyl. Evidence for the *p*-polyphenyl structure is based upon elemental analyses, infrared spectrum, X-ray diffraction pattern, insolubility, and thermal stability. The mechanistic aspects of the various reactions are discussed.

286. POLYMERIZATION OF NON-CONJUGATED DIYNES BY COMPLEX METAL CATALYSTS

Stille, J. K., Frey, D. A.
***American Chemical Society, Journal of the*, v. 83, no. 7,**
pp. 1697–1701, April 5, 1961

The polymerization of 1,6-heptadiyne by Ziegler-type catalysts leads to soluble, highly colored polymers of 10,000–20,000 molecular weight, which contain alternating double and single bonds along the backbone of the polymer chain and a cyclic recurring unit as the main structural features. Polymerization of 1,7-octadiyne and 1,8-nonadiyne under the same conditions, however, affords mostly cross-linked polymers.

287. NEW ORGANOMETALLIC SEMICONDUCTOR

Dewar, M. J. S., Talati, A. M.
***American Chemical Society, Journal of the*, v. 85, no. 12, p. 1874, June 20, 1963**

The expected electrical properties of coordination polymers are discussed, and the synthesis of a new organometallic semiconductor of this kind is reported, the cupric derivative of the dioxime of 1,5-diacetyl-2,6-dihydroxynaphthalene. The conductivity of the polymer was measured in compressed disks (prepared at about 9×10^4 psi) at room temperature. Three samples of the polymer, prepared in different experiments, had resistivities of 8.6×10^7, 7.4×10^7 and 8.0×10^7 ohm-cm.

288. POLYMERIC CONDUCTORS AND SEMICONDUCTORS

Becher, M., Mark, H. F.
***Angewandte Chemie*, v. 73, pp. 641–646, 1961**

Preparation of electrically conducting polymers by building ionogenic groups into the structure or by introducing mobile electrons through conjugated systems is explained. Work on the electrical and magnetic properties, as well as the preparation, of polymers containing heteroatoms, metal chelate polymers, and polyvinylenes is summarized.

289. DONOR-ACCEPTOR COMPLEXES

Mulliken, R. S., Person, W. B.
In "Annual Review of Physical Chemistry," Volume 13, pp. 107–126
Eyring, H., Editor
Annual Reviews, Inc., Palo Alto, Calif., 1962

Very recent material not fully covered in Briegleb's book (Entry #334) is reviewed, and current thinking, which in some respects goes beyond or differs from that in the literature and in Briegleb's book, is presented.

290. SEMICONDUCTING POLYMERS CONTAINING COORDINATED METAL IONS

Bolto, B. A., Weiss, D. E.
***Australian Journal of Chemistry*, v. 15, pp. 653–667, 1962**

Conducting compounds thought to be polycoordinated quinoxalophenazine derivatives were prepared by heating chloranil (I) (1 mole) *o*-phenylenediamine (II) (2 moles), and a metal salt (0.67 mole) in N at 250–400°C for 30 min, grinding the reaction mass and extracting with EtOH until the extract was colorless. Of the metals examined (Cr, Mn, Fe, Co, Ni, Cu. Zn, Cd, Mg, Ca, Ba, Ru, and Os), Fe as $FeCl_2$ gave the best conductor (resistivity 38,000 ohm-cm for preparation temperatures from 350 to 450°C). At 250–350°C, I, II, and $FeCl_2$ gave compounds whose conductivities were 20 times greater than those prepared with $FeCl_3$. The conductivity of these polymers is attributed to interaction between donor N atoms and acceptor groups, such as the metal ion, quinones, and quaternary N atoms linked within a fully conjugated polycyclic system. The existence of the metal in more than one oxidation state, as may occur in the $FeCl_2$ polymer, may be of further benefit.

291. CYCLIZING TRIMERIZATION OF ALKYNES BY MEANS OF CARBONYL COMPOUNDS

Hübel, W., Hoogzand, C.
***Chemische Berichte*, v. 93, pp. 103–115, 1960**
(For full abstract, see *Chemical Abstracts*, 1960, Entry 9839f)

Conversion to benzene derivatives of mono- and disubstituted acetylenes by heating with small amounts of metal carbonyl derivatives, with or without solvent, is reported. Unsymmetrical alkynes of the type RC:CR′ yielded under these conditions exclusively benzene derivatives with identical substituents in the 1,2,4- and 3,5,6-positions, respectively. It was postulated that the trimerization proceeded via an intermediate organic metal carbonyl complex.

292. ON THE SYNTHESIS AND ELECTRONIC PROPERTIES OF POLYACETYLENIC HYDROCARBONS

Okamoto, Y., Gordon, A., Movsovicius, F., Hellman, H., Brenner, W.
***Chemistry & Industry*, London, no. 49, pp. 2004–2006, December 9, 1961**

Phenylacetylene was thermally polymerized under oxygen-free, dry nitrogen at reflux temperatures for 20–65 hr in the absence of solvent as well as in 10–20 wt.% solutions of decalin, xylene, diethylene glycol dimethyl ether (diglyme), and chlorobenzene. In all cases deep red solids were obtained in near quantitative yields, which became yellow-orange powders upon reprecipitation from benzene, acetone, carbon tetrachloride, or chloroform solutions by adding methanol, ethanol, or petroleum ether. To determine the electroconductivity of the material, a temperature-resistivity profile was made under purified nitrogen on compressed pellets. The bulk polymer appears to obey the usual exponential law for a semiconductor, $\rho \alpha \exp(E/kT)$, where $\rho =$ resistivity, ohm-cm; E apparent energy gap, ev; k is Boltzmann's constant; and T is absolute temperature. The low molecular weight materials obtained to date do not show conductivities significantly lower than those of many other non-conjugated polymer systems. A room temperature resistivity of 10^{16} ohm-cm and a high apparent energy gap of 0.963 ev place the polymer in the dielectric category, even though it conducts better than linear polystyrene by a factor of 1000. Further studies on such polymers are now in progress.

293. POLYMERISATION OF DICYANOACETYLENE

Beneš, M., Peskǎ, J., Wichterle, O.
***Chemistry & Industry*, London, no. 12, pp. 562–563, March 24. 1962**

Polymerization of acetylenic monomers to linear polyconjugated polymers has attracted increasing interest in recent years. Dicyanoacetylene (DCA) prepared according to Moureu and Bongrand was chosen for these polymerization experiments. The darkening of this compound induced by caustic soda as described by the French authors indicates an ability to undergo base-catalyzed polymerization. According to this extended investigation, DCA is polymerized easily by many other anionic catalysts, e.g., *N*-ethylpiperidine, triethylphosphine, butylmagnesium bromide, potassium benzophenone, sodium naphthalene in tetrahydrofuran (THF), butyllithium in THF or hexane, sodium cyanide in dimethylformamide.

The paramagnetic behavior of this polymer, prepared with THF, was given by ESR spectrum which shows a narrow signal with a half-line width of approximately 7.5 gauss. The g value was found to be 2.0029 ± 0.0003 and the amount of unpaired spins of the order 10^{18}/g, as calculated by comparison with a standard of diphenylpicrylhydrazyl. Further work on the polymerization of DCA and related compounds, and the investigation of the structure and electric and magnetic properties of the polymers formed, are in progress.

294. POLYMÉRISATION DU PHÉNYLACÉTYLÈNE SOUS L'INFLUENCE DES CATALYSEURS ORGANO-MÉTALLIQUES (POLYMERIZATION OF PHENYLACETYLENE UNDER THE INFLUENCE OF ORGANOMETALLIC CATALYZERS)

Champetier, G., Martynoff, M.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 252, no. 5, pp. 633–636, January 30, 1961**

Contrary to acetylene, the phenyacetylene is not polymerized in an appreciable quantity by the catalyzers obtained by the action of ferric chloride on the organomagnesia compounds mixed or symmetric. In using the tetrachloride of titanium and a symmetric organomagnesia, it is possible to obtain soluble yellow polyphenylacetylenes containing, as an average, thirteen monomers, and insoluble orange polymers of higher molecular masses.

295. CATALYSE PAR LE POLYACRYLONITRILE PYROLYSÉ (CATALYTIC ACTION OF PYROLYZED POLYACRYLONITRILE)

Gallard, J., Traynard, P.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 254, no. 20, pp. 3529–3531, May 14, 1962**

Polyacrylonitrile needles heated to 400°C become black, and the powder formed dark red-brown, the two forms being very stable to heat and semiconducting. They give a paramagnetic signal of about 10^{18} centers/g. Only NiO semiconductor had a higher catalytic activity with N_2O than the powder form of pyrolized polyacrylonitrile.

296. SYNTHESIS OF POLYMERIC MATERIALS POSSESSING SEMICONDUCTOR PROPERTIES

Geyderikh, M. A., Davydov, B. E., Krentsel, B. A., Kristanovich, I. M., Polak, L. S., Topchiev, A. V., Voitenko, R. M.
In "Mezhdunarodnyi Simpozium po Makromolekulyarnoi Khimii, Mezhdunarodnyi Soyuz Chistoi i Prikladnoi Khimii, Komissiya Makromolekulyarnoi Khimii, Doklady i Avtoreferaty (International Symposium on Macromolecular Chemistry, The International Union of Pure and Applied Chemistry, Committee on Macromolecular Chemistry, Papers and Summaries), Moscow, June 14–18, 1960," v. 3, pp. 85–92
Izdatelstvo Akademii Nauk, SSSR, Moscow, 1960 (English translation available in AEC-tr-4470, 1961, pp. 22–28, U.S. Atomic Energy Commission, Technical Information Service Extension, Oak Ridge, Tenn.)

Among the materials synthesized are: polycondensation products of phthalic anhydride with hydroquinone and with *p*-phenylenediamine; the substances obtained by dehydrochlorination of polyvinyl chloride; and the products of thermal conversion of polyacrylonitrile. Paramagnetic and electrical properties of the polymers are tabulated and graphed. The conductivity mechanism is considered.

297. SYNTHESIS AND PROPERTIES OF SOME AROMATIC POLYMERS

Berlin, A. A., Liogonkii, B. I., Parini, V. P.
In "Mezhdunarodnyi Simpozium po Makromolekulyarnoi Khimii, Mezhdunarodnyi Soyuz Chistoi i Prikladnoi Khimii, Komissiya Makromolekulyarnoi Khimii, Doklady i Avtoreferaty (International Symposium on Macromolecular Chemistry, The International Union of Pure and Applied Chemistry, Committee on Macromolecular Chemistry, Papers and Summaries), Moscow, June 14–18, 1960," v. 3, pp. 115–123
Izdatelstvo Akademii Nauk, SSSR, Moscow, 1960

Linear polynuclear aromatic compounds were synthesized on decomposing bisdiazo compounds by a cuprous ammoniacal solution. Equivalent quantities of the bisdiazo salt, based on benzidine and 3,3′-benzidinedicarboxylic acid, and of the cuprous ammoniacal solution were used. The procedure was performed both by the addition of the salt to the solution and by the reverse addition of the materials.

298. POLYMERIZATION OF BENZENE TO *p*-POLYPHENYL BY MOLYBDENUM PENTACHLORIDE

Kovacic, P., Lange, R. M.
***Journal of Organic Chemistry*, v. 28, no. 4, pp. 968–972, April 1963**

Benzene is polymerized by molybdenum pentachloride under mild conditions to *p*-polyphenyl. The polymer, which contained a small amount of chlorine, was identified by elemental analyses, infrared spectrum, X-ray diffraction pattern, pyrolysis products, oxidative degradation, insolubility, and thermal stability. The low molecular weight organic product, present in trace amounts, contained 4,4′-dichlorobiphenyl, dichlorobenzene, and chlorobenzene. Facile dehydrogenation of 1,4-cyclohexadiene to benzene by molybdenum pentachloride lends support to the proposal that the reaction proceeds by oxidative cationic polymerization. The polymer formed under more drastic conditions possessed a darker color and a higher C/(H + Cl) atomic ratio

299. REACTION OF ANTIMONY PENTACHLORIDE WITH MONOALKYLBENZENES

Kovacic, P., Sparks, A K.
***Journal of Organic Chemistry*, v. 28, no. 4, pp. 972–974, April 1963**

The products formed from antimony pentachloride and monoalkylbenzenes included chloroalkylbenzenes, diarylmethane-type hydrocarbons, disproportionation products, and polymeric material. Ethylbenzene yielded chloroethylbenzene, 1-(ethylphenyl)-1-phenylethane, and polymer. Cumene gave chlorocumene, benzene diisopropylbenzene, 2-(isopropylphenyl)-2-phenylpropane, and polymer. Evidence was found for a cocatalytic effect in the cumene–antimony pentachloride reaction involving side-chain attack.

300. POLYBENZIMIDAZOLES, NEW THERMALLY STABLE POLYMERS

Vogel, H., Marvel, C. S.
***Journal of Polymer Science*, v. 50, no. 154, pp. 511–539, April 1961**

Wholly aromatic polybenzimidazoles were synthesized from aromatic tetraamines and difunctional aromatic acids and characterized as new thermally stable polymers. The melt polycondensation of aromatic tetraamines and the diphenyl esters of aromatic dicarboxylic acids was developed as a general procedure of wide applicability. Polybenzimidazoles containing mixed aromatic units in the chain backbone were prepared from 3,3′-diaminobenzidine, 1,2,4,5-tetraaminobenzene, and a variety of aromatic diphenyl dicarboxylates. Phenyl 3,4-diaminobenzoate could also be polymerized by melt condensation to give poly-2,5(6)-benzimidazole. The polymers were characterized by a high degree of stability, showing great resistance to treatment with hydrolytic media and an ability to withstand continued exposure to elevated temperatures. Most of the polymers were infusible, but some had melting points above about 400°C. Many of the polymers exhibited no change in properties on being heated to 550°C and showed a weight loss of less than 5% when heated under nitrogen for several hours to 600°C. The polymers were soluble in concentrated sulfuric acid and formic acid, producing stable solutions. Many of the polymers were soluble in dimethyl sulfoxide and some also in dimethylformamide. The inherent viscosities of a number of polymers in 0.5% dimethyl sulfoxide solution ranged from approximately 0.4 to 1.1. The higher polymers could be cast into stiff and tough films from formic acid and dimethyl sulfoxide solutions.

301. COLLECTIVE INTERACTIONS IN POLYMERIZATION PROCESSES AT LOW TEMPERATURES AND IN POLYMERS WITH CONJUGATED BONDS

Semenov, N. N.
***Journal of Polymer Science*, v. 55, no. 162, pp. 563–596, December 1961**

The first part of the paper is concerned with low-temperature polymerization, and a hypothesis explaining its mechanism is proposed. Physical properties of new classes of polymers are discussed in the second part. The importance of electron collectivization and energy levels both in polymerization processes and in physical properties is emphasized.

302. POLYMERS WITH SYSTEMS OF CONJUGATED BONDS AND HETEROATOMS IN THE CONJUGATED CHAIN

Berlin, A. A.
***Journal of Polymer Science*, v. 55, no. 162, pp. 621–641, December 1961**
(Paper presented at the IUPAC International Symposium on Macromolecular Chemistry, Moscow, June 1960)

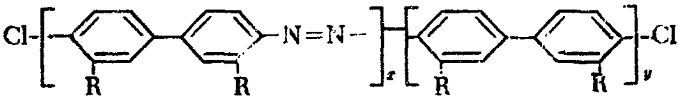
Review and discussion are presented of the synthesis and study of the properties of polymers having conjugated bond systems and heteroatoms (in particular, metal atoms) in the conjugated chain. A characteristic feature of such polymeric substances is the great degree of delocalization of the π-electrons in the macromolecule. The decrease in the internal energy due to the delocalization of π-electrons and the energy gain in the unpairing of the π-electrons in the conjugated chain are responsible to a considerable degree for the high thermostability of macromolecules containing systems of conjugated bonds. The decrease in the energy of excitation to the triplet state and the decrease in the ionization potential for long conjugated chains give rise to semiconductivity and specific magnetic, electron-exchange, optical, and chemical properties of these substances.

The polymers are divided into those with acyclic conjugated systems (polyvinylenes), those containing aromatic structures in the conjugated chain, and those containing heterocyclic and metallocyclic structures in the conjugated chain.

303. SYNTHESIS AND PROPERTIES OF SOME AROMATIC POLYMERS

Berlin, A. A., Liogonkii, B. I., Parini, V. P.
***Journal of Polymer Science*, v. 55, no. 162, pp. 675–682, December 1961**

Multinuclear aromatic compounds are distinguished by considerable thermostability. In a number of cases they have been shown to be endowed with semiconductor properties. In view of this, the development of a method of synthesis and investigation of aromatic polymers with a common system of conjugated bonds has both theoretical and practical interest. Such substances have been synthesized by the authors on decomposing bisdiazo compounds by an ammoniacal solution of univalent copper, and also on decomposition of bisnitroso acetates. In particular, 4,4′-bisdiazobiphenyl, 4-4′-bisdiazobitolyl, 4-4′-bisdiazobiphenyl-3,3-dicarboxylic acid, and benzidine, *N,N′*-bisnitroso acetate were employed. On decomposition of the bisdiazo compounds, a powder of orange to brown color was formed, soluble in concentrated sulfuric acid and insoluble in most organic solvents. Analysis showed it probably to possess the composition:



where R may be H, COOH, or CH_3. On the average one azo group is present for each 4–10 benzene rings and two chlorine atoms for each 10–20 rings. The mean molecular weight determined for one of the carboxylated polymer specimens was found to be 3000. On heating to 400°C the polymer decarboxylates. At 450°C decomposition sets in. Viscosity curves of the solutions (plots of η_{sp}/C vs. C) exhibit an anomalous rise within the limits $C = 0.1–1\%$. The concentration of unpaired electrons in the polymers was shown by the electron resonance method to be $\sim 10^{19}$/g. Heating the substances leads to an increase in concentration of unpaired electrons by 1–2 magnitudes. The spectra and X-ray diagrams of the substances were obtained. Evidently the formation of polymers from bisdiazo compounds is of a radical nature, leading to the formation of stable radicals of low activity. Low molecular fractions isolated from the polymers are fusible and soluble in benzene. They are capable of reacting with diethynylbenzene with the formation of nonmelting and insoluble thermostable products. Carboxylated polymers form salts with transition elements that evidently are of the nature of intracomplex compounds with intermolecular cross-linkage. Products of the decomposition of benzidine bisnitroso acetate are in general similar to those resulting from bisdiazodiphenyl, but contain less unpaired electrons.

304. SOME RESULTS OF CESIUM-INITIATED DIENE POLYMERIZATION AND COPOLYMERIZATION

Rembaum, A., Ells, F. R., Morrow, R. C., Tobolsky, A. V.
***Journal of Polymer Science*, v. 61, no. 171, pp. 155–165, September 1962**

A study of the homogeneous polymerization of isoprene and butadiene by means of alkali aromatic complexes confirmed the influence of polarity of the medium on the microstructure of the homopolymer. Cesium naphthalene in tetrahydrofuran yielded a high concentration of the 1,2-adduct (29%) and 3,4-adduct (43%) in polyisoprene, but a comparatively low concentration of 1,2-structures (74.5%) in polybutadiene. Practically pure, 1,2-polybutadiene was synthesized by means of Li naphthalene. A gradual decrease in the concentration of 1,2-polybutadiene structures was noted as the electropositivity of the alkali counterion increased. The influence of solvent, temperature, and molecular weight on the structure of polybutadiene was examined. Copolymerization of the isoprene-styrene monomer pair yielded block polymers. The determination of the torsional modulus–temperature spectrum afforded a simple method for distinguishing block from random copolymers.

305. SYNTHESIS AND SOME ELECTROPHYSICAL PROPERTIES OF POLYMERS WITH SYSTEM OF CONJUGATED BONDS

Korshak, V. V., Vinogradova, S. V., Sosin, S. L., Sladkov, A. M.
Preprint 69, presented at the International Symposium on Macromolecular Chemistry, Paris, France, July 1–6, 1963, sponsored by the International Union of Pure and Applied Chemistry, under the patronage of Monsieur le Ministre d'État chargé de la Recherche Scientifique, under the auspices of the Délégation Générale à la Recherche Scientifique et Technique, and the National Committee for Chemistry
(To be published in *Journal of Polymer Science, Part C: Polymer Symposia*)

Polymers with a conjugated system of carbon–nitrogen and carbon–carbon bonds have been obtained by the treatment of aliphatic and aromatic nitriles, aromatic diamines, and diphenols with *tert*-butyl peroxide (polyrecombination reaction). By this reaction polymers containing iron (polyferrocene) and germanium have also been obtained. Polymers and copolymers with conjugated system of carbon–carbon and carbon–other element bonds have been obtained from acetylene and bisethynyl derivatives of silicon, germanium, and tin by the oxidative polydehydrocondensation reaction. By means of the polycoordination reaction some polymers with chelate bonds have been synthesized which contain metals in the main chain such as copper, zinc, cobalt, beryllium, nickel, and others. In the polymers with a conjugated system of bonds thus obtained, the presence and the intensity of a single line of the ESR spectrum were determined to be due to the electron delocalization along the chain; the dependence of the electric conductivity on the temperature has been shown to have an exponential character. The values of the activation energy for conductivity and magnetic susceptibility were determined. The data obtained indicate that the polymers studied have some properties characteristic of semiconductor materials.

306. CONDUCTING POLYMERS FROM CYCLOPENTADIENE

Blatz, P. E.
Preprint 71, presented at the International Symposium on Macromolecular Chemistry, Paris, France, July 1–6, 1963, sponsored by the International Union of Pure and Applied Chemistry, under the patronage of Monsieur le Ministre d'État chargé de la Recherche Scientifique, under the auspices of the Délégation Générale à la Recherche Scientifique et Technique, and the National Committee for Chemistry
(To be published in *Journal of Polymer Science, Part C: Polymer Symposia*)

Similar infrared spectra are observed when cyclopentadiene is polymerized with any of the following catalysts: stannic chloride, titanium tetrachloride, or the combination of titanium tetrachloride and aluminum alkyl. When the resulting polymer is brominated, it spontaneously undergoes a spectacular dehydrobromination which gives a series of color changes and finally a black carbonlike material that is insoluble in common laboratory solvents. Consideration of the remaining bromine content of the dehydrobrominated polymer along with the visual spectrum produced by the actively dehydrobrominating polymer, the infrared and ultraviolet spectra and the visual spectrum of the original and isomerized polycyclopentadiene indicate the structure of the polymer and the mode of polymerization. The bromodehydropolycyclopentadiene shows unusual physical properties; it has a resistivity of 10^6 ohm-cm and an electron spin density of 10^{18} spins/g. The polymer also exhibits unusual thermal stability. In a nitrogen atmosphere at 900°C it is still 50% intact and is not completely pyrolyzed until a temperature of 1100°C is reached.

307. POLYMÈRES À LONGUES SÉQUENCES DE DOUBLES LIAISONS CONJUGUÉES: PRÉPARATION ET PROPRIÉTÉS (POLYMERS WITH LONG SEQUENCES OF CONJUGATED DOUBLE BONDS: PREPARATION AND PROPERTIES)

Roth, J. P., Rempp, P., Perrod, J.

Preprint 72, presented at the International Symposium on Macromolecular Chemistry, Paris, France, July 1–6, 1963, sponsored by the International Union of Pure and Applied Chemistry, under the patronage of Monsieur le Ministre d'État chargé de la Recherche Scientifique, under the auspices of the Délégation Générale à la Recherche Scientifique et Technique, and the National Committee for Chemistry

(To be published in *Journal of Polymer Science, Part C: Polymer Symposia*)

Macromolecular chain molecules bearing long sequences of double bonds cannot be readily obtained by polymerization reactions, but it is possible to create such unsaturated blocks on suitable saturated polymers by an elimination reaction. It appears that polyvinyl halides are quite suitable for this purpose. An attempt was made to get compounds as well defined as possible. Therefore, thermal dehydrohalogenation was not used as it usually yields cross-linked samples, nor was elimination by means of organic bases, which leads to substitution side-reactions. Lithium chloride (and some other salts) is quite effective, in dimethylformamide (DMF) solution, on polyvinyl halides; this reaction, if carried out at moderate temperature, creates very long polyenic sequences on the PVC macromolecules. These substances are usually dark violet powders and exhibit strong light absorption near 550 mμ. To elucidate further the dehydrohalogenation mechanism systematic experiments have been carried out, and it has been shown that the chloride anion behaves in DMF solution as a strong base, and is responsible for the observed reaction. Electrical conductivity measurements have been undertaken on the dehydrohalogenated polymers at constant frequency (1520 cps). Resistivities at room temperature are quite high, but typical semiconductive behavior has been observed for their thermal variation. The activation energies have been found to decrease with increasing insaturation.

308. POLYDICYANOACETYLENE: PREPARATION AND PROPERTIES

Beneš, M., Peška, J., Wichterle, O.

Preprint 74, presented at the International Symposium on Macromolecular Chemistry Paris, France, July 1–6, 1963, sponsored by the International Union of Pure and Applied Chemistry, under the patronage of Monsieur le Ministre d'État chargé de la Recherche Scientifique, under the auspices of the Délégation Générale à la Recherche Scientifique et Technique, and the National Committee for Chemistry

(To be published in *Journal of Polymer Science, Part C: Polymer Symposia*)

Synthesis of conjugated polymers by direct catalytic polymerization of suitable monomers is studied. Polymerization of dicyanoacetylene (DCA) with which formation of polymers analogous to the well-known "black Orlon" could be expected is described in detail. DCA polymerizes by the action of anionic polymerization catalysts. The reaction is strongly exothermal and requires a large amount of catalyst. The method of gradual addition of the catalyst to the solution of the monomer was therefore adopted. Under these conditions a low molecular weight ($< 10^3$) polymer is formed, and the conversion is directly proportional to the amount of the catalyst (butyllithium). With Li naphthalene or benzophenone-Li-ketyl, initiation by electron transfer was observed, as neither naphthalene nor benzophenone is bound to the polymer. The polymer has apparently the structure of polycyanopolyene, as strong CN absorption is found in the infrared spectrum, persisting up to 200°C. The polymer is soluble in water and in polar organic solvents. It is paramagnetic and the ESR spectrum shows a single narrow signal (7 gauss) without any fine structure. Electric conductivity in the solid state was measured in pressed disks between Pt electrodes under pressure in high vacuum. Conductivity at room temperature σ_{20} was found to be in the range 10^{-9}–10^{-12} ohm^{-1} cm^{-1}, and the activation energy ($E/2kT$) was 0.8–1.2 ev, differing according to the method of synthesis.

309. CATALYSE SUR POLYMÈRES PRÉSENTANT DES PROPRIÉTÉS DE RÉSONANCE PARAMAGNÉTIQUE ÉLECTRONIQUE (CATALYSIS OF PRESENT POLYMERS WITH PROPERTIES OF ELECTRON PARAMAGNETIC RESONANCE)

Dawans, F., Gallard, J., Teyssie, Ph., Traynard, Ph.

Preprint 75, presented at the International Symposium on Macromolecular Chemistry, Paris, France, July 1–6, 1963, sponsored by the International Union of Pure and Applied Chemistry, under the patronage of Monsieur le Ministre d'État chargé de la Recherche Scientifique, under the auspices of the Délégation Générale à la Recherche Scientifique et Technique, and the National Committee for Chemistry

(To be published in *Journal of Polymer Science, Part C: Polymer Symposia*)

New polymers synthesized by condensation of unsaturated polymers (polydienes) with chloranil and benzoquinone exhibit a strong electron spin resonance signal (2×10^{21} spins/g) comparable to that of thermally treated polyacrylonitrile. All these polymers have a noticeable catalytic activity on the decomposition of N_2O, the dehydration of cyclohexanol, and the isomerization of 1-butene. An interesting parallel was established between the catalytic activity of all these products and their spin concentrations.

310. POLYVINYLANTHRAQUINONE REDOX RESINS (ELECTRON EXCHANGE POLYMERS)

Manecke, G., Storck, W.

Preprint 81, presented at the International Symposium on Macromolecular Chemistry, Paris, France, July 1–6, 1963, sponsored by the International Union of Pure and Applied Chemistry, under the patronage of Monsieur le Ministre d'État chargé de la Recherche Scientifique, under the auspices of the Délégation Générale à la Recherche Scientifique et Technique, and the National Committee for Chemistry

(To be published in *Journal of Polymer Science, Part C: Polymer Symposia*)

Polycondensation redox resins (electron exchange polymers) with *p*-quinone/hydroquinone redox groups show at the potentiometric titration, in comparison with comparable monomer redox systems, higher normal redox potentials and also raised index potentials. To investigate the reason for this behavior, hydroquinone, phenol, and formaldehyde redox compounds of low and uniform molecular weight were synthesized and their redox properties studied. The titration curves were analyzed theoretically. As the structure of the polycondensation redox resins is not uniform and as they are also chemically not very stable, new redox resins with uniform structure and better chemical properties were synthesized. For this purpose 2-methyl-3-vinyl-1,4-naphthoquinone and 2-vinyl-9,10-anthraquinone were synthesized. The naphthoquinone compound polymerized very badly. The new synthesis of the 2-vinylanthraquinone yielded a very pure monomer which showed very good polymerization- and copolymerization-properties. A cross-linked copolymer of styrene, divinylbenzene, and 2-vinylanthraquinone was sulfonated. The so-produced swellable redox resins of relative uniform structure are resistant to mild oxidizing agents and chemically stable at all pH regions. The cation exchange capacity, the redox capacity, the normal redox potentials, and the infrared absorption were investigated as functions of the composition of the redox resins. The possibility of catalyzing the slow establishment of equilibrium of the redox resins during the redox reactions is discussed.

311. FORMATION DE COMPLEXES MOLÉCULAIRES SUR HAUTS POLYMÈRES (FORMATION OF MOLECULAR COMPLEXES OF HIGH POLYMERS)

Smets, G., Balogh, V., Castille, J. P.

Preprint 82, presented at the International Symposium on Macromolecular Chemistry, Paris, France, July 1–6, 1963, sponsored by the International Union of Pure and Applied Chemistry, under the patronage of Monsieur le Ministre d'État chargé de la Recherche Scientifique, under the auspices of the Délégation Générale à la Recherche Scientifique et Technique, and the National Committee for Chemistry

(To be published in *Journal of Polymer Science, Part C: Polymer Symposia*)

The 2,4-dinitropolystyrene, obtained by nitration of polystyrene, supplies the EDA complexes with hydrocarbons and naphthalene amines (α-naphthylamine). Similarly, the polystyrene *p*-dimethylamine binds the dinitro- and trinitrobenzene with formation of pairs of contact and complex. The behavior of the polymers is compared to that of the homologs of low molecular weights, such as 2,4-dinitrocumene, and cumene *p*-dimethylamine. The equilibrium constants of complexing are compared among themselves, and discussed. Their spectrometric evaluation is made difficult by the changing in position of the maxima and coefficients of absorption. In a similar way, the absorption power of the hydrocarbons has been studied with regard to the coordination complexes obtained by adding nickel thiocyanate to poly-4-vinylpyridine. Although it is not possible to obtain a coordination complex from two bases by the nickel ion, nevertheless the electronic assessment of aromatic hydrocarbons is important enough, and essentially a function of the wealth of different new aromatics. The aliphatic hydrocarbons are only very feeble adsorbers. The adsorption of alcohols and amine has been equally considered.

312. NEW FERROUS-CONTAINING POLYMERS BASED ON FERROCENE AND THEIR ELECTROPHYSICAL PROPERTIES

Paushkin, I. M., Polak, L. S., Vishnyakova, T. P., Patalakh, I. I., Machus, F. F., Solinskaya, T. A.

Preprint 83, presented at the International Symposium on Macromolecular Chemistry, Paris, France, July 1–6, 1963, sponsored by the International Union of Pure and Applied Chemistry, under the patronage of Monsieur le Ministre d'État chargé de la Recherche Scientifique, under the auspices of the Délégation Générale à la Recherche Scientifique et Technique, and the National Committee for Chemistry

(To be published in *Journal of Polymer Science, Part C: Polymer Symposia*)

A number of new polymers based on ferrocene were prepared and their electrophysical properties investigated. The polymers were obtained from the polyrecombination, i.e., by linkage of the primary monomers of ferrocene with a number of aromatic compounds (naphthalene bromide, *p*-dichlorobenzene, quinoline, benzonitrile, diphenyl, diphenylamine) in the presence of *tert*-butyl peroxide. The prepared polymers are black powders infusible up to 500°C. Approximately ⅓–¼ of a polymer is a soluble product and correspondingly ⅔–¾ are insoluble parts. Molecular weights of the soluble polymers are within the range of 2000–3000; elementary composition and Fe content are in good agreement with the given formulae. The polymers give a peak in the EPR spectrum. Polymers obtained from alkyl ferrocenes (from *i*-$C_4H_9C_5H_4FeC_5H_5$-$C_8H_{17}C_5H_4FeC_5H_5$), e.g., *tert*-butylferrocene, are soluble, and melt at 290–300°C, but these polymers do not give a peak in the EPR spectrum. Unlike benzene and its homologs, ferrocene forms high molecular compounds by polycondensation with acetone; these polymers have molecular weights of 3000–3200, melting points of 320–360°C, and give a peak in the EPR spectrum. Polycondensation of acetyl, alkyl acetyl, and diacetyl ferrocenes forms soluble and insoluble polymers giving a peak in the EPR spectrum. For a number of the prepared polymers electrophysical properties have been defined.

Measurements of conductivity were made in vacuum (1×10^{-4} mm Hg) by the compensation method within the temperature range of 20–200°C. All samples have a positive thermal coefficient of conductivity and in the investigated range of temperature are subjugated to the exponential dependency of conductivity on temperature $\sigma = \sigma_0 e^{-E/kT}$ which is characteristic of usual semiconductors. The value of specific electroconductivity at 50°C is $1 \times 10^{-15} - 5 \times 10^{-8}$ ohm^{-1} cm^{-1} and the activation energy is 1.74–0.47 ev.

313. MOBILE ELECTRON-CHARGE-TYPE MOLECULAR COMPLEXES

Tsubomura, H., Kuboyama, A.
***Kagaku To Kogyo*, Tokyo, v. 14, no. 6, pp. 537–547,**
June 1961

Mulliken's theory initiated experimental as well as theoretical studies on mobile electron-charge-type molecular complexes, and led to the present level of works. A significant contribution in this field was the elucidation of electron structure and bonding characteristics of molecular complexes, and an understanding of electron and vibration spectra was further deepened. Information obtained is being utilized for analyses of reaction mechanisms, action of solid catalysis, and solid-state physics.

314. SYNTHESIS AND PROPERTIES OF POLYMERS WITH SYSTEMS OF CONJUGATED BONDS

***Khimicheskaya Promishlennost*, v. 5, pp. 23–30,**
July–August 1960
(One page translation available as "Theoretical Information on the Manufacture of Polymers With Desired Semiconducting and Heat-Resistance Properties,"
AID 60-81, Library of Congress, Air Information Div.,
Washington, D. C., November 7, 1960)

This article is a theoretical discussion based on materials published recently or unpublished at the time of the appearance of the article. In this review emphasis is placed on the synthesis of polymers with structures and distributions of energy on the bonding electrons which display desired physicochemical properties. Such properties include high thermal stability, increasing conductivity, and good semiconducting, magnetic, electrical, and ion-exchange properties.

315. SYMPOSIUM ON NEW SYNTHETIC POLYMERS

***Kogyo Kagaku Zasshi*, v. 65, pp. 658–742, 1962**

A number of the polymers for which syntheses were presented at the symposium are semiconducting. Specific papers concerning these are referenced in the following entries.

316. PARAMAGNETIC AND ELECTRIC PROPERTIES OF POLYACETYLENE

Hatano, M., Kambara, S., Okamoto, S.
***Kogyo Kagaku Zasshi*, v. 65, pp. 716–719, 1962**

The authors have obtained high molecular weight, crystalline or amorphous polyacetylene by the use of various catalyst systems of Ziegler–Natta type. The resultant polyacetylene had a stereoregular structure of substantially *trans*-conjugated C = C double bonds. Since it was expected that these polymers containing long chains of conjugated double bonds might have stable free radicals, paramagnetic and semiconducting properties of the polymers were measured. An appreciable concentration of unpaired electrons has been found in all of the polyacetylenes by means of electron spin resonance spectroscopy. Thus the authors had the figure, in spins/g, for amorphous polyacetylene, 10^{16}, for crystalline polyacetylene, 10^{19}, and for oxidized polyacetylene, 10^{17}. Each of these spectra consisted of a narrow singlet having 8 to 10 gauss of the line width. The *g*-factor of the spectra of polyacetylene was 2.0028. Hence, the unpaired electrons in polyacetylene would be expected to be unlocalized electrons which are stabilized via resonance in high conjugations. Then the conductivities of the pressed samples were measured at various temperatures by a direct current method. The variations of resistance of polyacetylenes with temperature were found to obey the usual equation for an intrinsic semiconductor.

317. POLYMERIZATION OF ACETYLENE BY BINARY SYSTEMS COMPOSED OF TRIETHYLALUMINUM AND VARIOUS ACETYLACETONATES OF TRANSITION METALS

Kambara, S., Hatano, M., Hosoe, T.
***Kogyo Kagaku Zasshi*, v. 65, pp. 720–723, 1962**

Recently, the authors have found that polyacetylene obtained by the use of Ziegler catalysts behaves as a typical organic semiconductor. In the present paper, a new catalyst system which is capable of synthesis of such polyacetylene as mentioned above has been studied. In the polymerization of acetylene, if catalyst systems are prepared from electrophilic transition metal compounds, e.g., $TiCl_4$, with $Al(C_2H_5)_3$, acetylene is converted to amorphous polymer. On the other hand, if a less electrophilic compound, e.g., $Ti(OC_4H_9)_4$, is used as a component of catalyst, high crystalline polyacetylene might be obtained from acetylene. The preferred catalyst components might be compounds containing no halogen atom rather than electrophilic compounds.

With these considerations in mind, the authors tried the polymerization of acetylene by the use of binary systems composed of triethylaluminum and some transition metal chelate compounds containing stable and neutral ligands. Various combinations of 2,4-pentadione compounds of metals of groups IV to VIII, e.g., Ti, V, Cr, Co, Fe, with $Al(C_2H_5)_3$ were used. In those combinations, the complex catalysts from $VO(CH_3COCHCOCH_3)_2$ $Al(C_2H_5)_3$ or $TiO(CH_3COCHCOCH_3)Al(C_2H_5)_3$ have been found to be very effective as the catalyst for the polymerization of acetylene to crystalline polymer. On the contrary, binary systems of the other combination were less effective or not at all effective.

318. THE STRUCTURE OF CRYSTALLINE POLYACETYLENE

Hatano, M.
***Kogyo Kagaku Zasshi*, v. 65, pp. 723–727, 1962**

The polymers obtained from acetylene by using catalysts of Ziegler type behave as a typical organic semiconductor and have unlocalized unpaired electrons. The author undertook the present study to learn more about the structure of these polymers as well as about the length of their conjugation, by means of the measurements of infrared spectra, specific resistances and X-ray diffraction patterns. It was supposed that the polyacetylene had a stereoregular structure of substantially *trans-trans* conjugated double bonds, and support for this view came from the data on infrared spectra and X-ray diffractions of the polymer. Thus, acetylene-d_2 was polymerized to poly(acetylene-d_2) by the catalyst, and infrared spectra of poly(acetylene-d_2) were compared with that of polyacetylene, and then each band of these polymers was assigned, respectively. This comparison showed that the polyacetylene had fully extended *trans*-conjugated double bonds. The X-ray diffraction patterns indicated that the molecular layers were kept separate from each other by 3.754 A. This value of intermolecular distance might be near enough to allow the electron in the crystallite to jump from one molecule to the next. A tentative consideration suggested that the conjugation might be more than 25 for the crystalline polymer, and less than 14 for the amorphous polymer.

319. RADIATION-INDUCED POLYMERIZATIONS BY TRIPLE BONDS

Okamura, S., Hayashi, K., Yamamoto, M., Nakamura, Y.
***Kogyo Kagaku Zasshi*, v. 65, pp. 728–731, 1962**

The mechanism of radiation-induced polymerization of monomers having a triple bond such as acetonitrile, propargyl alcohol, propargyl bromide, and phenylacetylene was investigated. The rate of polymerization is proportional to the first order of dose rate and not influenced by the existence of air. The activation energy is very small. As compared with the results of radical, cationic and anionic polymerization using catalysts, it may be concluded that polymerization of acetonitrile proceeds by the anionic mechanism. In the case of other monomers, it is not clear which mechanism is predominant. The g-values and degrees of polymerization are small.

Produced polymers have conjugated double bonds and are colored dark brown.

320. RADIATION-INDUCED LIQUID- AND SOLID-PHASE POLYMERIZATIONS OF ACETYLENE

Tabata, Y., Saito, B., Shibano, H., Sobue, H., Oshima, K.
***Kogyo Kagaku Zasshi*, v. 65, pp. 731–734, 1962**

Radiation-induced polymerization of acetylene was investigated in the liquid and solid states of monomer. It was concluded from these experimental results that the liquid phase polymerization proceeds by cationic mechanism.

It was found that the structures of the polymer obtained in the liquid and the solid state polymerizations are quite different, that is, in the former, *cis*-form polyacetylene is rich, and in the latter, *trans*-form is rich. These facts confirm that a stereospecific polymerization is possible in solid state polymerization, using ionizing radiation, as was previously pointed out by the authors.

The authors proposed a new mechanism, "electronic polymerization," for solid-state polymerizations at low temperatures.

321. PREPARATIONS AND ELECTRICAL CONDUCTIVITIES OF POLY(VINYLANTHRACENE) AND OF ITS MOLECULAR COMPLEXES

Inoue, H., Noda, K., Takiuchi, T., Imoto, E.
***Kogyo Kagaku Zasshi*, v. 65, pp. 1286–1290, 1962**

9-Vinylanthracene (I), m.p. 64.5–67°C, and 1-vinylanthracene (II), m.p. 64–66°C, were synthesized from corresponding acetylanthracenes through 1-(1-anthryl)ethanol. II gave a polymer in 75% yield at 76°C for 72 hr by using 0.1–1.0 mole % $(BzO)_2$ as an initiator. I gave 10–50% polymer in 24–94 hr when 0.2–1.0 mole % (*tert*-BuO$)_2$ was used as an initiator at 115–140°C. The degree of polymerization and melting point of these polymers were in the region 4–6 and 120–180°C, respectively. For the purpose of obtaining the steroregulated polymer, I was polymerized by Ziegler catalysts with various ratios of $AlEt_3$ to $TiCl_4$. The yield of the polymer at 80°C increased from 20 to 90% according to a decrease of the ratio from 4 to 2. Even with $TiCl_4$ alone, poly-I was obtained in an approximate 90% yield at 80°C. BF_3 OEt_2 also gave poly-I in a 91% yield even at room temperature. The repeated addition of iodine to poly-I prepared by the radical-type initiator finally gave a molecular complex (III) having a mole ratio of anthracene to iodine of 1.7. By a similar procedure, a molecular complex (IV) having the ratio 2.8 was obtained from poly-I prepared by Ziegler catalysis. Resistivity (ρ) of the polymers and their molecular complexes was determined at various temperatures and the energy gap

(ϵ) was calculated from $\rho = \rho_0 \exp(\epsilon/2kT)$. Values of ρ at 20°C were 1×10^{15}, 4.6×10^{13}, 2.1×10^{6}, and 3.7×10^{6} ohm-cm and ϵ values were 1.59, 1.32, 1.02, and 1.03 ev with respect to poly-I prepared by the radical initiator and poly-I prepared by Ziegler catalyst, III, and IV, respectively. The low ϵ value of poly-I prepared by Ziegler catalyst in comparison with poly-I prepared by the radical initiator is thought to be due to the difference in polymer structure as suggested by the X-ray diffraction diagram. Values of ϵ and ρ generally increased with the decrease in the iodine content of the complexes. Trinitrobenzene and Br also gave complexes with poly-I prepared by Ziegler catalysis, having ρ 1.2×10^{13} and 7.2×10^{12} ohm-cm and ϵ 1.03 and 1.50 ev, respectively.

322. PREPARATION AND ELECTRICAL CONDUCTIVITIES OF METAL CHELATE POLYMERS

Inoue, H., Hatashi, S., Takiuchi, T., Imoto, E.
***Kogyo Kagaku Zasshi*, v. 65, pp. 1622–1626, 1962**

Thirty-one metal chelate polymers were prepared by combining five different ligands, 2,3-diacetylresorcinol (DAR), 2,4-diacetylresorcinol oxime (DOR), 1,4- and 1,5-dihydroxyanthraquinone (1,4-DOA, 1,5-DOA) and 1,5-dihydroxyphenazine (DOP), with metal ions, Cu^{++}, Zn^{++}, Fe^{++}, Ni^{++}, Co^{++}, Cr^{+++}, Pb^{++}, Sn^{++}, and Sn^{++}. Electrical conductivities were studied. The electrical resistivity is 10^{11}–10^{16} ohm cm at 20°C with an energy gap 1–3 ev. With each ligand, the energy gap is smaller as the ionization tendency of the metal ion is higher, and, with each metal ion, (DOP) > (DOR) > (1,4-DOA), (1,5-DOA) > (DAR).

323. SEMICONDUCTING POLYMERS

April 12, 1961
Library of Congress, Air Information Division,
Science and Technology Section, Washington, D. C.
AID 61-49
AD-255,791
(Also available through U.S. Dept. of Commerce, Office of Technical Services, Washington, D. C.)

This report, a brief analysis of current Soviet experiments on chelate-type semiconducting polymers, presents translations from (1) "Some Electrophysical Properties of Polymer Complexes Formed by Tetracyanoethylene With Metals," *Akademiya Nauk SSSR, Doklady*, v. 136, pp. 1127–1129, 1961; (2) "Letter to the Editor," *Akademiya Nauk SSSR, Izvestiya, Otdeleniye Khimicheskikh Nauk*, v. 12, p. 2261, December 1959; and (3) "Method of Obtaining Chelate Polymer Compounds" (Authors' Certificate 126612), *Byulleten Izobretenii*, v. 5, p. 38, 1960. Source 1 describes experiments in which thoroughly cleaned copper, iron, or nickel plates are exposed to vapors of tetracyanoethylene at 150 to 400°C and covered with thin films of a polymer consisting of carbon, nitrogen, and metal bound with ordinary and chelate-type valences into an assumedly azoporphyrin structure. Similar polymers were obtained by A. A. Berlin and associates in 1959 (source 2) by the condensation of copper-acetonylacetonate with tetracyanoethylene at 160–300°C. Source 3 lists an Authors' Certificate (126612) for a method of manufacturing heat-resistant chelate polymers, issued April 7, 1959. This method provides both for film production on metal plates and for hot pressing of tetracyanoethylene with finely dispersed metals.

324. CONJUGATED POLYMERIC SCHIFF'S BASES. THERMALLY STABLE POLYMERS WITH LOW ELECTRICAL RESISTIVITY

Akitt, J. W., Kaye, F. W., Lee, B. E., North, A. M.
***Makromolekulare Chemie*, v. 56, pp. 195–199, 1962**
(in English)

Polymeric Schiff's bases have been obtained by the condensation of conjugated dialdehydes, such as glyoxal and terephthalaldehyde, with conjugated diamines such as phenylene diamine or diamino phenol. Low molecular weight colored polymers are obtained from aqueous systems, while high molecular weight black polymers are obtained by dilute solution condensation in dimethyl sulphoxide. The electrical conductivities of these polymers at room temperature range from 10^{-7} to 10^{-11}ohm^{-1}cm^{-1}. Spectroscopic, electron spin resonance, and conductivity measurements all suggest considerable electron delocalization both through the $-CH{=}N-$ linkage and across the meta positions of the aromatic nucleus. The high molecular weight compounds exhibit remarkable thermal stability.

325. ORGANIC SEMICONDUCTORS

Biehl, E. R., Deebel, G. F., Dolle, R. E., Wildi, B. S.
December 30, 1961
Monsanto Research Corporation, Dayton, Ohio
Semiannual Scientific Report 1 for May–December 1961,
AFCRL 62-245, AF 19(604)-8497
AD-281,892
(Also available through U.S. Dept. of Commerce, Office of Technical Services, Washington, D. C.)

The synthesis, purification, and single crystal growth of coronene, perylene/iodine complex and chloranil/durenediamine complex are described. The usual purification methods of organic chemistry, i.e., chromatography, crystallization, and vacuum sublimation, have been employed. Attempted analytical methods for determination of impurities in the above compounds are described. The polymer of 2,4,6-tricyano-*s*-triazine was prepared and shown to be a semiconductor.

326. ORGANIC SEMICONDUCTORS

Wildi, B. S., Biehl, E. R.
May 15, 1962
Monsanto Research Corporation, Dayton, Ohio
Final Report for May 1, 1961–April 30, 1962,
MRC DA-3, AFRCL 62-600, AF 19(604)-8497
AD-277,494
(Also available through U.S. Dept. of Commerce, Office of Technical Services, Washington, D. C.)

The synthesis, purification, and single crystal growth of coronene, perylene/iodine complex and chloranil/durenediamine complex are discussed. The usual purification methods of organic chemistry, namely, chromatography, recrystallization, sublimation and zone refining where applicable, were employed. Purification of coronene contaminated with 1:12-benzoperylene-1:12-C-14 (11,000 ppm) and coronene 1:2-dicarboxylic-1:2-C-14 anhydride (15,000 ppm) reduced the impurity concentration to 57 and 0.25 ppm, respectively. Attempted analytical methods for determination of trace impurities in the above compound are described. IR, UV, and fluorescence spectra apparently cannot determine impurity levels of the order of 1 ppm. X-ray analysis of coronene crystals, perylene/iodine crystals, and chloranil/durenediamine crystals revealed considerable strains and distortions. The electrical properties of the single crystals of the above semiconductors are described. Polymers of 2,4,6-tricyano-s-triazine and terephthalonitrile were prepared and shown to be semiconductors.

327. PURIFICATION AND CRYSTALLIZATION OF SOME ORGANIC COMPOUNDS [ABSTRACT]

Sloan, G. J.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 66–67
National Research Council, Ottawa, Canada, 1962

Zone refining and normal freezing have been applied not only to the purification of anthracene but to the quantitative estimation of purity. Gas chromatographic analysis of zone refined commercial anthracene showed at least 12 impurities, although only four were detectable in the starting material. Effective segregation coefficients were determined from normal freezing experiments at various rates for fluorene, anthraquinone, tetracene, and carbazole in anthracene, both with and without stirring.

A technique has been developed for zone refining anthracene in an inert atmosphere in a sealed system, and for transferring the purest fraction to a crystallizing tube for crystallization in vacuum, without opening the tube to the atmosphere. New techniques for crystallizing from solution are described.

328. RESEARCH ON THE PREPARATION OF PURE METALS

Brenner, W., Marsel, C. J.
March 15, 1963
New York University, College of Engineering, N. Y.
Final Report, AFCRL-63-97, AF 19(604)-4124

...Basic research on the preparation and characterization of organic semiconductors is discussed, with emphasis on the effect of chemical purity on the electronic properties of a series of polycyclic aromatic hydrocarbons. The preparation and electronic properties of certain acetylenic polymers are discussed. 70 references. (*STAR*, 1963, N63-16739)

329. TRAPPED RADICALS IN ORGANIC DEPOSITS

Mangiaracina, R., Mrozowski, S.
In "Proceedings of the 5th Conference on Carbon, Pennsylvania State University, University Park, June 19–23, 1961," Volume II, pp. 89–96
Pergamon Press, Inc., London, England, and The Macmillan Co., New York, N. Y., 1963

Polymeric deposits showing an electron spin resonance absorption were made by passing an electrical discharge through vapors of relatively simple organic compounds. Very high spin concentrations (10^{20}/g) were obtained in films formed using naphthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$) vapors. Paramagnetic spin centers were also found in films deposited from vapors of decalin ($C_{10}H_{18}$) and of secondary butyl alcohol ($C_4H_{10}O$) but with much lower concentration. The free radical structures are either formed in the discharge itself and then trapped in the deposit or created by bombardment of the film after deposition, and seem to be predominantly of an aromatic nature. By studying the heat-treatment dependence of the spin resonance in the temperature range 0–1000°C, differences are noted from films charred at temperatures above 400°C.

330. SYNTHESIS OF ACENAPHTHYLENE, ITS POLYMERS, AND COPOLYMERS WITH OTHER MONOMERS

Golubeva, A. V., Neĭmark, O. M., Usmanova, N. F., Sivograkova, K. A., Bezborodko, G. L., Meerzon, A. A.
***Plasticheskie Massy*, no. 8, pp. 3–6, 1960**

Acenaphthylene (I) was synthesized in 88% yield by catalytic dehydrogenation of acenaphthene at 640–650°C. Polymers of I were very brittle, but the 20:80 copolymer with styrene (II) had better heat resistance than polystyrene and good dielectric and mechanical properties. I was polymerized by the block method in the presence of Bz_2O_2 and by the emulsion method with $K_2S_2O_8$ initiator and sulfanol emulsifier. Copolymers of II and I were prepared by the block method in a sealed ampul and by emulsion in a stream of N at 80–85°C. The copolymer was separated by coagulation with a 5% solution of K alum, washed, and dried to constant weight. Properties were determined for the 50:50–10:90 copolymers and for polystyrene. The 20:80 copolymer and polystyrene show the following: power factor at 10^6 cps 0.0005, 0.0003; dielectric constant at 10^6 cps 2.6, 2.5; volume resistivity (ohm cm) 4×10^{16}, 1×10^{16}, and surface resistivity (ohms) 3.0×10^{16}, 1×10^{17}.

331. DEPOSITION OF THIN FILMS OF HYDROCARBON POLYMERS OF VARYING CONDUCTIVITIES

Pagnia, H.
***Physica Status Solidi*, v. 1, pp. 90–93, 1961 (in German)**

During ion or electron impact from glow discharge in a benzene atmosphere, polymeric layers are built up on exposed surfaces from the molecular fragments produced. The polymer layers vary with the pressure in the discharge vessel, the electrode distance, the strength of current and voltage, and the temperature. In particular, low temperatures and voltages produce hydrocarbon films of conductivities $\geqq 10^{-10}$/ohm cm; high temperatures and voltages produce carbon films with conductivities up to 100/ohm cm. The temperature stability upholds the conclusions.

332. CHARGE-TRANSFER MOLECULAR COMPLEXES AND THEIR ROLE IN CHEMICAL REACTIONS
Booth, D.
***Science Progress*, v. 48, no. 191, pp. 435–455, July 1960**

333. POLYMERS AS CONDUCTORS AND SEMICONDUCTORS
Atlas, S. M., Becher, M., Mark, H. F.
***SPE (Society of Plastics Engineers), Transactions of the*, v. 1, no. 4, pp. 169–173, August 1961**

The introduction of mobile ions (conduction by ion pairs), the introduction of mobile electrons (polymers with conjugated double bonds), the preparation of polymers with metallo-cyclics in the chain of conjugation, and the preparation of polymers containing heteroatoms are explained as methods of increasing polymer conductivity to the point of semiconduction and even conduction for low-frequency operation. The paramagnetic as well as electrical properties are discussed for polymers prepared by the four methods above.

334. ELEKTRONEN-DONATOR-ACCEPTOR KOMPLEXE (ELECTRON-DONOR-ACCEPTOR COMPLEXES)
Briegleb, G.
Springer-Verlag, Berlin, Germany, 1961

335. CONDUCTIVE MATERIAL
Gul, V. E., Kap'unov, Ya. N., Maizel, N. S., Ostryakov, I. A.
December 27, 1960 (application date)
U.S. Department of Commerce, Washington, D. C.
USSR Patent 140,110
(See also *Byulleten Izobretenii*, no. 15, p. 25, 1961)

The material is based on a furfurolacetone polymer, acetylene soot, and acetone.

336. SEMICONDUCTOR DEVICE MADE FROM ORGANIC SEMICONDUCTORS
Bohlmann, F., Dexheimer, H., Fuchs, O., Kraemer, H.
April 20, 1961 (patent application, September 28, 1957)
U.S. Department of Commerce, Washington, D. C.
German Patent 1,091,657 (assigned to Farbwerke Hoechst A.-G.)

Polynes of the formula $R(C \vdots C)_n R'$ exposed to light or heat form semiconductors. An example of heated 3-(1-naphthylcarbamoyloxy)propyl is detailed; the resistivities at 50 and 200°C were 10^{10} and 10^5 ohm cm, respectively.

337. ORGANIC SUBSTANCES WITH SEMICONDUCTIVE ELECTRICAL PROPERTIES
Ratusky, J., Sorm, F., Ulbert, K.
September 15, 1961 (patent application, May 28, 1960)
U.S. Department of Commerce, Washington, D. C.
Czechoslovakian Patent 100,972

Semiconductive materials which are more chemically and thermally stable than the corresponding inorganics are formed by thermal decomposition of salts of acetylene- and polyacetylenecarboxylic acids. An example is detailed.

338. VOLATILE ORGANIC LIQUIDS OF INCREASED ELECTRICAL CONDUCTIVITY
van der Minne, J. L., Hermanie, P. H. J.
December 12, 1961 (Netherlands patent application, December 30, 1952)
U.S. Department of Commerce, Washington, D. C.
U.S. Patent 3,012,969 (assigned to Shell Oil Co.)

Increase in electrical conductivity of an organic liquid containing 90 mole % C_{12} and having a dielectric constant less than 9 is claimed by the use of certain additives. Two additives are used for the compound, one a multivalent metal organic salt of molecular weight $\geqq$ 200, the other an O-containing compound of molecular weight $\geqq$ 200 and in which the product of this molecular weight and the specific conductivity in C_6H_6 at 1 g/l is $\geqq 10^{10}$. The two additives should not have an ion in common. Use of Cr diisopropylsalicylate and Na dioctyl sulfosuccinate increases the conductivity of the solution containing both to 165 times as great as the sum of the conductivities of the solutions containing only one of each.

339. ELECTRICALLY CONDUCTIVE POLYMERIC FIBERS AND FILMS
Campbell, T. W.
December 26, 1961 (patent application, December 9, 1957)
U.S. Department of Commerce, Washington, D. C.
U.S. Patent 3,014,818 (assigned to E. I. du Pont de Nemours & Co.)

A claim is made for production of electrically conductive polymers by mixing a solution of a synthetic hydrophobic polymer with a reducible salt of Ni, Co, Cu, or Fe, forming the mixture into a shared article, and then reducing the metal salt to the free metal by $NaBH_4$ or other reducing agent. The metals, which are more electronegative than Cr, are finely divided particles having an average diameter of $< 1\mu$. The amount of metal is 0.1–35% by weight of the article. The shaped articles, preferably films or fibers, can be plated with Ni, Co, Cu or any metal more electronegative than Mn. An example is given of a copolymer of acrylonitrile, Me acrylate and Na styrenesulfonate mixed with $FeCl_2$ and $HCONMe_2$.

340. SEMICONDUCTING POLYMERS FROM THE CONDENSATION OF ALDEHYDES AND KETONES

Lomonosov, M. V.
March 12, 1962 (patent application, January 4, 1961)
U.S. Department of Commerce, Washington, D. C.
French Patent 1,277,189 (assigned to Moscow State University)

Preparation of a heat-resistant polymer which has semiconducting properties is claimed, by polycondensation of Me_2CO in the presence of a Lewis acid. Me_2CO with anhydrous $ZnCl_2$ as a catalyst yields a dark purple polymer heat-resistant at 500°C. Other polymers are obtained by the following carbonyl compounds and catalysts: Me_2CO, $TiCl_4$; Me_2CO, $FeCl_3$; PhAc, $ZnCl_2$; and AcH, $ZnCl_2$.

341. SEMICONDUCTING POLYMERS

Okamura, S., Hayashi, K., Ohdan, K.
August 8, 1962 (patent application, June 21, 1960)
U.S. Department of Commerce, Washington, D. C.
Japanese Patent 10,594 (assigned to Japanese Association for Radiation Research on Polymers)

A claim is made for preparation of a red-brown, transparent elastomer with specific resistance (ρ) of 3×10^4 ohm-cm at 20°C, and a pale-yellow transparent resin with ρ of 4×10^4 ohm-cm. The former is composed of acrylonitrile, $HCONMe_2$, and $AgNO_3$ irradiated by gamma irradiation of 1.2×10^6 r; the latter consists of acrylonitrile, a lesser amount of $HCONMe_2$, and $AlCl_3$.

342. SEMICONDUCTIVE POLYMERS

Topchiev, A. V., Krentsel, B. A., Kargin, V. A., Davydov, B. E., Makhova, I. E.
February 13, 1963 (patent application, May 30, 1961)
U.S. Department of Commerce, Washington, D. C.
British Patent 918,368 (assigned to Institut Neftekhimicheskogo Sinteza, Akademiya Nauk, SSSR)

Semiconductive polymers were produced by condensation of phthalic anhydride (I) with hydroquinone (II) in the presence of metal salts, such as $CdCl_2$, $ZnCl_2$, or $AlCl_3$. An example is given of equimolecular amounts of I and II heated to 238–252°C in the presence of 10 wt. % $ZnCl_2$ for 17–21 hr, the polymer formed washed and dried and then pressed into tablets which showed a specific conductivity of $10^{-6} - 10^{-5}$ $ohm^{-1}cm^{-1}$ at room temperature and an activation energy of 0.6–0.8 ev.

343. ELECTRICAL CONDUCTIVITIES OF POLYCONDENSED BENZOPYRAZINE AND RELATED COMPOUNDS

Inoue, H., Imoto, E.
***University of Osaka Prefecture, Bulletin of the, Series A—Engineering and Natural Sciences*, v. 10, pp. 61–70, 1961**

Heteroaromatic compounds in which benzene rings fused alternately with dihydropyrazine rings were formed by the reaction of 4,5-dichlorocyclohexene-3,6-dione with NH_3 (resistivity ~ 10^{11}–10^{16} ohm-cm). Dehydrogenation changed resistivity to the order 10^{13}–10^{14} ohm-cm. Metal chelates of this material showed resistivity of ~ 10^{12}–10^{13}, and iodine complexes of the material, ~ 10^{7}–10^{8}.

344. ON THE POLYMERS OF CHELATE COMPOUNDS

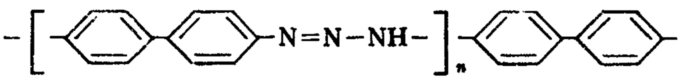
Berlin, A. A.
***Uspekhi Khimii i Tekhnologii Polimerov, Sbornik,* v. 3, pp. 3–13, 1960**

The synthesis of metal chelate polymers is proposed as one answer to the current search for polymer compounds with high thermal stability, electroconductivity, magnetic permeability, electrono-ionic exchange capacity, and other properties. Syntheses are described for a number of the chelate polymers, and the relative merit of using Cu^{++}, Co^{++}, Zn^{++}, Ni^{++}, and Cd^{++} for the metal is pointed out.

345. AROMATIC POLYTRIAZENES

Berlin, A. A., Liogonkii, B. I., Parini, V. P.
***Vysokomolekulyarnye Soedineniya*, v. 3, no. 10, pp. 1491–1494, October 1961**
(Translated from the Russian in *Polymer Science U.S.S.R.*, v. 3, no. 6, pp. 1000–1004, 1962; published May 1963)

The present communication deals with the preparation and study of aromatic polytriazenes of the general formula



Aromatic polytriazenes have been prepared, of evidently linear structure and of greater heat resistance than monomeric triazenes. Anomalous viscosities suggest association of rigid macromolecules in solution. The strength and nature of the ESR spectra of the polymers indicate that conjugation is maintained along the macromolecules and that unpaired electrons exist in the ground state of the material. The rigidity of the macromolecules, manifested in the anomalous viscosities, also confirms the preservation of conjugation. At room temperature the aromatic polytriazenes are virtually insulators. At higher temperatures their electrical conductivity increases considerably.

The method of preparation described may be considered to be applicable generally for derivatives of aromatic polytriazines with different substituents in the benzene ring.

346. POLYMERIZATION KINETICS OF HYDROCARBONS WITH CONJUGATED BONDS—II. POLYMERIZATION OF PHENYLACETYLENE AND THE PARAMAGNETIC PROPERTIES OF THE POLYMERS

Shantarovich, P. S. Shlyapnikova, I. A.
***Vysokomolekulyarnye Soedineniya*, v. 3, no. 10, pp. 1495–1499, October 1961**

(For Part I, see Entry #707, AI/LS 341.) The products of the thermal polymerization of phenylacetylene have been investigated. The polymer has a chain length of 6–17 monomer units. All specimens exhibit durable EMR spectra in the form of a narrow-line singlet without hyperfine structure. With elevation of temperature the mean molecular weight of the polymer falls and the EMR signal increases. At temperatures of 400–450°C carbonization takes place, accompanied by a sharp increase in the EMR signal to 10^{19}–10^{20} active particles per gram.

347. ELECTRICALLY CONDUCTING SYSTEMS BASED ON POLYMERS—I. INVESTIGATIONS OF THE STRUCTURE OF CONDUCTIVE SYSTEMS BASED ON UNCURED RESINS

Gul, V. E., Maizel, N. S., Kamenskii, A. N., Fodiman, N. M.
***Vysokomolekulyarnye Soedineniya*, v. 4, no. 5, pp. 642–648, May 1962**
(Translated from the Russian in *Polymer Science U.S.S.R.*, v. 4, no. 2, pp. 207–214, July 1963)

The structure of current conducting compositions consisting of unsolidified phenol formaldehyde resin of the resol type and of epoxide resin E-40 together with varying amounts of acetylene black has been investigated. It has been shown that when the concentration of the black reaches a value of 30% an abrupt fall in the specific electrical resistance takes place. The structural and mechanical properties of the composition showed that at sufficiently high degrees of filling a difference arises in the yield value of the filled resins. This indicates structuration of the black. The structure formation was confirmed by electron microscope studies which revealed chain structures of the black particles at a concentration of about 30% carbon black. The reason for the higher conductivity of compositions based on phenol formaldehyde resin than upon epoxide resin for equal black contents is due to better compatibility of the former resin with the black. Electron microscope studies confirmed the fact that the chemical nature of the binder has an important influence on the electroconductivity of the composition.

348. ELECTRICALLY CONDUCTING SYSTEMS BASED ON POLYMERS—II. INVESTIGATIONS OF THE STRUCTURE OF CONDUCTIVE COMPOSITIONS BASED ON HARDENED RESINS

Gul, V. E., Maizel, N. S., Kamenskii, A. N., Fodiman, N. M.
***Vysokomolekulyarnye Soedineniya*, v. 4, no. 5, pp. 649–654, May 1962**
(Translated from the Russian in *Polymer Science U.S.S.R.*, v. 4, no. 2, pp. 215–221, July 1963)

The present work is concerned with the examination of the hardening process whereby the materials under examination pass gradually from the viscous-flow to the solid state during the period of observation. The authors followed the structural changes occurring during the hardening of compositions based on a phenol–formaldehyde resole resin and the epoxide resin E-40 containing various proportions of acetylene black, and compared the results with the results of the measurement of electrical properties.

In experiments on the hardening of the resins, the specimens were held for a suitable time at a high temperature—the phenol–formaldehyde compositions at +150°C and the epoxide compositions at +80°C.

In order to study the structural changes occurring during the curing process, an apparatus was designed which, in conjunction with a Polyani dynamometer and a PMT-3 micro hardness gauge, enabled the variation in viscosity of the polymeric systems during hardening to be followed. The apparatus was a modification of the Volarovich and Tolstoi dynamometer in conjunction with a Polyani dynamometer. By measuring the limiting load P required to stretch rods of the hardened compositions, it is possible to determine the absolute shear stress.

349. NITROGEN-CONTAINING POLYMERS WITH PARAMAGNETIC PROPERTIES

Maltsev, V. I., Lebedev, V. B., Itskovich, V. A., Petrov, A.A.
***Vysokomolekulyarnye Soedineniya*, v. 4, no. 6, pp. 848–850, June 1962**

Insoluble powders with paramagnetic and semiconductor properties have been obtained on oxidizing aromatic amines (aniline, diphenylamine and triphenylamine). The intensity of the EPR signal increases after heating or UV irradiation of the specimens or after passing an electric current through them, or cooling them to −180°C. The products obtained apparently contain quinoid and amine groupings, interaction of which in the solid polymer is of the same nature as that taking place in paramagnetic mixtures of quinone and amine powders or in polyphenylaminoquinones.

350. CONJUGATED BOND POLYMERS WITH HETEROATOMS IN THE CONJUGATED CHAIN. XIX. SOME PROPERTIES OF ANILINE BLACK

Parini, V. P., Kazakova, Z. S., Berlin, A. A.
***Vysokomolekulyarnye Soedineniya*, v. 3, no. 12, pp. 1870–1873, December 1961**

It has been shown that aniline black obtained by dichromate oxidation of aniline gives electron paramagnetic resonance spectra containing a wide line (*ca* 450 oersteds) with superposition of a narrow (11–12 oersteds) signal. The wide line disappears on heating the specimen. Removal of chromium by treatment with hydrochloric acid and reprecipitation from acetic acid does not change the nature of the EPR spectrum. Aniline black possesses catalytic properties and is a semiconductor. The electroconductivity of the base is 10^{-13}–10^{-5} ohm^{-1}cm^{-1} and of hydrochlorides 10^{-5}–10^{-2}ohm^{-1}cm^{-1}. The authors associate these properties of aniline black with the accumulation in the molecule of quinonodiimine groupings.

351. CONJUGATED BOND POLYMERS WITH HETEROATOMS IN THE CONJUGATED CHAIN. XX. SYNTHESIS OF POLYMERIC PHTHALOCYANINES AND INVESTIGATION OF THEIR BASIC PHYSICOCHEMICAL PROPERTIES

Berlin, A. A., Cherkashina, L. G., Balabanov, E. I.
***Vysokomolekulyarnye Soedineniya*, v. 4, no. 3, pp. 376–382, March 1962**

Polymeric phthalocyanines were synthesized on the basis of pyromellitic acid and 3,3′, 4,4′-tetracarboxydiphenyl ether as well as mixtures of each of the compounds with phthalic-anhydride, and their principal magnetic and electrical properties were investigated. The synthesis was carried out with the objective of obtaining substances with semiconductor properties. It was found that the polyphthalocyanines being relatively thermostable (300–350°C) possess enhanced electroconductivity $\sigma_{300°K} = 10^{-7}$–10^{-8} ohm^{-1} cm^{-1} with $E = 7$–9 kcal/mole and are characterized by wide electron paramagnetic resonance lines of high intensity (10^{19}–10^{20}). A definite correlation has been found to exist between the EPR signals and the electroconductivity of these substances.

352. CONJUGATED BOND POLYMERS WITH HETEROATOMS IN THE CONJUGATED CHAIN. XXI. POLYMERIC COMPLEXES OF TETRACYANETHYLENE

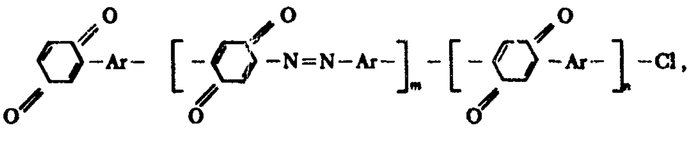
Berlin, A. A., Matveeva, N. G., Sherle, A. I., Kostrova, N. D.
***Vysokomolekulyarnye Soedineniya*, v. 4, no. 6, pp. 860–868, June 1962**
(Translated from the Russian in *Polymer Science U.S.S.R.*, v. 4, no. 2, pp. 260–269, July 1963)

Polymeric complex compounds have been obtained for the first time on reaction between tetracyanethylene with copper, iron and magnesium acetylacetonates, both in the presence and absence of solvents as well as with various metals. The polymers are black, non-melting substances, partially soluble in dimethylformamide, pyridine, triethanolamine and concentrated sulfuric acid. The polychelates are stable up to 400–450°C, possess enhanced magnetic susceptibilities, conductivities from 10^{-5} to 10^{-12} ohm^{-1} cm^{-1} and activation energies of conductivity 10–15 kcal/mole. The infrared spectrum shows no absorption bands in the region 700–1200 cm^{-1}, but a $-\mathrm{C{\equiv}N}$ vibration peak at 2210 cm^{-1} that disappears on heating.

353. CONJUGATED BOND POLYMERS WITH HETEROATOMS IN THE CONJUGATED CHAIN. XXII. PRODUCTS OF THE REACTION BETWEEN *bis*-DIAZO COMPOUNDS AND QUINONES

Parini, V. P., Kazakova, Z. S., Okorokova, M. N., Berlin, A. A.
***Vysokomolekulyarnye Soedineniya*, v. 4, no. 4, pp. 510–515, April 1962**

Polymers of the proposed general formula



where Ar is the corresponding aromatic group with possible substituents, have been obtained by reaction of *p*-benzoquinone with *bis*-diazo compounds prepared from *p*-phenylenediamine, benzidine and benzidine-3,3′dicarboxylic acid. The polymers contain 0.55–11.6% N and 2.0–6.4% Cl. They possess electron exchange properties and give a narrow ESR signal. Some of them lose not more than 3% of their weight at 300°C, possess electroconductivities of the order of 10^{-10} ohm^{-1} cm^{-1} at room temperature, and react with heavy metal salts with the probable formation of cross-linked chelate structures.

354. CONJUGATED BOND POLYMERS WITH HETEROATOMS IN THE CONJUGATED CHAIN. XXIV. SYNTHESIS AND INVESTIGATION OF THE PROPERTIES OF LINEAR AROMATIC POLYMERS WITH METHYLENE GROUPS BETWEEN THE BENZENE RINGS

Berlin, A. A., Liogonkii, B. I., Parini, V. P., Leikina, M. S.
***Vysokomolekulyarnye Soedineniya*, v. 4, no. 5, pp. 662–669, May 1962**
(Translated from the Russian in *Polymer Science U.S.S.R.*, v. 4, no. 2, pp. 221–230, July 1963)

Aromatic polymers with $-\mathrm{CH_2}-$ and $-\mathrm{CH_2}-\mathrm{CH_2}-$ groups between the benzene nuclei, and including some azo groups, have been prepared by the reduction of the products of *bis*-diazotization of 4,4′-diaminodiphenylmethane and 4,4′-diaminodibenzyl. The average molecular weight of the unfractionated products was 1200–1600 and 2400–2600, respectively. The absence of significant anomalies in the viscosity of the solutions bore evidence of a less rigid structure for the molecules of the polymers than that possessed by polyphenylenes. The polymers exhibit electron resonance absorption, the intensity of which diminishes with increase in the number of methylene groups in the backbone. They possess a high temperature dependence of electroconductivity which in combination with their high thermal stability makes them promising stock for the preparation of materials with considerable electroconductivity at high temperatures.

355. CONJUGATED BOND POLYMERS WITH HETEROATOMS IN THE CONJUGATED CHAIN. XXVI. POLYAZOPHENYLENFERROCENES

Berlin, A. A., Liogonkii, B. I., Parini, V. P.
***Vysokomolekulyarnye Soedineniya*, v. 5, no. 3, pp. 330–337, March 1963**

The reaction of ferrocene with salts of diphenylbisdiazonium-4,4′-dicarboxylic-3,3′-acid and diphenylbisdiazonium-4,4′-dicarboxylic-3,3′-acid affords polymers apparently of ribbon structure, containing 3–6 diphenyl residues per 1 atom of Fe. The resultant compounds are partially soluble in organic solvents and completely soluble in concentrated sulfuric acid, whereas the carboxyl-containing polymers dissolve also in dimethylformamide. All are capable of compression molding (the carboxyl-containing polymers being inferior in this respect). The benzene-soluble fraction possesses a mean molecular weight of about 1000–1400 and yields films from solutions. Of much higher molecular weights are the benzene insoluble fractions. The polymer fractions insoluble in organic solvents are nonmelting and of high thermal stability in an inert atmosphere, losing in weight about 2% at 400°C, about 4% at 500°C, about 7% at 600°C, and about 8% at 700°C. They are not thermostable in air. All the polymers give EPR signals and possess static paramagnetism. The electroconductivity of these polymers at room temperature is 10^{-10}–10^{-16} ohm^{-1} cm^{-1}.

356. SYNTHESIS OF ELECTROCONDUCTIVE POLYMERS WITH A SYSTEM OF CONJUGATED DOUBLE BONDS

Pshenitsyna, G. M., Shantarovich, P. S.
***Vysokomolekulyarnye Soedineniya*, v. 5, no. 8,**
pp. 1228–1231, August 1963

The polycondensation of benzidine and quinone has been investigated. Conditions have been shown for preparing organic materials of high electroconductivity.

357. SYNTHESES OF HIGH-POLYMERIC SEMICONDUCTORS

Hatano, M.
***Yuki Gosei Kagaku Kyokai Shi*, v. 20, pp. 326–342,**
1962

A review is presented. 121 references.

APPLICATION

358. GRAPHITE, A BADLY KNOWN SEMICONDUCTOR; ITS USE IN THE PREPARATION OF PURE METALS AND SEMICONDUCTORS [SI,GE]

Millet, Y.
***Bulletin de la Société Française des Électriciens*, v. 2,**
Series 8, no. 13, 1961

A review is presented.

359. ORGANIC SEMICONDUCTOR CHALLENGE

Pohl, H. A.
***Chemical Engineering*, v. 68, no. 22, pp. 104–110,**
October 30, 1961

Potential applications for organic semiconductors include catalysis, sea water conversion, electron exchange resins, thermoelectric power, solid-state batteries, solid-state electrolytes, and information storage components. This survey considers conductivity factors, electronic properties of monomers, coordination polymers and molecular complexes, polymers as semiconductors, and organic superpolymers. (*EI*, 1962)

360. INDUSTRIAL APPLICATIONS OF THE METAL ORGANIC COMPOUNDS

Harwood, J. H.
***Chemistry & Industry*, London, no. 11, pp. 430–436,**
March 16, 1963

This article is concerned mainly with the non-electric usable properties of these compounds. It is mentioned, however, that cyclopentadienyl compounds of transition elements show promise in printed electrical circuits; titanium alkoxides are usable in electrical equipment; and antimony ethoxide may be used to produce an electrically conductive mirror coating.

361. ENERGY CONVERSION STUDY OF SEMICONDUCTOR ELECTRODES

Tannenbaum, I. R.
June 1962
Electro-Optical Systems, Inc., Pasadena, Calif.
Final Report for February–December 1961, EOS-1640,
ASD TDR-62-89, AF 33(616)-7939
AD-282,849

This work is a preliminary investigation of the parameters of semiconductor electrodes. Four electrodes—lithiated nickel oxide, zinc oxide, anthracene, and phenanthrene—have been studied. Sample preparation is described; overvoltage, specific reaction rate constants, stoichiometric number, rate limiting steps, exchange currents and equilibrium potentials are determined; and the application of these data to fuel cell technology is discussed.

362. CONDUCTIVE ADHESIVES

Wentzel, H.
***Fertigungstechnik und Betrieb*, v. 12, no. 8, pp. 520–524,**
1962

These compounds were prepared by mixing 50-μ Al plates, 12-μ Ag powder, 40-μ Cu platelets and 1.5–1.6 μ Ni powder with various organic castable resins, and applying pressures of 0.3–3 kg/cm^2. Resistance was independent of casting time, but was lower with finer power. The lowest resistance, 3 milliohms cm^2, was found for 3-μ Ni with a powder-to-resin ratio of 3:10. Conductive bonds were tested in humidity chambers, under SO_2, in vacuum, and with high current flow, deterioration with increased joint resistance occurring in each case.

363. RESEARCH AND DEVELOPMENT OF HIGH TEMPERATURE STRUCTURAL ADHESIVES

Ruetman, S. H., Wrasidlo, W. J., Levine, H. H.
November 30, 1962
Narmco Industries, Inc., San Diego, Calif.
Final Summary Report for November 1, 1961–October 31, 1962, NOw 61-0254-c
AD-291,711

Constructive pyrolysis of silicone-phenolic laminates in argon at 1800°F resulted in semiconducting specimens with increased oxidation resistance and improved high temperature strengths. Constructive pyrolysis of silicone-phenolic laminates in the presence of small amounts of hydrogen sulfide further improved their high temperature performance. Several arsenic compound cured epoxy-novolac adhesive systems were developed which offer useful strengths after 30 min at 1000°F or after 1000 hr at 500°F. Mechanistic studies of ortho-linked phenolic model compounds showed the ether and the direct carbon–carbon linkages to be most stable under oxidative conditions at elevated temperatures. A material containing organic groups and showing outstanding oxidation resistance was obtained when silicone dioxide in the "E" glass formula was replaced by a phenyl silicone resin. Improvement in oxidation resistance of a commercial novolac was obtained after treatment with certain arsenic compounds. Synthesis of sulfur containing phenolics by reaction of thiophenol with formaldehyde of phenol with sulfur dichloride resulted in very low molecular weight products.

364. ELECTRICALLY CONDUCTIVE PLASTIC COMPOSITIONS

Lewis, A. S.
November 26, 1958 (application date)
U.S. Department of Commerce, Washington, D. C.
U.S. Patent 3,003,975 (assigned to Myron A. Coler)

Molded, electrically conductive plastic articles are claimed, which are usable for multi-contact switches. Spaces within the network are filled with a conductive material comprising fine conductive powder in a synthetic organic plastic. Preparation of the material is described.

365. POINT CONTACT RECTIFIER DEVICE

Epstein, A. S.
April 18, 1961
U.S. Department of Commerce, Washington, D. C.
U.S. Patent 2,980,833 (assigned to Monsanto Chemical Co.)

Fabrication of organic point contact devices employing monomeric metal phthalocyanine, formed from tetrafunctional pyromellitonitrile, is described. The degree of *p*-type or *n*-type conductivity will vary with the excess of deficiency of the metal stoichiometrically required. A device produced from copper polyphthalocyanine, employing a point contact of gold-plated copper, gives a rectification ratio of about 3 to 1. (*SSA*, #11,073)

366. ELECTRICALLY CONDUCTIVE ORGANIC BONDED GRINDING WHEEL

Norton Grinding Wheel Co., Ltd.
December 20, 1961 (U.S. patent application, December 30, 1958)
U.S. Department of Commerce, Washington, D. C.
British Patent 885,192

Formation is claimed of an electrically conductive grinding wheel, or other abrasive article, from abrasive grains, an organic bond for the grains, a filler of solid particles of electrically conductive material, and an electrically conductive liquid selected from formamide, dimethylformamide, diethylformamide and their mixtures. The grinding wheel has a resistivity $\leqq$ 1 meg cm. An example is given of the use of Al_2O_3, phOH-HCHO resin, powdered graphite, CaO powder, and dimethylformamide to form a grinding wheel.

367. SHEET MAGNETIC PARTICLE CARRIER WITH IMPROVED ELECTRICAL CONDUCTIVITY

Eichler, W., Brueck, R., Abeck, W., Kranes, F.
January 23, 1962 (patent application, November 14, 1959)
U.S. Department of Commerce, Washington, D.C.
German Patent 1,122, 725 (assigned to Agfa A.-G.)

A claim is made for a sheet magnetic particle carrier with improved conductivity. One form is a 15-μ foil of terephthalic acid-glycol polyester coated on one side with 0.1 μ of Ag, in turn covered with 1 μ of lacquer. On the opposite side of the foil is a magnetizable layer of cubic lattice of Fe_2O_3 in a mixed polymer—poly(vinyl chloride) and poly(vinyl acetate)—about 10 μ thick. The whole structure has a resistance of 10^{12} to 10^{11} ohms, and no static charging can be detected. An improvement over the former two-foil structure is noted.

368. ELECTRICALLY CONDUCTIVE WEBS

Pattilloch, D. K., Polowczyk, C.
February 20, 1962 (patent application, February 13, 1958)
U.S. Department of Commerce, Washington, D. C.
U.S. Patent 3,022,213 (assigned to Michigan Research Laboratories, Inc. and Electro-Chem Fiber Seal Corp.)

Preparation of a conductive suspension, which is formed into a web and may be used for laminated panels and other structures, is claimed. An aqueous suspension of fibrous web-forming material (cellulose asbestos) is treated with 0.5–5% of dicyandiamide-HCHO condensation product. The treatment with an aqueous colloidal silica solution containing 1–40% of silica is followed by addition of up to 300% by weight of a finely divided conductive material (graphite, Zn).

369. HIGH-VOLTAGE SHIELDING COMPOSITION

Anaconda Wire and Cable Co.
April 11, 1962 (U.S. patent application, February 10, 1959)
U.S. Department of Commerce, Washington, D. C.
British Patent 893,587

A claim is made for an O_3-resistant, elastically resilient, electrically semiconductive composition suitable for use in shielding high-voltage electric power cables. Chlorosulfonated polyethylene, a copolymer of isobutylene, and a small proportion of a diene, a finely dispersed metallic conductor, and 0.1–3% by weight of an antioxidant, *N,N′*-dialkyl-*p*-phenylenediamine, of at least eight C atoms are combined and the product cured.

370. CONDUCTIVE COATING

Price, J. E.
April 17, 1962 (patent application, September 15, 1959)
U.S. Department of Commerce, Washington, D. C.
U.S. Patent 3,030,237 (assigned to North American Aviation, Inc.)

A conductive coating is claimed, which exhibits good adhesion to a nonconducting lightweight base material and also possesses decreased resistivity. It is composed of carrier resins, such as phenolics, polyesters, and alkyds, and metallic pigment particles. The pigment particles should be approximately 44 μ or less in size, and a combination of flakes and ball particles. The preferred pigment is Ag, although Al, Cu, and Au may also be used. The ratio of pigment to carrier resin should be approximately 150:40 to prevent settling and provide maximum adhesion Metallic driers are used to produce the desired end product.

371. POLYACRYLONITRILE FIBERS OR FABRICS WITH SEMICONDUCTING PROPERTIES

Vseso Yuznyi Nauchno-Issledovatelskii Institut Iskusstvennogo Volokna and Institut Neftekhimicheskogo Sinteza, Akademii Nauk USSR
April 20, 1962 (patent application, May 15, 1961)
U.S. Department of Commerce, Washington, D. C.
French Patent 1,291,163

The fibers were heat-treated in two steps (at 200°C and 500–1100°C) while they were stretched to 10–25 times their original length. The conductivities can be changed from 10^{-6} to 10^{2} ohm^{-1} cm^{-1} by varying the temperature and the duration of the heat treatment as well as the atmosphere in which the fibers are heated. Fibers with increased electrical conductivity brought about by combined heat treatment and stretching are claimed.

372. SEMICONDUCTIVE VARNISH

Nicolas, H.
May 28, 1962 (French patent application, March 9, 1955)
U.S. Department of Commerce, Washington, D. C.
East German Patent 23,202 (assigned to Compagnie Generale d' Electricité)

A varnish usable in semiconductive coatings on high-frequency cables, wires, or insulated conductors is claimed, which is prepared by dissolving, in MeCOEt, 15–20 wt. % of a copolymer of vinyl chloride and vinyl acetate, in the presence of a plasticizer, such as tritolyl phosphate, adding 6–10% acetylene black, and stirring.

373. ORGANIC SEMICONDUCTOR THERMOELECTRIC DEVICE

Wildi, B. S.
July 24, 1962 (patent application, March 7, 1960)
U.S. Department of Commerce, Washington, D. C.
U.S. Patent 3,046,322

Preparation of pyrolyzed pyromellitonitrile-H_2S reaction products is claimed, which are usable as components or elements in thermoelectric devices. The resistivity on one of the samples, measured under vacuum of 10^{-1} mm, was found to be 190 ohm/cm at 23°C. Thermoelectric power (TEP) of −24 μv/°C was determined. The sample had *n*-type conductivity, as shown by the negative sign. A second pellet was given a further heat treatment at 560°C and 0.2 mm pressure for 40 hr, and exhibited conductivity of 22 ohm-cm and a TEP of +1.6 μv/°C. Thus, it can be seen that by the additional heat treatment a pyrolyzed pellet can be produced which has a *p*-type conductivity. Maximum *p*-type conductivity can be obtained by using optimum treating temperatures and time of treatment. Methods of fabricating thermoelectric generating or cooling devices from these elements are described.

374. SEMICONDUCTIVE POLYACRYLONITRILE MOLDINGS

Ohdan, T.
September 4, 1962 (patent application, April 3, 1961)
U.S. Department of Commerce, Washington, D. C.
Japanese Patent 12,933 (assigned to Shin-Etsu Chemical Industry Co., Ltd.)

Powdered polyacrylonitrile was heated *in vacuo* at 150°C for 4 hr, crushed, and then molded. The product was again heated *in vacuo* at 500°C for 2 hr to give a solid article having a specific electric resistance of 6.5×10^{6} ohm-cm. The molding is carried out at 1000 kg/cm^2, and the dimensions of the mold should be decided on the basis of the volumetric contraction caused by secondary heating. The time and temperature limits acceptable in primary and secondary heating are mentioned.

375. THERMOPLASTIC MANUFACTURE OF MECHANICALLY STABLE HIGH-MOLECULAR-WEIGHT ORGANIC SEMICONDUCTORS

Schlosser, E. G., Fuchs, O.
November 15, 1962 (patent application, April 27, 1961)
U.S. Department of Commerce, Washington, D. C.
German Patent 1,139,586 (assigned to Farbwerke Hoechst A.-G.)

A claim is made for the shaping of formerly patented organic powders (German Patent 1,097,037) into films, tablets, or rods for transistors or rectifiers, without binding agents. Molding is done at about 300°C, which is below melting point. Hard bodies are produced which have a conductivity of about 2×10^{-12} ohm^{-1} cm^{-1} at 30°C and 10^{-7} ohm^{-1} cm^{-1} at 300°C, i.e., 500 times and 10 times, respectively, that of the original material.

PHOTOCONDUCTIVITY

GENERAL REFERENCES

376. PHOTOCONDUCTIVITY OF ACETYLENE POLYMERS

Mylnikov, V. S., Putseiko, E. K., Terenin, A. N.
***Akademiya Nauk SSSR, Doklady*, v. 149, no. 4, pp. 897–900, April 1, 1963**

377. ELEKTRONENÜBERFÜHRUNG DURCH LICHTABSORPTION UND -EMISSION IN ELEKTRONEN-DONATOR-ACCEPTOR-KOMPLEXEN (ELECTRON TRANSFER BY MEANS OF LIGHT ABSORPTION AND EMISSION IN ELECTRON-DONOR-ACCEPTOR-COMPLEXES)

Briegleb, G., Czekalla, J.
***Angewandte Chemie*, v. 72, no. 12, pp. 401–413, June 1960**

A review with 58 references is presented.

378. PROCEEDINGS OF THE 1961 INTERNATIONAL CONFERENCE ON PHOTOCONDUCTIVITY, NEW YORK, AUGUST 21–24

Levinstein, H., Editor
***Journal of Physics and Chemistry of Solids*, v. 22, December 1961**

The conference was sponsored by the International Union of Pure and Applied Physics, the American Physical Society, and the Office of Naval Research. (*FA*, 1962, #6486)

379. ELECTRICAL PROPERTIES OF ORGANIC SOLIDS

Kearns, D.
***Radiation Research*, Supplement 2, pp. 407–431, 1960**
(Proceedings of Bioenergetics Symposium, Brookhaven National Laboratory, Upton, N. Y., October 12–16, 1958, sponsored by the U.S. Atomic Energy Commission)

Discussions are included of: materials; kinetics of photocurrent decay; flash photoconductivity rise; results with sandwich cells and annealed samples; temperature and voltage dependence of steady-state photocurrent and dark current; spectral response of steady-state photoconductivity; effect of ambient illumination on flash photoconductivity; experimental procedure; results of experiments on dark conductivity, steady-state photoconductivity, electron spin resonance, light-induced polarization, thermoelectric power, and flash-induced photoconductivity; special results with tetracene and pentacene; and conclusions reached.

THEORY

380. CARRIER GENERATION IN PHOTOCONDUCTING ANTHRACENE

Silver, M., Moore, W.
In "Proceedings of the International Conference on Semiconductor Physics, Prague, August 29–September 2, 1960," pp. 854–857
Academic Press, Inc., New York, N. Y., and London, England, 1961

An analysis based on recently reported results on the spatial distribution of trapped charge in anthracene is presented. This analysis shows that anthracene is an extrinsic rather than an intrinsic photoconductor. Further experimental evidence is presented which indicates that most of the free electrons are injected into the anthracene at the negative electrode. (*PA*, 1962, #23,449)

381. THE PHOTOCONDUCTIVITY OF MOLECULAR CRYSTALS

Murrell, J. N.
***Faraday Society, Discussions of the*, no. 28, pp. 36–47, 1959**

Theoretical expressions are derived for the photocurrent of a molecular crystal in the form of a power series in the light intensity, which includes the first- and second-order terms. The current depends in the first instance on the relative values of the potential difference across the crystal, the extinction coefficient of the crystal, and the rate at which free carriers are trapped. It is shown that the experimental results can only be understood if it is assumed that the trapping of charge carriers is more important in limiting the carrier concentration than the discharge of the carriers at the electrodes. From the sign of the rectifying effect it is deduced that the positive carriers are the more mobile. (*PA*, 1961, #2419)

382. ORGANIC PHOTOCONDUCTORS. V. A MODEL FOR PHOTOCONDUCTIVITY IN CATIONIC DYES

Nelson, R. C.
***Journal of Chemical Physics*, v. 30, no. 2, pp. 406–409, February 1959**

(For Part IV, see AI/LS 341, Entry #163.) It is shown that there is a close relationship between the excited state associated with the lowest optical transition of the molecule in solution and that associated with photoconductivity in the solid dye. The model considers the solid dye as a periodic array of potential wells having discrete bands of allowed energies corresponding to the ground state and excited state of the molecule. In the case of dyes whose conductive properties are strongly temperature-dependent, it is assumed that an excited electron can move in the array by passing over the inter-molecular barrier. Extension of this assumption to dyes in which the conductive properties depend only slightly on temperature leads to contradictions, and it is assumed in this case that electrons move through the array by tunneling. It is shown that in such a system the diffusivity will be very large and the mobility very small, and that the Einstein diffusivity–mobility relationship does not hold. The model has properties which are in accord with those observed for the two classes of dyes (*PA*, 1959, #3500)

383. **PHOTOCONDUCTIVITY OF ORGANIC MOLECULAR CRYSTALS AND THE TRIPLET STATE**
Kleinerman, M., McGlynn, S. P.
***Journal of Chemical Physics*, v. 37, no. 6, pp. 1369–1370, September 15, 1962**

Arguments are presented to refute the triplet-state theory of conductivity and the correlation of photoconduction activation energies with a vibrational quantum or two. (*PA*, 1963, #4951)

384. **SOME COMMENTS ON THE PHOTOCONDUCTIVITY OF ORGANIC MOLECULAR CRYSTALS AND THE TRIPLET STATE**
Rosenberg, B.
***Journal of Chemical Physics*, v. 37, no. 6, pp. 1371–1372, September 15, 1962**

The criticisms of Kleinerman and McGlynn (preceding abstract) are answered. (*PA*, 1963, #4952)

385. **EXCITON-EXCITON INTERACTIONS AND PHOTOCONDUCTIVITY IN CRYSTALLINE ANTHRACENE**
Choi, S., Rice, S. A.
***Journal of Chemical Physics*, v. 38, no. 2, pp. 366–373, January 15, 1963**

The mechanism of photoconductivity in crystalline anthracene is considered. It is shown that two excitons may interact to form a pair of charge carriers and an unexcited molecule. The computed rate of generation of charge carriers is 3.7×10^8 cm^{-3} sec^{-1} in satisfactory agreement with the (approximate) experimental value of 7.2×10^8 cm^{-3} sec^{-1} when the exciton concentration is 1.2×10^{10} cm^{-3}. Other qualitative features of the proposed mechanism are in agreement with observation if electron-hole recombination is accounted for. Recent experiments by Silver demonstrating a photocurrent proportional to the square of the light intensity, and by McGlynn demonstrating the necessity for singlet states as the kinetic intermediate in charge-carrier generation, are in agreement with the model proposed. (*PA*, 1963, #8568)

386. **ORGANIC PHOTOCONDUCTORS. VI. THE NATURE OF THE CONDUCTIVE EXCITED STATES**
Nelson, R. C.
***Journal of Molecular Spectroscopy*, v. 7, no. 6, pp. 439–448, December 1961**

(For Part V, see Entry #382.) By means of measurements of the work function and electron affinity of solid dye films, it is shown that the energy of an electron in the conductive excited state is very nearly equal to that of one in the first singlet excited state of the dye molecule. This substantiates the feature of the author's model for photoconduction in dyes which postulates a close relationship between the two states. It is also shown that the values of the energy levels associated with photoconduction in cationic dyes are affected only slightly by the choice of the anion. (*PA*, 1962, #6493)

387. **ORGANIC PHOTOCONDUCTORS. VII. COLLECTIVE AND LOCALIZED CONDUCTION PROCESSES**
Nelson, R. C.
***Journal of Molecular Spectroscopy*, v. 7, no. 6, pp. 449–459, December 1961**

Although the photoconductive behavior of cationic dyes is little affected by the nature of the anion, the dark conductivity is highly dependent upon it. In certain cases the anion has the formal character of a donor impurity. No materials were found in which intrinsic semiconductivity was indisputably present, and one type of film was observed in which it was certainly absent. In the latter case, the character of the photovoltaic effect at a dye–cadmium sulphide junction was consistent with a localized process model for conduction; where substantial dark conductivity existed, the photovoltaic effect was consistent with a collective or band model. (*PA*, 1962, #6492)

388. **THE INTERACTION OF RADIATION WITH MATTER**
Mohanty, S. R.
***Journal of Scientific Research of the Banaras Hindu University*, v. 12, pt. 2, pp. 299–316, 1961–1962**

The interaction of radiation with solids produces effects depending upon the nature of the solid and upon the nature and energy of the incident radiation. The effects are primarily excitation, ionization, the displacement of atoms from lattice sites, and transmutation of nuclei. Interstitials and vacancies from displacement events, and holes, electrons, and excitons generated in excitation and ionization, are capable of migration through the crystal. The holes, electrons, and excitons produce chemical damage in molecular crystals and ionic solids with polyatomic ions. (*PA*, 1963, #2841)

389. **EXCITON–EXCITON INTERACTIONS AND PHOTOCONDUCTIVITY IN CRYSTALLINE ANTHRACENE [ABSTRACT]**
Choi, S., Rice, S. A.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 50–52
National Research Council, Ottawa, Canada, 1962
(See also *Physical Review Letters*, v. 8, no. 10, pp. 410–415, May 15, 1962)

Of the various suggestions for the origin of photoconductivity in organic crystals, that of Northrop and Simpson is selected for discussion. These investigators conclude from studies of photoconductance and fluorescence quenching in doped anthracene that exciton–exciton interactions are responsible for the promotion of electrons into conducting states. To render this mechanism plausible, it must be demonstrated that the transfer of excitation energy between two excited molecules with nonoverlapping electronic wave functions has a significant probability. In this paper the properties of crystalline anthracene are considered. It is found that a transfer of excitation energy between degenerate states can occur very readily and therefore that exciton–exciton interaction can lead to photoconductivity.

The manner of calculation is detailed. From the calculations it is estimated that under the conditions used by Northrop and Simpson where the density of excitons is about 3.5×10^{12} the rate of carrier generation $= 3.2 \times 10^{13}$ cm^{-3} sec^{-1}. Northrop and Simpson estimated the rate of production of charge carriers in anthracene to be 1.2×10^{17} sec^{-1} and concluded that the mobility of the positive charge carrier has to be 5×10^{-3} cm^{-2} v^{-1} sec^{-1}. Their value for the rate of production, when corrected to yield the result of recent measurements of the mobility, is 3.5×10^{12} cm^{-3} sec^{-1}, in agreement (the uncertainties introduced in the theory coupled with the experimental error make order of magnitude agreement satisfactory; note that the theory predicts a rate of carrier generation which is larger than the crude observed value) with the theoretical estimate quoted. Because Northrop and Simpson's determination of the rate of carrier production is subject to considerable uncertainty, the results presented here should be regarded as a demonstration of the plausibility of the mechanism whereby charge carriers are produced from exciton–exciton interactions in a molecular crystal.

390. THE PHOTOCONDUCTIVE AND EMISSION SPECTROSCOPIC PROPERTIES OF ORGANIC MOLECULAR MATERIALS

Kleinerman, M., Azarraga, L., McGlynn, S. P.
In "Luminescence of Organic and Inorganic Materials," International Conference Proceedings, New York University, N. Y., 1961, pp. 196–225
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N. Y., 1962

The initiating act in the generation of a photocurrent is the absorption of a light quantum or quanta. Thereafter, three energy-dissipative processes ensue: (1) luminescence emission, (2) nonradiative degradation into vibrational motion of lattice and/or molecule, and (3) production of current carriers. It is noted that processes 1 and 2 are subtractive with respect to 3. Despite this, it is the thesis of the present paper that (a) the better photoconductors will be found among luminescent species, (b) the occurrence of intermolecular interaction, as exemplified for instance by fluorescence self-quenching, enhances process 3, and (c) a significant triplet state population density, somewhat contrary to existing belief, indicates improbability of process 3.

391. EIN REAKTIONSKINETISCHES MODELL MIT FÜNF ÜBERGÄNGEN FÜR PHOTOLEITER UND LUMINOPHORE (A REACTION-KINETIC MODEL WITH FIVE TRANSITIONS FOR PHOTOCONDUCTORS AND PHOSPHORS)

Böer, K. W., Voigt, J.
***Zeitschrift für Naturforschung*, v. 16a, no. 9, pp. 873–879. September 1961**

A simple reaction-kinetic model is proposed which shows electron transitions to the conduction band and also considers transitions to the valence band by a single effective transition parameter. This model is discussed at steady-state conditions for the conductance-electron concentration and the luminescence intensity and seems to fit the experimental data more closely than do other models.

392. ON THE MECHANISM OF THE OPTICAL SENSITIZATION OF SEMICONDUCTORS BY ORGANIC DYES

Terenin, A., Akimov, I.
***Zeitschrift für Physikalische Chemie*, Leipzig, v. 217, no. 5–6, pp. 307–320, June 1961 (in English)**

The different theories for the mechanism by which the inner photoeffect in semiconductors can be sensitized by adsorbed dyes are discussed. On the basis of experimental data, it is shown that the excitation energy of the dye molecule is transferred to electrons in surface traps, and not an electron from the excited dye molecule to the conduction band of the semiconductor. (*PA*, 1962, #6488)

EXPERIMENT

393. ELECTRON SPIN RESONANCE (ESR) INVESTIGATIONS ON RADIATION-INDUCED CHEMICAL EFFECTS IN BIOLOGICAL SPECIES

Blyumenfeld, L. A., Kalmanson, A. E.
In "The Initial Effects of Ionizing Radiations on Cells," pp. 59–68
Harris, R. J. C., Editor
Academic Press, Inc., London, England, and New York, N.Y., 1961
(Proceedings of a symposium held in Moscow, October 1960, supported by UNESCO and IAEA, sponsored by Academy of Science, USSR)

The ESR method may be used to investigate radiation-produced unpaired electrons in lyophilized biological structures. The authors have studied nearly all the amino acids, a number of di- and tripeptides and various proteins, nucleoproteins, and tissues.

The number of free radicals produced in γ-irradiated lyophilized proteins is some two or three orders of magnitude less than in amino acids and peptides. It is suggested that "conductive channels" may exist and that electrons can migrate along these, thus "healing" the injuries.

394. COMPARISON OF CERTAIN PROPERTIES OF SOLID AND LIQUID DIELECTRICS DURING IRRADIATION

**Kolomoitsev, F. I., Mitskevich, P. K., Bobyl, V. G.,
Yakunin, A. Ya.
In "Fizika Dielektrikov Sbornik," pp. 510–517
Akademii Nauk SSSR, Moscow, 1960
(See also *Referativnyi Zhurnal Fizika,* 1961, #9E157)**

Electrical conductivity curves of solid dielectrics (mica, quartz, polyethylene, polystyrene, polytetrafluoroethylene, poly(methyl methacrylate)) and liquid dielectrics ($CHCl_3$, $CHBr_3$–Et_2O, $CHBr_3$-anisole, CHI_3–Et_2O, chlorophenol, PhBr) are compared. The increase in σ during irradiation is shown to depend on the nature and intensity of irradiation and on the purity of the dielectric and is due to fixing of the current carrier on metastable levels. The decrease with time in σ after cessation of irradiation is shown to be proportional to the thermal liberation of the current carrier from metastable levels. At fields up to 10^4 v/cm, $\Delta\sigma$ is proportional to the field strength. For liquid dielectrics $\Delta\sigma$ is two to three orders of magnitude higher than for solid dielectrics.

395. DETERMINATION OF THE CURRENT IN DIELECTRICS BEING IRRADIATED WITH GAMMA-RAYS

**Vul, B. M.
Akademiya Nauk SSSR, Doklady, v. 139, no. 6,
pp. 1339–1341, August 21, 1961
(Translated from the Russian in *Soviet Physics—Doklady,*
v. 6, no. 8, pp. 725–726, February 1962)**

Gamma irradiation of dielectrics produces ionization which gives rise to an increase in the electrical conductivity of the material. The increase in conductivity is directly proportional to the intensity of the radiation. A mechanism for the phenomenon is proposed, and expressions are derived that agree with the results of measurements on quartz, polyethylene, sulphur, ceramics, and other materials. (*PA*, 1962, #21,205)

396. THE SEMICONDUCTING PROPERTIES OF BLOOD PIGMENTS

**Vartanyan, A. T.
Akademiya Nauk SSSR, Doklady, v. 143, no. 6,
pp. 1317–1320, April 21, 1962
(Translated from the Russian in *Soviet Physics—Doklady,*
v. 7, no. 6, pp. 332–335, October 1962)**

The temperature dependence of electrical conductivity for layers of haemin, haematin, and haematoporphyrin was investigated in vacuum and in oxygen. The dependence of photocurrent and of optical absorption on wavelength for haemin and haematoporphyrin was measured for 350–650 μ. Both properties exhibited a peak at ~ 400 μ. (*PA*, 1962, #16,718)

397. PHOTOSEMICONDUCTIVE PROPERTIES OF ACETYLENE POLYMERS

**Mylnikov, V. S., Sladkov, A. M., Kudryavtsev, Yu. P.,
Luneva, L. K., Korshak, V. V., Terenin, A. N.
Akademiya Nauk SSSR, Doklady, v. 144, no. 4,
pp. 840–843, June 1, 1962
(Translated from the Russian in *Proceedings of the
Academy of Sciences of the USSR—Physical Chemistry
Section,* v. 144, no. 1–6, May–June 1962)**

Six out of eight acetylene polymers synthesized at the authors' laboratories were found to possess photoelectric properties with either *p*- or *n*-type conductivity, the maximum photo EMF observed amounting to 10 mv/mw. Photo-EMF spectra obtained for two of the substances studied had a maximum at $\lambda \cong 780$ mμ. Illumination of the *p*-type specimens with ultraviolet light ($\lambda \leq 366$ mμ) in vacuum brought about a considerable increase in their photo EMF which, however, decreased again when the specimens were exposed to the action of atmospheric oxygen, this being a reversible effect. (*PA*, 1962, #23,371)

398. OPTICAL AND PHOTOELECTRIC PROPERTIES OF Mg PHTHALOCYANINE AS INFLUENCED BY ELECTRON-ACCEPTING ADDITIVES

**Putseiko, E. K.
Akademiya Nauk SSSR, Doklady, v. 148, no. 5,
pp. 1125–1128, February 11, 1963**

The absorption and photoelectric sensitivity spectra of amorphous and microcrystalline layers of Mg phthalocyanine, either deposited *in vacuo* (10^{-5} mm Hg) on mica and quartz or precipitated from concentrated acetone and ether solutions, activated by electron-accepting additives, were studied. Experimental apparatus is explained. Layers deposited *in vacuo* on mica or quartz (20°C) are amorphous. In their absorption spectrum, maxima at 680 and 690 mμ appear. The evaporation method, temperature of mica and quartz, and the pressure influence the state of aggregation. After the deposition on mica and quartz (100–150°C), on which previously a Au or a Pt layer had been deposited, a new absorption maximum at 820–840 mμ appears. The same maximum appears when layers are treated with liquid acetone, ether, or EtOH, or when precipitated from concentrated acetone solution. This effect is attributed to the presence of a crystalline form (possible β-form) with included molecules of the solvent. The thermal activation in water vapors *in vacuo* or the treatment by solvents causes an increase of photoelectric effect and the formation of a new photoelectric effect with the maximum at 840 mμ. Adsorption of quinone from dilute EtOH on amorphous layers raises the photoelectric sensitivity 100–1000 times; at the same time the new photoelectric effect maximum at 840 mμ appears, attributable to the formation of superficial impurity centers on which electrons are fastened. The analogous effect can be observed in deposition on cells of photoelectric resistors. The conductivity increases by three to five orders under the action of moisture, and the photosensitivity decreases by two to three orders, but regeneration is possible by means of adsorption of quinone from EtOH solution.

399. SPECTRAL DISTRIBUTION OF CHLOROPHYLL-A PHOTOCONDUCTIVITY AS DEPENDENT ON THE THICKNESS OF THE CHLOROPHYLL LAYER

Vartanyan, A. T.
***Akademiya Nauk SSSR, Doklady*, v. 149, no. 3, pp. 563–565, March 21, 1963**

400. ACTIVATION ENERGY OF DARK CONDUCTIVITY AND PHOTOCONDUCTIVITY OF CHLOROPHYLL-A

Vartanyan, A. T.
***Akademiya Nauk SSSR, Doklady*, v. 149, no. 4, pp. 812–815, April 1, 1963**

The photocurrents induced in amorphous chlorophyll-*a* film by exposure to light from an incandescent lamp operating at various temperatures of the filament were measured. The thermal activation energy was found to be 1.74 ev; that for chlorophyll $(a + b)$ was 1.77. The activation energy obtained from photoelectric curves was determined at 1.77 ev for chlorophyll-*a*. After two days of exposure to O atmosphere in the dark the activation energy dropped to 1.63 ev while the conductivity rose by a factor of 10, providing an explanation for the anomalous results reported by Rosenberg and Camiscoli. Temperature dependence of photocurrent in the chlorophyll-*a* layer was measured *in vacuo* at various levels of illumination. Explanation of the data is given.

401. AN INVESTIGATION OF THE INTERMOLECULAR ELECTRON TRANSFER IN TETRAPYRROLE PIGMENTS UNDER PULSED ILLUMINATION

Shakhverdov, P. A., Terenin, A. N.
***Akademiya Nauk SSSR, Doklady*, v. 150, no. 6, pp. 1311–1314, June 21, 1963**

402. PHOTOSEMICONDUCTING PROPERTIES OF METAL ACETYLIDES

Mylnikov, V. S., Terenin, A. N.
***Akademiya Nauk SSSR, Doklady*, v. 153, no. 6, pp. 1381–1384, December 21, 1963**

403. MICROWAVE PROPAGATION IN AROMATIC COMPOUNDS

Kusnezov, N.
June 1961
California, University of, Electronics Research Lab., Berkeley
Series 60, Issue 369, AFOSR-1187, AF 49(638)-1043
AD-265,790
(Also available through U.S. Dept. of Commerce, Office of Technical Services, Washington, D. C.)

An investigation of those electrical properties of aromatic compounds which are related to their potential uses as microwave modulators or mixers is presented. The study includes: repeat measurements of conductivity and variations of conductivity of aromatic materials as function of the intensity and frequency of the irradiating light; measurement of the Hall constants of the materials; investigation of the variation of the dielectric constant of the materials in X-band range in the dark and while irradiated by light; and investigation of the X-band magneto-optical properties of the materials. Interest is in the photosemiconducting compounds, and anthracene, naphthalene and phthalocyanine are the materials.

404. PHOTOCONDUCTION OF CRYSTALLINE 9,10-DIBROMOANTHRACENE AND 9,10-DICHLOROANTHRACENE

Smith, I. C., Bock, E.
***Canadian Journal of Chemistry*, v. 40, no. 6, pp. 1216–1218, 1962**

In order to facilitate the elucidation of the role played by the triplet state in the photoconduction process, it was decided to investigate the photoconductivity of 9,10-dibromoanthracene, and also the temperature dependence of the photocurrent in 9,10-dichloroanthracene—a dependence not hitherto determined.

All measurements were made on optically clear crystals grown from solution by cooling or by recirculating supersaturated solvent over seed crystals.

Only dc conductances were measured. The electrodes were always mounted on the same face of the prismatic crystals—a "surface cell" arrangement. Contact was made by thin platinum wires attached to the crystals by means of an alcoholic suspension of graphite. Except in special cases, all measurements were made *in vacuo* or under dry nitrogen. The dependence of the surface photocurrents on applied field was found to be linear up to 3000 v cm^{-1} for all crystals studied of each compound. The variation of the photocurrent in 9,10-dibromoanthracene with light intensity was also linear for the wavelengths 3650, 4050, and 4360 A. The temperature dependence of the photocurrent fitted an expression of the form $i = i_0 \exp(-\Delta E/kT)$. For crystals stored under nitrogen, $\Delta E = 0.14 \pm .01$ ev. Crystals stored in air showed a discontinuity in a plot of log i vs. $1/T$, yielding two straight lines of different slope. The high-temperature portions of these curves yielded $\Delta E = 0.11 \pm .01$ ev. The low-temperature portions gave $\Delta E = 0.20 \pm .01$ ev. The level of photoconductivity in the chloro compound was several orders of magnitude higher than that in the bromo compound under similar conditions.

These results show that 9,10-dichloroanthracene and 9,10-dibromoanthracene are easily oxidized on exposure to air, and that the oxidation products affect their surface photoconductivities. The reversibility with respect to adsorbed gases shows that the gases also affect the photocurrent through electrical double-layer formation.

The relative orders of magnitude of the photocurrents are not what one would expect on the basis of the triplet-state theory. Further measurements on the dark conductivities are being made to confirm this statement. The effect of gases on the surface photocurrent shows the majority charge carriers to be positive holes.

405. THE PHOTOVOLTAIC BEHAVIOR IN ORGANIC COMPOUNDS

Inokuchi, H., Maruyama, Y., Akamatu, H.
***Chemical Society of Japan, Bulletin of the*, v. 34, no. 8,**
pp. 1093–1096, August 1961

Photovoltages of about 10 mv were produced with white light, using aromatic compounds between two conducting layers, one of which was partially transparent. The latter layer, when irradiated, became negative. The type of metal used for contacts influenced the decay.

406. PHOTOCONDUCTIVITY OF POLYCYCLIC AROMATIC COMPOUNDS

Sano, M.
***Chemical Society of Japan, Bulletin of the*, v. 34, no. 11,**
pp. 1668-1673, November 1961

The voltage, light intensity, and temperature dependence for photocurrent in polycyclic compounds (pyranthrene, violanthrene, and perylene) were studied as well as the effect of limiting the area of illumination. The photocurrent was ohmic at 100–7000 v/cm, increasing linearly with the intensity of light in the region of low light intensity, up to 10^{16} photons/sec cm^2, and increasing as the fractional power of the light intensity in the region of high intensity (perhaps caused by a trapping process for charge carriers). Photocurrent increased with an increase of temperature at 175–293°K. Activation energy was independent of wavelength and light intensity. The results indicated that conduction in polycyclic aromatic compounds was due predominately to electrons which were generated in the bulk of the aromatic films.

407. CHARGE CARRIERS IN PYRENE CRYSTALS

Inokuchi, H., Ohki, K.
***Chemical Society of Japan, Bulletin of the*, v. 36, no. 1,**
pp. 105–107, January 1963

The sign of the charge carriers in molecular crystals of an organic semiconductor has been investigated by observing the rectifying behavior of photoconduction. The ratio of forward to reverse photocurrent corresponds to the ratio of mobilities μ_e/μ_h, where μ_e is the mobility of electron, and μ_h is that of hole. The ratio for pyrene crystals exceeds unity with repeated purification, i.e., the predominant charge carrier is changed from hole to electron with increasing purity of the crystals. (*SSA*, #18,541)

408. PHOTOCONDUCTIVITY IN AN ORGANIC LIQUID SOLUTION

Sano, M., Akamatu, H.
***Chemical Society of Japan, Bulletin of the*, v. 36, no. 4,**
pp. 480–481, April 1963

In the present experiment the photoconductivity of solutions was investigated preliminarily in relation to the intermolecular energy transfer. Measurement was made with benzene solutions of pyranthrene (3.3×10^{-5} mole/l), tetracene (2.0×10^{-5} mole/l), and pyrene (1.3×10^{-1} mole/l), all of which show intense absorption spectra in the range of 370 ~ 500 mμ. A photocell was made of teflon, with two parallel Nesa-glass electrodes (1.3 cm^2 in area), forming a sandwich-type cell. The distance between the electrodes was fixed at 3 mm. Through one of the electrodes the solution was illuminated by monochromatized light. The currents were measured by a dc method. The dark currents through the solutions, as well as the benzene, followed Ohm's law below the electric field of 10^2 v/cm. The specific conductivity of benzene was $6.4 \times 10^{-14} \Omega^{-1}$ cm^{-1}, judging from the observed current in this ohmic range. Beyond the electric field of the above value, the current increased nonlinearly and showed a tendency to saturate in accordance with an applied voltage. Similar behavior was found in the photocurrent in the solutions. Benzene itself did not show any response to illumination in the visible spectral region; the benzene solution of pyranthrene exhibited a remarkable photocurrent in the spectral region between 400 and 500 mμ. Some explanation is presented for the observed phenomena.

409. CONTRIBUTION À L'ÉTUDE DES PROPRIÉTÉS ÉLECTRIQUES DU POLYÉTHYLÈNE IRRADIÉ (CONTRIBUTION TO THE STUDY OF THE ELECTRICAL PROPERTIES OF IRRADIATED POLYTHENE)

Fallah, E., Coelho, R.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 256, no. 4, pp. 946–949, January 21, 1963**

Observations of the conductivity induced by low intensity X-rays were used to study the permanent changes in samples of high pressure polythene effected by irradiation in a reactor or with a cobalt source. (*PA*, 1963, #10,866)

410. PHOTOCONDUCTIVITY IN THIN ORGANIC FILMS

Bradley, A., Hammes, J. P.
***Electrochemical Society, Journal of the*, v. 110, no. 6,**
pp. 543–548, June 1963

Organic films of approximately 1 μ thickness were prepared by glow-discharge polymerization of monomers containing nitrogen, sulfur, selenium, and certain metals, and tested for photosensitivity. Conductivities (in the dark ranging from 10^{-17} to 10^{-13} mho/cm at room temperature) were enhanced by as much as three orders of magnitude by 10 w/in.^{2} of white light excitation. Nitrile groups and sulfur appeared most promising as chemical substituents in the polymer films for promoting conductivity to useful levels. Addition of traces of iodine to the discharge during the deposition of a polynaphthalene film increased its dark and photoconductivity over 1000-fold. Activation energies of photoconduction of the order of 0.25 ev were found (25–175°C). Short-circuit photocurrents of consistent polarity in all films were observed and attributed to a photovoltaic effect at the interface between the film and the transparent electrode.

411. PHOTOCONDUCTIVITIES OF α AND β FORMS OF METAL-FREE PHTHALOCYANINE

Liang, C. Y., Scalco, E. G.
Electrochemical Society, Journal of the, v. 110, no. 7, pp. 779–783, July 1963

Some experimental results on the photoconductivities of α and β forms of metal-free phthalocyanine are presented and discussed. It is found that the photocurrent threshold energy is lower for the α sample than that for the β sample. The activation energies for dark conduction are about 1.9 ev for the β sample and 1.4 ev for the α sample, while the activation energies for photoconduction are about 0.34 ev for the β and 0.42 ev for the α. All these differences are interpreted as due to the disordered structure of the α sample.

412 THE EFFECT OF GAMMA RADIATION ON THE ELECTRICAL CONDUCTIVITY OF INSULATORS

Vul, B. M.
Fizika Tverdogo Tela, v. 3, no. 8, pp. 2264–2274, August 1961
(Translated from the Russian in *Soviet Physics—Solid State*, v. 3, no. 8, pp. 1644–1650, February 1962)

Under the influence of ionizing radiation the concentration of free charges in the dielectric can be significantly increased, causing an increase in the electrical conductivity. A description is given of measurements made on various materials, including fused quartz, glass, ceramics, sulphur, polyethylene, and rubber used as insulation for electrical cables. Effects of intensity of irradiation, temperature of surrounding medium, and duration of irradiation are discussed. (*PA*, 1962, #3996)

413. INFLUENCE OF CRYSTAL STRUCTURE ON THE OPTICAL AND PHOTOELECTRIC PROPERTIES OF PHTHALOCYANIN WITHOUT METAL

Mylnikov, V. S., Putseiko, E. K.
Fizika Tverdogo Tela, v. 4, no. 3, pp. 772–779, March 1962
(Translated from the Russian in *Soviet Physics—Solid State*, v. 4, no. 3, pp. 566–571, September 1962)

A study was made of the effect of the crystal structure on the absorption, photo-EMF and photoconductivity spectra, and on the sign of photocurrent carriers in vacuum-sublimated layers and powders of phthalocyanin without metal. It was found that the two different crystal modifications, α and β, of the pigment have different absorption and photoelectric spectra. In crystals of the β-modification, which have closer molecular packing, *n*-type conduction was observed due to overlapping of intermolecular potential barriers.

The spectrum of the photoconduction quantum yield of vacuum-sublimated layers was also investigated.

414. PHOTOELECTRIC SENSITIVITY SPECTRA IN SEMICONDUCTORS DETERMINED BY VARIOUS METHODS

Akimov, I. A., Putseiko, E. K.
Fizika Tverdogo Tela, v. 4, no. 6, pp. 1542–1548, June 1962
(Translated from the Russian in *Soviet Physics—Solid State*, v. 4, no. 6, pp. 1133–1137, December 1962)

The spectral characteristics of the internal photoeffect in a number of organic and inorganic semiconductor layers of different thicknesses were investigated by different methods, namely, photoconductivity, condenser photo EMF, contact potential and photodielectric loss methods.

Analysis of the curves obtained and comparison with the corresponding absorption spectra provided information concerning the nature of the photoresponse in these materials.

415. SPECTRAL DISTRIBUTION OF THE INTERNAL PHOTOEFFECT IN PHOTOCHEMICALLY SENSITIVE SEMICONDUCTORS

Akimov, I. A.
Fizika Tverdogo Tela, v. 4, no. 6, pp. 1549–1558, June 1962
(Translated from the Russian in *Soviet Physics—Solid State*, v. 4, no. 6, pp. 1138–1144, December 1962)

A velocity method was used to investigate photoconductivity and photo-EMF spectra in dyed and undyed silver halides in microcrystalline powder form. Cyanine dyes were used and the measurements were carried out in the region from 350 to 1000 mμ. The semiconductor was irradiated with energies of the order of 10^{-6} w/cm^2.

The change in the photoeffect in the region of the semiconductor absorption edge is explained by the formation of electron trapping levels as a result of chemical decomposition of the silver halide. Experiments with dyed layers confirm the mechanism of energy transfer from the dye to the semiconductor and the importance of acceptor levels in the semiconductor in regard to optical sensitization.

416. NON-UNIFORM PHOTOCONDUCTIVITY IN ORGANIC SEMICONDUCTORS

Burshtein, A. I.
Fizika Tverdogo Tela, v. 5, no. 5, pp. 1264–1278, May 1963

417. THE CONDUCTIVITY OF POLYTHENE UNDER GAMMA IRRADIATION

Wintle, H. J.
International Journal of Applied Radiation and Isotopes, v. 8, no. 2–3, pp. 132–134, July 1960

The increase in electrical conductivity of polythene per unit of gamma irradiation at 0.014 rad/min is comparable to the increases obtained by others at much higher dose rates. However, in contrast to previous works, the rise and decay times were of the same order. (*PA*, 1961, #17,636)

418. GAMMA-RAY INDUCED CONDUCTIVITY IN POLYETHYLENE AND TEFLON UNDER RADIATION AT HIGH DOSE RATE

Yahagi, K., Danno, A.
Journal of Applied Physics, v. 34, no. 4, pt. 1, pp. 804–809, April 1963

The conductivity induced by gamma radiation from Co^{60} has been measured for polyethylene and teflon as functions of temperature, dose rate, and applied voltage. The range of dose rates was from about 10^3 to 10^5 r/hr and of the temperature from 190 to 300°K. The value of Δ, which shows the dependence of the induced current i on the dose rate R, i.e., $i \propto R\Delta$, varies from 1 (characteristic of the monomolecular recombination) to ½ (characteristics of the bimolecular recombination) with decreasing temperature. In both polymers, below about 240°K the induced current at thermal equilibrium was independent of temperature, although it was slightly increased with decreasing temperature. From the investigation of temperature and dose-rate dependences, it is considered that the thermal electrons are dominant as charge carriers above 230°K, but fast electrons at below that temperature. (*PA*, 1962, #10,874)

419. ELECTRICAL PROPERTIES OF ORGANIC SOLIDS IV. CHARGE CARRIER DIFFUSIVITY IN METAL-FREE PHTHALOCYANINE

Kearns, D. R., Calvin, M.
***Journal of Chemical Physics*, v. 34, no. 6, pp. 2022–2025, June 1961**

The pulsed light technique has been applied to determine the charge carrier mobility in microcrystalline or amorphous, metal-free phthalocyanine layers. This appears to be of the order of 10^{-3} to 10^{-2} cm² sec⁻¹ v⁻¹, and the positive holes are the majority carriers. The low values are attributed to the physical state of the layer.

420. PHOTOCARRIER GENERATION IN ANTHRACENE

Hoesterey, D. C.
***Journal of Chemical Physics*, v. 36, no. 2, pp. 557–558, January 15, 1962**

Crystals between conducting electrodes were excited by 2-μsec sparks in air. The crystal surfaces were contaminated by various organic substances to determine their effects on the hole photocurrent and the electron photocurrent perpendicular to the *ab* plane, relative to their value for a clean crystal. In general, the hole current was increased and the electron current decreased by the electrophilic impurities, which act as electron traps. Photocarriers were generated only at the surface. (*PA*, 1962, #4059)

421. TEMPERATURE DEPENDENCE OF PHOTOCONDUCTIVITY OF METAL-FREE PHTHALOCYANINE

Liang, C. Y., Scalco, E. G., Oneal, G., Jr.
***Journal of Chemical Physics*, v. 37, no. 2, pp. 459–460, July 15, 1962**

After the sample was pressed into a disk, two electrodes were attached to one side of the disk with about 1-mm separation. Into one side of the sample, a small hole was drilled and a thermocouple inserted. This assembly was put in a container with the electrode side facing its quartz window. The container was evacuated during measurement. The resistance and photocurrent were measured by a General Radio electrometer. Using a tungsten light source, the quartz prism monochromator was set at about 1000 mμ, where the sample was highly photosensitive. A measuring resistance R_m was used and a bias potential was connected to the ground terminal in order to balance the dark current for photoconductivity measurement. The sample resistances R_s measured between 0 and 100°C obeyed the equation $R_s = R_o \exp(\Delta E/2kT)$ with an activation energy for dark conduction $\Delta E = 1.9$ ev. In studying the photoconductivity, the voltage across the sample in the temperature range studied was maintained at essentially 90 v, the voltage of the battery supply. The activation energy $\Delta\epsilon$ proved to be about 0.34 ev.

Another method was used to observe the temperature dependence of photoconduction with constant voltage across the sample. The sample was kept at constant temperature; photocurrents were measured at various values of applied voltage, and the voltage across the sample was computed; and the activation energy $\Delta\epsilon$ was again 0.34 ev.

422. SPECTRA AND PHOTOCONDUCTION OF PHTHALOCYANINE COMPLEXES (I)

Day, P., Williams, R. J. P.
***Journal of Chemical Physics*, v. 37, no. 3, pp. 567–570, August 1, 1962**

Reflection spectra of Co, Ni, Cu, Zn, and metal-free phthalocyanines were measured. The Davydov splitting of the main absorption peak in the metal compounds correlates with the relative tendencies of the metals to out-of-plane bonding. Photoconduction response curves were measured between 1500 and 300 mμ for single crystals of these compounds. Besides a high response following the crystal absorption, metal-free Ni and Cu phthalocyanines also had considerable photosensitivity in the near infrared, peaking at 900–1100 mμ. The effect on the short-wavelength photoconduction of measuring *in vacuo* instead of in air also correlates with the ability of the metals to bond out-of-plane groups. (*PA*, 1962, #18,751)

423. EMISSIVITY AND PHOTOCONDUCTIVITY OF ORGANIC MOLECULAR CRYSTALS

Kleinerman, M., Azarraga, L., McGlynn, S. P.
***Journal of Chemical Physics*, v. 37, no. 8, pp. 1825–1834, October 15, 1962**

The materials investigated in this work were of three extreme types with regard to their fluorescence characteristics: (1) materials which are strongly fluorescent at room temperature in both the solid and the dilute neutral solution, and in which quenching of all sorts is small; (2) materials which are nonfluorescent in both solid and dilute neutral solution at room temperature and also at −190°C, but which are strongly phosphorescent at −190°C, and in which the intersystem crossing-rate constant is very large ($k_{IS} \sim 10^{12}$ sec^{-1}); (3) materials which fluoresce strongly in dilute neutral solution at room temperature, but in which the fluorescence efficiency decreases markedly with increasing concentration until in the single crystal it may be absent or weak, and in which the self-quenching rate constants of a bimolecular or higher-order process must be very large. Many materials intermediate in their luminescence behavior between these extremes were investigated, and, in particular, materials in which k_{IS} was increased by a number of different ways were studied. These methods all function by increasing the spin–orbital coupling in the molecule and are: (a) appending a heavy atom, as a substituent, to the molecular framework; (b) decreasing the $S^1 \leftrightarrow T$ energy split; (c) forming charge-transfer complexes; (d) designing the molecule such that η, π^* levels intervene between $S_{\pi,\pi'}$ and $T_{\pi,\pi}$ states. The conclusions to be drawn, with reservations, are as follows: (1) Photogeneration of carriers proceeds with significantly higher probability from the lowest singlet excited state than for the lowest triplet state. (2) As a corollary of 1 it may be concluded that the better photoconductors will be found among those species which have simultaneously the highest quantum yield of fluorescence and the lowest fluorescence rate constant. (3) The difference in probability quoted in 1 is such that the intersystem crossing process leading to triplet-state population may be considered in a kinetic sense to be competitively concurrent with charge carrier formation. (4) Photoconductivity increases in a fashion which corresponds roughly to the extent of increasing intermolecular interaction in the solid. (5) As one corollary of 4 it is not surprising that the best photoconductor investigated, namely rubene, shows complete self-quenching of fluorescence in the solid. (6) The process which provides energy for the carrier generation act is predominately, or perhaps even completely, communal; it requires the participation of two or more molecules. It may be first order, but it is not monomolecular. It is possible that conclusion 2 is relevant only because the singlet exciton is more mobile than the triplet exciton and can more readily attain the surface or an appropriate defect where it then degrades to a triplet, or because a biphotonic bimolecular process is involved, one molecule being a S' species, the other a triplet species. The simple biphotonic process, in which the second photon causes excitation entirely within the triplet manifold of a previously excited molecule, is not excluded either. (*PA*, 1963, #3060)

424. PHOTOCONDUCTIVITY IN METAL-FREE PHTHALOCYANINE SINGLE CRYSTALS

Heilmeier, G. H., Warfield, G.
***Journal of Chemical Physics*, v. 38, no. 4, pp. 897–901,**
February 15, 1963

The spectral response of photoconductivity in metal-free phthalocyanine crystals was obtained in the region 2500–25,000 A, and was found to have the same response edges as the optical absorption spectrum. The correspondence between the valley-to-valley separation of the structure found in the strong response regions of the spectral response of photoconductivity and the peak-to-peak separation of the infrared optical absorption spectrum has been used to formulate a model for photoconductivity in metal-free phthalocyanine crystals which involves the direct creation of carriers by suitable radiation. An expression for the effective lifetime of a photoexcited carrier in a crystal with a finite surface recombination velocity was derived. This was found experimentally to be approximately 0.9 × 10^{-8} sec. Using this lifetime and the mobility determined by Hall effect measurements, the diffusion length for electrons was calculated to be 5 × 10^{-8} cm. A comparison of this diffusion length with the reciprocal of the extinction coefficient indicates that the free carriers excited by 7300-A radiation are produced further from the surface than a diffusion length. Thus, the lifetime of the free carriers should be more nearly characteristic of the bulk. The experimentally determined lifetime is in rough agreement with the theoretical decay time for fluorescence. This emphasizes the importance of the first excited singlet state in the conduction process. The structure of the spectral response of photoconductivity was used in conjunction with previous discussions of the applicability of the band model to infer the nature of the conduction band in metal-free phthalocyanine crystals. (*PA*, 1963, #10,890)

425. GAMMA-RADIATION-INDUCED CONDUCTANCE IN LIQUID HYDROCARBONS

Freeman, G. R.
***Journal of Chemical Physics*, v. 38, no. 4, pp. 1022–1023,**
February 15, 1963

The conductance of n-hexane under the influence of gamma radiation was measured as a function of voltage. The fact that the conductance values are unaltered by the addition of oxygen is an indication that escaped electrons behave as massive ions even in "pure" n-hexane. Electron mobility, $u = 1.40 \times 10^{-3}$ cm^2 v^{-1} sec^{-1}, and yield of escaped electrons are given for n-hexane.

426. PHOTOELECTRIC PHENOMENA IN HEMOGLOBIN AND DYED GELATIN

Nelson, R. C.
***Journal of Chemical Physics*, v. 39, no. 1, pp. 112–115,**
July 1, 1963

Hemoglobin shows photoconductivity with a threshold at about 3.9 ev. A similar phenomenon is found in dyed gelatin films. In the latter case, the response arises from light absorbed by the protein rather than by the dye, and it is suggested that the energy is transferred to the dye by a nonradiative resonance process involving the aromatic amino acid residues in the protein, and that the dye functions only as a relatively easily ionizable center in the solid. The same is presumably true of the porphyrin group in hemoglobin. No evidence for the existence of band-model structure in these proteins could be inferred from the data.

427. ELECTRON SPIN RESONANCE STUDY OF SOME ORGANIC PHOTOCONDUCTORS

Cho, B.-Y., Nelson, R. C., Brown, L. C.
***Journal of Chemical Physics*, v. 39. no. 3, pp. 499-503,**
August 1, 1963

In dye photoconductors which have a very high density of traps, such as rhodamine B and crystal violet, it is possible to build up a density of spins $\sim 10^{16}/\text{cm}^3$ in strong illumination. The kinetics of rise and decay of these spins can be directly related to those of photoconductivity, and the spins are believed to be associated with trapped conduction electrons. Since the magnitude of the ESR signal is a measure of the number of electrons, the assumptions regarding mobility which have been made to account for the conductive behavior can be tested. In general, the conclusion that the mean or drift mobility has an exponential temperature dependence corresponding to a monoenergetic trap depth has been confirmed. The mean mobility of electrons is estimated to be $\sim 1 \times \exp(-E_t/kT)$ cm^2/v-sec. The previously observed irregularities in the photoconductive behavior of rhodamine-B arise from the existence of a considerable population of unpaired electrons which do not contribute directly to conduction, but interchange with those which do. Some salts of crystal violet which have appreciable semiconductivities were found to have spin densities $\sim 10^{17}/\text{cm}^3$ in the dark.

428. PHOTOCONDUCTIVITY IN ORGANIC SINGLE CRYSTALS

Kommandeur, J.
***Journal of Physics and Chemistry of Solids*, v. 22,**
pp. 339–349, December 1961
(Paper presented at the International Conference on Photoconductivity, New York, N.Y., August 21–24, 1961—Entry #378)

In general, it is very difficult to define a "band gap" in organic materials. The ultraviolet spectrum of the solid is almost identical to that of the molecules in the vapor phase. Therefore, light absorption is essentially determined by the single molecules. Thus, no relation between thermal and optical band gap is to be expected or found. Phenomenologically, anthracene can be used for an illustration of most of the properties encountered. Surface currents and bulk currents were observed and separated experimentally. Under inhomogeneous illumination, space charge effects, the Dember effect and many other related phenomena were detected. The photoresponse is closely related to the absorption spectrum and depends critically on the geometrical arrangement. The material is exceedingly sensitive to neutron irradiation. The high impedance of the material precludes measurements of the Hall or photoelectromagnetic effects, but recently the hole and electron mobilities were measured by a pulsed photoconductivity technique. It was found that the mobilities are of the order of 1 cm^2/v-sec and anisotropic. A theoretical calculation of this anisotropy is successful. The magnitude of the photocurrents and their spectral sensitivity can be changed markedly by absorption of electron acceptors, or donors, on the surface of the crystals. This leads to the conclusion, already inferred from other work that most of the charge carriers are generated in the surface layer. (*PA*, 1962, #8428)

429. TRANSIENT SPACE-CHARGE-LIMITED PHOTOCURRENTS IN ANTHRACENE

Silver, M., Swicord, M., Jarnagin, R. C., Many, A., Weisz, S. Z., Simhony, M.
***Journal of Physics and Chemistry of Solids*, v. 23,**
pp. 419-422, April 1962

The interpretation of transient photocurrents in the absence and presence of space-charge effects is discussed. Theory suggests that for the space-charge-limited case (1) the initial amplitude varies as (applied voltage)^2; (2) the transit time t_1 of the first front of carriers is about 20% more than the transit time in the absence of space-charge; (3) the form of the photocurrent versus time curve represents a combination of the rise with time due to space-charge effects and the decay due to trapping and surface recombination; and (4) for $t > t_1$ the photocurrent decays even in the absence of trapping. Measurements in anthracene crystals were found to be in agreement with the theoretical predictions. Space-charge effects were observed at very low current densities due to the very low carrier mobility. (*PA*, 1962, #14,578)

430. SYNTHESIS AND STUDY OF THE PHOTOELECTRIC PROPERTIES OF POLYAZINES AND SCHIFF POLYBASES

Topchiev, A. V., Korshak, V. V., Popov, U. A., Rosenstein, L. D.
Preprint 68, presented at the International Symposium on Macromolecular Chemistry, Paris, France, July 1–6, 1963, sponsored by the International Union of Pure and Applied Chemistry, under the patronage of Monsieur le Ministre d'État chargé de la Recherche Scientifique, under the auspices of the Délégation Générale à la Recherche Scientifique et Technique, and the National Committee for Chemistry
(To be published in *Journal of Polymer Science, Part C: Polymer Symposia*)

The method of linear polycondensation of dicarbonyl compounds with hydrazine or with its salt in organic acids or in a water-alcohol medium with addition of hydroxides of alkali metals as catalysts has been used to produce a number of polyazines. They are colored substances with a relatively low molecular weight and with a very limited solubility in organic solvents. The structure of many polyazines is crystalline. Their resistance depends on temperature and is governed by an exponential law; the energy of activation ranges from 1.56 to 2.82 ev and their specific electroconductivity σ_{20} varies from 7.08×10^{-12} to 1.12×10^{-18} ohm^{-1} cm^{-1}. A number of Schiff polybases with a system of conjugated bonds have been synthesized from *p*-phenylenediamines and 2,6-diaminopyridine with carbonyl derivatives: diacetyl, benzyl, glyoxal, terephthalic dialdehyde, maleic dialdehyde, diacetylphenyl oxide, and diacetyldiphenyl sulfide. The color of the resulting polymers was black to grey. The polymers are soluble in dimethylformamide and acetic, formic, and sulfuric acids. The electric properties of Schiff polybases were investigated. The temperature dependence is governed by the equation $\sigma = \sigma_0 e^{-\Delta E/kT}$ and the energy of activation varies from 3.6 to 0.8 ev. Photoelectric sensitivity has been found in a number of compounds. The voltampere, luxampere, and temperature dependence of photocurrent has been established. The phenomenon of polarization was investigated in the polymer product of the polycondensation of benzyl with *p*-phenylenediamine.

431. MODIFICATION OF ELECTRONIC PROPERTIES OF SOME SYNTHETIC POLYMERS

Kryszewski, M., Skorko, M.
Preprint 76, presented at the International Symposium on Macromolecular Chemistry, Paris, France, July 1–6, 1963, sponsored by the International Union of Pure and Applied Chemistry, under the patronage of Monsieur le Ministre d'État chargé de la Recherche Scientifique, under the auspices of the Délégation Générale à la Recherche Scientifique et Technique, and the National Committee for Chemistry
(To be published in *Journal of Polymer Science, Part C: Polymer Symposia*)

Changes in electronic properties of ultraviolet-irradiated chlorine-containing vinyl polymers (saran and PVC) on addition of Zn and Cd ions and Tn and Cd sulfides were investigated. The Zn and Cd ions were introduced into polymer films by swelling in appropriate mixtures of solvent and aqueous salt solution. The sulfides were formed in the swollen films by diffusion of H_2S (amorphous sulfides) or introduced by casting or pressing of films from mixtures with crystalline ZnS or CdS. It was found that the Zn and Cd ions accelerate the ultraviolet degradation, causing discoloration and a large decrease in resistance. The presence of these ions in the studied films yields the disappearance of photoconductivity found in pure irradiated films. The amorphous and crystalline sulfides influence the resistance only very slightly but enhance the photoconductivity of irradiated films, especially those containing crystalline semiconducting powders. Films containing ZnS showed a larger polarization than the pure irradiated films. Some experiments carried out with polystyrene suggest that these effects are not only related to the presence of small amounts of semiconducting compounds, but to intrinsic changes in the polymeric materials during irradiation. Some suggestions are given in order to explain the observed phenomena.

432. SENSITIZED PHOTOCONDUCTIVITY IN ANTHRACENE

Steketee, J. W., de Jonge, J.
***Koninklijke Nederlandse Akademie van Wetenschappen, Proceedings, Series B: Physical Sciences,* v. 66, no. 2, pp. 76–79, 1963 (in English)**

The photoconductivity of anthracene single crystals has been studied in a sandwich type of cell with electrolytic electrodes. If very small amounts of certain water-soluble organic dyes are added to the positive electrode compartment, photocurrents can be observed due to light that is absorbed by the dyes. (*PA*, 1963, #13,129)

433. ELECTRONIC TRANSPORT IN ORGANIC SOLIDS AND LIQUIDS [ABSTRACT]

LeBlanc, O. H., Jr.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 81–83
National Research Council, Ottawa, Canada, 1962

Electronic mobility measurements in hydrocarbon crystals and liquids have revealed a remarkable dependence of the transport mechanism on phase. Transport in the crystal is described by the band model; transport in the liquid by the hopping model. The liquid data, which are relatively unfamiliar, are reviewed briefly. As in the pulsed photoconductivity experiments, transit times are determined from transient currents produced by charge carrier pulses. The method of generating the carrier pulses has usually been different in the liquid experiments, however, since those hydrocarbons that are liquids at room temperature are usually not photoconducting to light in the visible or near ultraviolet regions. Many different carrier generation techniques have been used. Reiss irradiated dilute solutions of anthracene in *n*-hexane with UV, presumably producing "free" electrons and anthracene mono-positive ions. The respective mobilities were $\mu_n = 1.3 \times 10^{-3}$ and $\mu_p = 9.9 \times 10^{-4}$ at 25°C. Gzowski and Terlecki ionized *n*-hexane directly with a spatially narrow, pulsed X-ray beam and measured $\mu_n = 1.3 \times 10^{-3}$ and $\mu_p = 4.1 \times 10^{-4}$ at 19°C.

The author injected electrons into *n*-hexane from a photocathode and measured $\mu_n = 1.4 \times 10^{-4}$ at 27°C. The mobility exhibited an Arrhenius temperature dependence with activation energy, $\Delta E = 0.14$ ev. Chong and Inuishi, using the same technique, found $\mu_n = 1.0 \times 10^{-3}$ at 20°C, $\Delta E = 0.16$ ev for *n*-hexane and $\mu_n = 4.5 \times 10^{-4}$ at 20°C, $\Delta E = 0.16$ ev for benzene.

The internal photoeffect was used to generate carriers in crystalline and liquid pyrene (surprisingly, the photoconductivity of liquid pyrene proved to be comparable to that of the solid). The hole mobility in the crystal just below the melting point (150°C) is ~0.3 and increases with decreasing temperature; the hole mobility in the liquid just above the melting point is $\sim 3 \times 10^{-4}$ and increases with increasing temperature. The decrease of three orders of magnitude and the change in temperature coefficient thus occur abruptly at the melting point. Paradoxically, the 1000-fold decrease in mobility at the melting point of pyrene is accompanied by a 100-fold increase in conductivity. Riehl and Bornmann have observed a similar increase in the conductivity of naphthalene upon melting, and a perusal of Bornmann's data is of interest. His results are fitted well by $\sigma = \sigma_0 \exp(-E/kT)$, but with different values of σ_0 and E for the solid and liquid. The parameter σ_0 is in fact two or three orders of magnitude lower in the liquid than in the solid, but the effect of σ_0 on σ is overwhelmed by a corresponding decrease in E. There is no necessary contradiction involved in the mobility and conductivity changes, although an explanation of the conductivity must now bridge quite a few orders of magnitude. Where before one had a factor of 10^2 in conductivity to account for, now one has a factor of 10^5 in carrier concentration. An explanation of this phenomenon must await the long-sought theory of dark conductivity.

Transport mechanisms are discussed.

434. ELECTRON AND HOLE MOBILITY IN ANTHRACENE CRYSTALS [ABSTRACT]

Kepler, R. G.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," p. 90
National Research Council, Ottawa, Canada, 1962

In an attempt to determine the intrinsic behavior of electrons and holes in anthracene, their drift mobilities have been measured in a large number of crystals as a function of crystal orientation, temperature, and pressure. The measurements were made using a pulsed photoconductivity technique.

435. TRAPPING OF PHOTOCARRIERS IN ANTHRACENE BY ANTHRAQUINONE, ANTHRONE, AND NAPHTHACENE [ABSTRACT]

Hoestery, D. C.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 91–93
National Research Council, Ottawa, Canada, 1962

To obtain a more quantitative measure of the effects of impurities, the bulk, transient photocurrents in anthracene crystals intentionally doped with anthraquinone, anthrone, and naphthacene have been studied. The apparatus in which the measurements were performed is similar to that described by Kepler. The 0.2-sec exposure comes from a condenser-powered air-spark whose output was controlled so that the photocurrents were not space-charge limited.

In the undoped crystals, the hole and electron trapping lifetimes range between 150 and 250 μsec. (With small electric fields, about 10^3 v/cm, no transit is observed and the photocurrents decay exponentially with time over their entire measurable range. The lifetime is defined as the time constant of this decay.) The decay of the photocurrent must arise from trapping and not recombination, since carriers are generated only at the illuminated surface and their relative motion separates them so that they cannot recombine.

The behavior of the anthraquinone- and anthrone-doped crystals is similar. Assuming that the trapping lifetime is an accurate indicator of the impurity concentration, these data show that both impurities (1) have a distribution coefficient in anthracene which is less than unity, (2) are more effective at trapping electrons than holes, and (3) in relatively small concentrations, are effective in controlling the photoconductive behavior of anthracene. These impurities are better electron acceptors than anthracene and it is not too surprising therefore that they are better traps for electrons than holes.

In the naphthacene-doped crystals, the impurity content in various portions of the ingots was determined by standard spectrophotometric methods. For naphthacene-in-anthracene the distribution coefficient is 0.01 and the saturation solubility appears to be about 100 ppm. Naphthacene is not an effective electron trap. For example, the electron lifetimes are 20 and 80 μsec in crystals containing 40 and 10 ppm of naphthacene, respectively. The behavior suggests that naphthacene is acting as a shallow trap and that the drift mobility of the hole is being controlled by multiple trapping. According to the free-carrier treatment of multiple trapping by Shockley and Read, the trap depth is 0.43 ev. Furthermore, the mobilities in the naphthacene-doped crystals are correctly predicted by this theory if it is assumed that (1) the microscopic mobility is that found in the undoped crystals, (2) all of the naphthacene molecules are effective as traps, and (3) the effective density of states in the hole band is equal to the density of anthracene molecules.

Additional measurements on the naphthacene-doped crystals show that (1) the quantum efficiency for carrier generation is the same as in undoped crystals, (2) no carriers are generated by light absorbed in the lowest energy absorption band of the naphthacene, and (3) the hole capture cross section is greater than 10^{-15} cm^2.

436. TRANSIENT PHOTOCURRENTS IN ANTHRACENE FROM LONG WAVELENGTH EXCITATION [ABSTRACT]

Silver, M., Olness, D., Swicord, M., Colby, G. H., Jarnagin, R. C.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 102–105
National Research Council, Ottawa, Canada, 1962

If the surface is the only source of free carriers, then under high intensity flash illumination the transient current will be space-charge-limited. Just such a result has been previously found. However, under extremely high intensity illumination, an initial transient over and above that prescribed by space-charge limitation has also been observed previously. One possible explanation for this result is that the fluorescent light is generating carriers throughout the bulk of the crystal. This possibility has been investigated by observing transient photocurrents in anthracene with microsecond flashes of high intensity fluorescent light and light of wavelengths longer than 4000 A. Three different electrode configurations have been used – electrolytic, blocking, and pressed tin oxide electrodes – the latter being used to observe the current transients as a function of temperature.

437. PHOTO-ELECTROLYSIS AT ANTHRACENE–ELECTROLYTE INTERFACES [ABSTRACT]

Gilliland, J., Jr., Jarnagin, R. C.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 117–124
National Research Council, Ottawa, Canada, 1962

Recent work employing electrolytic solutions as contacts to anthracene crystals and demonstrating the enhancement of photocurrent by selected electrolytes has made it desirable to better understand the processes occurring during conduction at the anthracene–electrolyte interfaces. A single crystal of anthracene sandwiched between two electrolytic solutions to which electrical connections are made via platinum wires is analogous to two electrolysis cells connected in series through a high value resistance. If positive current is passed through the cells from left to right, then a net oxidation must occur in interfacial regions 1 and 3, and a net reduction must occur in interfacial regions 2 and 4. Some aspects of the oxidation(s) which occur at the anthracene–electrolyte interface analogous to region 3 during photoelectrolysis have been examined.

Anthracene single crystals cleaved and polished in the *ab* (001) plane have been subjected to photoelectrolysis. The O_2 concentration in the dark electrolyte solution (illuminated only by light transmitted through anthracene) was monitored polarographically. Two classes of experiments were done: (1) high O_2 case, in which the dark solution was initially air-saturated and the cell maintained in an ambient air atmosphere; and (2) low O_2 case, in which the dark solution was initially N_2 scrubbed and the cell maintained in an ambient N_2 atmosphere. Results are presented and interpreted.

438. ELECTRONIC CONDUCTION IN TWO CRYSTALLINE FORMS OF HEXAMETHYLBENZENE [ABSTRACT]

Kronick, P. L.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," p. 128
National Research Council, Ottawa, Canada, 1962

Electronic conduction perpendicular to the lamellae in films of this material as it passes through its transition is continuous with no change in slope. Small changes in crystalline packing and large changes in symmetry are then not significant in determining the thermal excitation and mobility of carriers.

Using electrolyte for electrodes, the conductivity is measured parallel and perpendicular to the molecular planes in single crystals. Studies are reported of photoconduction excited by ultraviolet light. The sign of the mobile photocarriers is deduced to be positive, since illumination of the cathode produces no photocurrent.

439. ELECTRONIC PROPERTIES OF QUATERRYLENE [ABSTRACT]

Inokuchi, H., Harada, Y., Maruyama, Y.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 129–132
National Research Council, Ottawa, Canada, 1962

The techniques of recrystallization from trichlorobenzene and also of sublimation in high vacuum were effectively applied to make specimens for measuring its electronic properties. The single crystal (0.2 × 0.2 × 5.0 mm) was grown by sublimation in a glass vessel which was evacuated to a pressure of 10^{-4}–10^{-5} mm Hg. The cells used in this work were sandwich type and surface type. To make an appropriate cell for an observation of photoelectromotive force, the evaporation of the metal (Al) and the organic compound was carried out *in vacuo* successively to avoid a contact of oxygen with intersurface of the films. The aromatic hydrocarbons have electrical resistivity as low as 10^5–10^6 ohm-cm for a direction along the *ab*-plane. From the results of two types of cells, a substantial anisotropy of the resistivity was found by a factor of 10^7–10^8; 10^5 ohm-cm for surface-type cells and 10^{13} ohm-cm for the sandwich type. The crystallites of quaterrylene are in alignment with their *ab*-planes parallel with the film surface. The nearest approach of neighboring molecules is found in the *ab*-plane, and the overlapping of molecular orbitals of π-electrons between neighboring molecules may take place along the direction parallel to the *ab*-plane. This result is consistent with that observed with single crystal. Comparison with other aromatic compounds is given.

440. THERMOELECTRIC AND PHOTOELECTRIC EVIDENCE FOR POSITIVE CHARGE TRANSFER IN FERROCENE CRYSTALS [ABSTRACT]

Mette, H., Loscoe, C.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 139–142
National Research Council, Ottawa, Canada, 1962

It was thought to be desirable to perform charge carrier determinations in a material by thermoelectric power, and to compare these results with the photoconductivity measurements. The material selected for the present investigation was ferrocene, a metallo-organic compound that crystallizes in the monoclinic lattice and possesses electrical properties in an accessible range. Single crystals were obtained from zone refined material by three methods: slow evaporation of a saturated benzene solution, growing from the vapor phase, and growing from the melt. The resistivity was measured as a function of temperature and showed the exponential behavior of organic solids with an activation energy of $\epsilon = 0.6$ ev. The room temperature resistivity is 1.2×10^{13} Ω cm, which is several orders of magnitude lower and therefore in a more accessible range than most other organic solids. The current-electric field strength characteristics of the material show the typical "soft" behavior of organic solids with deviations from Ohm's law beginning at 3000 v/cm. Electrical contacts to the material were made with silver paint.

The measurement of the photoconductivity was performed in a manner similar to that reported earlier by Kepler and Boroffka. The photoconductive cell is connected in series with a dc battery and fed directly in a Tektronix Type 121 preamplifier. Strong microsecond Strobotac light pulses release from the cell electric current pulses that produce a voltage drop across the 10-meg input of the preamplifier and are amplified and reproduced on the screen of a Tektronix Type 545 oscilloscope. The samples were single crystals with areas of 0.7 × 0.7 cm^2 and 1 to 15 mils thick. One side was glued with silver paint to a strip of conducting glass. The other (illuminated) surface of the crystal was provided with a semitransparent but well conducting contact by the application of either a thin Ag or Cu_2I_2 suspension. An alternate method of preparing photocells consisted of pressing ferrocene powder between either conducting glass or transparent CsI (Tl) single crystal disks and heating them for a short moment above the melting point of ferrocene. Upon solidification, large area cells with good contacts to the conducting glass were obtained.

It is indicated that photoconductivity in organics cannot be interpreted on the basis of a simple model where photocarriers are generated at one electrode and leave the crystal at the other electrode, but that other mechanisms, e.g., replenishment of carriers at one electrode upon leaving the other electrode, or trapping processes may be taken into account.

441. PHOTOCONDUCTIVITY OF METAL FREE PHTHALOCYANINE SINGLE CRYSTALS [ABSTRACT]

Heilmeier, G., Warfield, G.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 153–155
National Research Council, Ottawa, Canada, 1962

The spectral response of photoconductivity in metal-free phthalocyanine crystals was obtained using ohmic contacts, and it was found to have the same spectral response edges as the optical absorption spectrum and thermal activation energy for conductivity. The correspondence between the "valley-to-valley" separation of the structure found in the strong response regions of the spectral response of photoconductivity and the "peak-to-peak" separation of the infrared optical absorption spectrum has been used to formulate a model for photoconductivity in metal-free phthalocyanine crystals which involves the direct creation of carriers by suitable radiation. The experimental results obtained for metal-free phthalocyanine crystals are consistent with a direct carrier producing absorption mechanism where the surface lifetime of free carriers is less than that of the bulk. The structure in the spectral response of photoconductivity data and the infrared absorption spectrum can also be used, in connection with the discussion on the applicability of a band model and the photoconduction process, to infer the general nature of the conduction bands in metal-free phthalocyanine crystals. The first one is seen to consist of discrete levels of width .014 ev and separation 395 cm^{-1} and 960 cm^{-1}. This band is located at 1.66 ev above the highest filled band. A second conduction band is found at 3.2 ev for which there is qualitative evidence for discreteness from photoconductivity data.

442. THE CONDUCTION STATE IN THE CHARGE-TRANSFER SOLID COMPLEXES [ABSTRACT]

Akamatu, H., Kuroda, H.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 181–185
National Research Council, Ottawa, Canada, 1962

Solid complexes of charge-transfer type which are poor semiconductors and do not show any appreciable ESR absorption are investigated. They are complexes between aromatic hydrocarbons (donors) and tetracyanoethylene (TCNE), 1,3,5-trinitrobenzene (TNB) or halogenated quinones (acceptors). They are of interest since a simple picture of the relation between the charge-transfer state and the conduction state may be anticipated for these loose molecular complexes, in contrast to the complexes with a strong interaction.

These solid complexes show photoconduction, and the spectral dependence of photoconductance is useful to clarify the relation between the exciton state and the conduction state.

443. PHOTOCONDUCTION AND SEMICONDUCTION IN SINGLE CRYSTALS OF CHARGE-TRANSFER COMPLEXES. THE 1:1 PERYLENE-FLUORANIL COMPLEX [ABSTRACT]

Kokado, H., Hasegawa, K., Schneider, W. G.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 186–189
National Research Council, Ottawa, Canada, 1962

Attempts were made to find a suitable complex which can be prepared conveniently in the form of single crystals and which is also a moderately good photoconductor. Several systems which approach these conditions were found. These include either perylene or pyrene as the electron donor, and chloranil, fluoranil, or tetracyanoquinodimethan as electron acceptors. In each case the crystals tend to be elongated along one axis and are bluish-black in color. Order of magnitude comparisons of the conductivities of some of these complexes are tabulated.

The perylene-fluoranil complex has been investigated in greater detail. Mono-crystals (approx. 10 × 2 × 2 mm) were grown from toluene solution. With polarized light the crystals are strongly dichroic. The complex has a 1:1 mole ratio of the components. An X-ray analysis carried out by Dr. A. Hansen shows the crystal to be monoclinic, with unit cell $a = 17.3$, $b = 7.49$, $c = 6.97$Å and $\beta = 90.4$ deg. There are four molecules, i.e., two complex units to the unit cell. The donor and acceptor molecules are alternately stacked, the stacking direction being the *c* crystallographic axis. (The crystals tend to be elongated along the *c*-axis.) The perpendicular interplanar spacing between donor and acceptor molecules is 3.27Å. The molecular planes are inclined at an angle of 69.7 deg to the *c*-axis.

The anisotropy in the electronic conduction was measured with the aid of a four-probe method. The results are tabulated, together with the thermal activation energy for semiconduction and photoconduction. There is roughly a three-to-ten-fold greater conductivity along the *c*-axis than that normal to this axis.

The spectral dependence of the photoconductivity of perylene-fluoranil monocrystals is illustrated. For these measurements electrodes were applied to the ends of the crystal, essentially a surface-cell arrangement, with current flow along the *c*-direction. It was established that the presence of oxygen had no effect on the photocurrents, and accordingly the measurements were made in dry air or nitrogen. The light source consisted of an Osram XBO-1001 xenon discharge lamp together with a Beckman monochromator.

444. ORGANIC PHOTOCONDUCTIVE SYSTEMS [ABSTRACT]

Mehl, W., Greig, H. G., Wolff, N. E.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 204–208
National Research Council, Ottawa, Canada, 1962

Organic photoconductive systems are described which consist of the solution of a photoconductor in an insulating polymer matrix. The polymer matrix itself does not show photoconductivity.

A large number of triphenylmethane and benzophenone derivatives have been used for the photoconductor. A small amount of dye (<1% by weight) derived from these uncolored dye precursors activates photoconductivity in the visible region. The unique property of these films is that they show photoconductivity although only short range order exists in them and although the photoconducting molecules are separated from each other by an insulating polymer. The investigation of these systems promises to give new information on the mechanism of charge transfer in organic photoconductors mainly because in these systems the distance between the photoconductor molecules can be varied over a wide range.

The photoconductivity of these films has been studied for the system bis(4,4′-dimethylaminophenyl) phenyl methane (compound I) in a vinyl chloride/vinyl acetate copolymer. Single crystals of compound I were grown from solution. They absorb in the UV and show photoconductivity. Dye sensitization of these crystals has not been obtained so far. Photoconductivity in the system here discussed was observed with 10 to 70% by weight of compound I in the polymer. The upper limit is given by the miscibility limit of the polymer and compound I. For all measurements reported here compound I constitutes 30% by weight of the total system. Sensitization in the visible was achieved by adding a small amount of the cationic dye malachite green, the oxidation product of compound I, as the chloride to the system. The concentrations were determined by optical absorption measurements. Photoresponse curves were determined with a calibrated monochromator and normalized for equal photons. The incident light was 2×10^{14} photons $cm^{-2}sec^{-1}$ at 6300 Å. To study the effect of concentration of the sensitizing dye on the photoresponse, films with different dye concentrations of malachite green were prepared. Within experimental error the photocurrent was directly proportional to the dye present. The quantum efficiency of these films was estimated.

445. PHOTOCONDUCTIVITY OF MANGANOUS PHTHALOCYANINE

Day, P., Scregg, G., Williams, R. J. P.
***Nature*, v. 197, no. 4867, pp. 589–590, February 9, 1963**

Manganous phthalocyanine differs in its behavior from the other members of the series of metal-free and transition-metal phthalocyanines in a striking manner. The measurements were made on the needle-shaped crystals using two electrodes. No guard ring was used, and the arrangement is therefore equivalent to a surface conductivity cell.

The dark resistivity of the manganous compound is much lower than that of the other phthalocyanines. While the photoconductive action spectra of compounds other than manganous phthalocyanine were generally similar, having two or more peaks in the region of 5000–8500 Å, and another, usually weaker, peak in the region 10,000–12,000 Å, manganous phthalocyanine showed its spectral response over the range 7000–20,000 Å (the limit of our monochromator) with broad maxima at 13,500 and 16,000 Å. The photocurrent in the infrared was stronger in this compound than in any of the others. The photocurrent is depressed in a remarkable way by gases.

446. PHOTOCONDUCTIVITY OF SODIUM DEOXYRIBONUCLEIC ACID IN THE DRY STATE

Liang, C. Y., Scalco, E. G.
***Nature*, v. 198, no. 4875, pp. 86–87, April 6, 1963**

A surface cell was prepared by attaching two electrodes about 1 mm apart to a quartz plate. A thin film from a Na-DNA water solution was then deposited and afterwards dried between the electrodes. Conductivity measurements were made *in vacuo*. For photocurrent observations, a tungsten light source was used.

The dark resistance of the sample is plotted against inverse absolute temperature, and the photocurrents of the sample observed at various temperatures and various applied voltages are also plotted. The activation energy for dark conduction, E_d, was found to be 2.43 ev. The activation energy for photoconduction, E_p, was found to be 0.89 ev. Equations are presented for the relations.

447 ENERGY TRANSFERS BETWEEN SENSITIZER AND SUBSTRATE. III. SENSITIZATION BY THICK DYE FILMS

Nelson, R. C.
***Optical Society of America, Journal of the*, v. 51, no. 11, pp. 1182–1186, November 1961**

Photoconductivity can be sensitized in cadmium sulphide films by specially prepared films of pinacyanole and kryptocyanine having a thickness $\sim 1\ \mu$. Preparations of this sort offer considerably more opportunity for experiment than those sensitized by monolayers of dyes. Their properties support the validity of the electron-transfer mechanism. (*PA*, 1961, #17,797)

448. ENERGY TRANSFERS BETWEEN SENSITIZER AND SUBSTRATE. IV. ENERGY LEVELS IN SOLID DYES

Nelson, R. C.
***Optical Society of America, Journal of the*, v. 51, no. 11, pp. 1186–1191, November 1961**

The work function, or ionization energy, for eight solid dyes was measured. In each case it was found that this energy was equal to the sum of the electron affinity of the dye, as previously measured by the author, and the energy required to produce a charge carrier in the solid dye. The data confirm the point of view that electron-transfer processes in dye sensitization are energetically possible. (*PA*, 1961, #17,798)

449. THE INFLUENCE OF THE RE-ABSORPTION OF LIGHT ON THE SPECTRAL DEPENDENCE OF PHOTOCONDUCTIVITY IN MOLECULAR CRYSTALS

Agranovich, V. M., Konobeev, Yu. V.
***Optika i Spektroskopiya*, v. 11, no. 4, pp. 498–503, October 1961**
(Translated from the Russian in *Optics and Spectroscopy*, v. 11, no. 4, pp. 269–272, October 1961)

The influence of the re-absorption of light on the spectral dependence of photoconductivity in molecular crystals is discussed. Considerable overlapping of absorption and emission spectra occurs in many crystals leading to more re-absorption. The re-absorption increases the photon lifetime in the crystal, and consequently increases the total number of excitons. This increase must be accompanied by an increase of photocurrent. The re-absorption effect is examined by use of a model of volume conductivity in anthracene proposed by Kommandeur and Schneider. It is demonstrated that the occurrence of re-absorption in an anthracene crystal increases the magnitude of the photocurrent and noticeably modifies its spectral curve. (*SSA*, #13,299)

450. PHOTOCONDUCTANCE AND SPECTRAL ABSORPTION OF ANTHRACENE

Steketee, J. W., de Jonge, J.
***Philips Research Reports*, v. 17, no. 4, pp. 363–381, August 1962**

The photoconductivity of anthracene crystals is measured in a sandwich type of cell, the crystals being illuminated through the positive electrolytic electrode with plane-polarized light. Photocurrent and spectral absorption of anthracene crystals are measured with the same optical system. A plot of the photocurrent per quantum of incident light against wavelength shows a close correspondence to the absorption spectrum, the current being a function of the extinction coefficient. The wavelength dependence observed confirms the theory that absorbed energy is transferred as excitons to the positive surface of the crystal where charge separation can take place. The electron is captured by the electrode while the positive hole moves through the crystal to the opposite negative electrode. The diffusion length of the exciton is about 1200 Å. A very small photocurrent found when the negative electrode is illuminated appears also to be due to the light absorbed in a region close to the positive electrode. (*PA*, 1963, #2970)

451. IMPERFECTION PHOTOCONDUCTIVITY IN DIAMOND

Elmgren, J. A., Hudson, D. E.
***Physical Review*, v. 128, no. 3, pp. 1044–1053, November 1, 1962**

The effect of monochromatic light throughout the visible region on the rate of decay of a persistent internal field in diamond was studied. The persistent field was generated by spacially separated trapped electrons and holes, and was sampled by the counting rate of the polarized diamond acting as a nuclear particle counter. Under the influence of light the internal field decayed exponentially with time in a fashion characterized by an intensity-dependent decay constant. The decay constants, normalized to a common photon flux density, varied over more than four orders of magnitude in the photon energy range from 1.8 to 3.5 ev. The results are interpreted in terms of imperfection photoconductivity arising from imperfection levels with photoionization energies of 2.5 and 3.0 ev. This photoconduction model utilizes a decay mechanism which has been overlooked in previous diamond work. An alternate conventional interpretation in terms of detrapping is also presented. (*PA*, 1963 #2975)

452. PHOTOGENERATION OF FREE CARRIERS IN ORGANIC CRYSTALS VIA EXCITON-EXCITON INTERACTIONS

Silver, M., Olness, D., Swicord, M., Jarnagin, R. C.
***Physical Review Letters*, v. 10, no. 1, pp. 12–14, January 1, 1963**

In this note, some results are presented which not only support the exciton-exciton theory, but also yield a bimolecular rate constant in good agreement with that calculated by Choi and Rice.

A current is observed which increases with the square of the light intensity and also increases with temperature in the superlinear region.

Transient current pulses for high- and low-intensity, weakly and strongly absorbed light in a 1.45-mm anthracene crystal (800 v applied, 10 μsec/cm) are graphed as is current density vs. incident light intensity for weakly absorbed light for 1000 v applied. Surface or near-surface generation of carriers is also considered.

453. DRIFT MOBILITY OF PHOTO-INJECTED ELECTRONS IN HEXANE-SILICONE MIXTURE

Chong, P., Inuishi, Y.
***Physical Society of Japan, Journal of the*, v. 16, no. 7, p. 1432, July 1961**

In this paper the mobility of photo-injected electrons in *n*-hexane–silicone oil mixture is mentioned. The silicone oil used has mean molecular weight 1200 and viscosity 6×10^{-2} poise at 20°C. The dependence of the drift mobility of photo-injected carrier on the viscosity of the mixture is shown.

454. EFFECT OF GASES ON THE PHOTOCONDUCTION OF ANTHRACENE

Nakada, I., Kaiyoh, H.
***Physical Society of Japan, Journal of the*, v. 17, no. 1, pp. 93–99, January 1962**

Measurements of photoconductivity in the *ab*-plane of an anthracene single crystal in various gas ambients are detailed. In order to examine the depth of the surface region in which the free carriers are influenced by absorbed gases, bulk and surface currents are measured separately. The magnitude of the surface current is increased by a factor of about three when the ambient is changed from nitrogen to oxygen. Water vapor eliminates the effect of the oxygen and approximately the same value as in the nitrogen ambient is obtained. Bulk current is only slightly influenced by adsorption. The range of influence of adsorption is estimated to be less than 0.1 mm from the crystal surface. (*SSA*, #15,218)

455. PHOTOCONDUCTIVITY OF HEAT-TREATED POLYACRYLONITRILE

Ohigashi, H.
***Reports on Progress in Polymer Physics in Japan*, v. 6, pp. 244–248, 1963 (in English)**
(Available through Kobayasi Institute of Physical Research, Kokubunji, Tokyo, Japan)

Although the photoelectric effects of organic molecular crystals of polynuclear aromatic hydrocarbons have been studied extensively, few investigations on the effect of semiconducting polymers have been reported. Therefore, there is much interest in obtaining information on the photoelectric effects of heat-treated PAN. In this work, spectral sensitivity of the photocurrent, its relation with optical absorption, and the temperature dependence of dark conductivity have been studied.

PAN powder, prepared by redox polymerization, was dissolved in dimethylformamide and made into a film on a glass plate. The film was heated in a quartz tube in various conditions as tabulated. The steady-state photocurrent was measured with a vibrating reed electrometer *in vacuo* ($< 10^{-5}$ mm Hg) for a surface-type cell with applied field of 10^3 v/cm. Aluminum was evaporated on the film as dc electrodes which were separated by a gap of 0.1 cm. The monochromatic light for photoconductivity measurements was obtained from a 50-w tungsten lamp dispersed by a quartz prism monochromator. Temperature dependence of the dark conductivity was measured in dry air for a sandwich-type cell at temperatures from 300 to 480°K. Thickness of the film in the cell was 0.1 to 0.2 mm, and the strength of the applied field was 5×10^3 v/cm.

456. COLOR SENSITIZATION OF PHOTOCONDUCTIVE MATERIALS BY DYES. SUPERSENSITIZATION OF ZINC OXIDE

Namga, S., Hishiki, Y.
***Rika Gaku Kenkyusho Hokoku*, v. 39, no. 1, pp. 27–34, 1963**

457. TRANSIENT PHOTOCONDUCTIVITY OF POLYSTYRENE AND POLYISOBUTYLENE EXPOSED TO PULSES OF NEUTRON AND GAMMA RADIATION

Coppage, F. N.
June 1962
Sandia Corporation, Albuquerque, N. Mex.
SCR-525
(Paper CP-62-1238, presented at the AIEE Summer General Meeting and Aero-Space Transportation Conference, Denver, Colo., June 1962)

Photoconductivity in polystyrene and polyisobutylene-impregnated Kraft paper dielectrics has been measured during and following exposures to short-duration, high-intensity pulses of nuclear radiation. Absorbed dose rates were $\leq 1 \times 10^7$ rad/sec. Temperatures of the dielectric samples were controlled in the range from −8 to +80°C. Radiation sources utilized were the Sandia Pulsed Reactor and the TRIGA Mk F. The prompt reactor periods for the study ranged from 30 to 300 μsec for the SPR and 4 msec for the TRIGA Mk F. (*STAR*, N63-18,972)

458. MEASURED BEHAVIOR OF GAMMA-RAY PHOTOCONDUCTIVITY IN ORGANIC DIELECTRICS

Harrison, S. E., Prouix, P. F.
June 1962
Sandia Corporation, Albuquerque, N. Mex.
SCR-526
(Paper CP-62-1251, presented at the AIEE Summer General Meeting and Aero-Space Transportation Conference, Denver, Colo., June 1962)

Photoconductivity measurements are reported for polyethylene, polystyrene, a mica-filled epoxy formulation, polypropylene, nylon, teflon, diallylphthalate, and H-film. The gamma-ray measurements were made at intensities within the interval from 1.0×10^{-3} rad (H_2O)/sec to 1.0×10^4 rad (H_2O)/sec, and at temperatures which ranged from 38 to 71°C. Conductivity was found to have distinct features in three time intervals. (*STAR*, N63-18,974)

459. A STUDY OF GAMMA-RAY PHOTOCONDUCTIVITY IN ORGANIC DIELECTRIC MATERIALS

Harrison, S. E.
1962
Sandia Corporation, Albuquerque, N. Mex.
SCDC-2580, AEC-TID-15482, AT(29-1)-789

The gamma-ray photoconductivities of polyethylene, polystyrene, polyvinylchloride, polypropylene, teflon, nylon, Kel-F, and three thermosetting resins denoted as Epoxy 1478-1, 1478-3, and 1478-22 were measured. Conductivity changes resulting from steady-state gamma-ray exposures were measured continuously throughout the exposure and after the exposure. The conductivity was found to exhibit distinct features in three time intervals: interval 1 is where photoconduction is responding to a step increase in radiation intensity; interval 2 is where the photoconductivity has reached an equilibrium value whose magnitude is defined by radiation intensity and temperature; and interval 3 is where the conductivity is recovering upon sample removal from the gamma-ray environment. The time required during interval 1 for the conductivity to reach the equilibrium values of interval 2 is defined as the rise time (τ_r) and was experimentally found to decrease with increased irradiation intensity according to the relationship $\tau_r = \tau_r' \dot{R}^{-\mu}$. The equilibrium conductivity values of interval 2 give a dependence of photoconductivity on irradiation intensity at a given temperature which is characterized to good approximation in one or more regions, within which conductivity (σ) is expressed as $\sigma = \sigma_0' \dot{R}^{\delta}$. Experimental values of δ range from 0.00 to 2.72. Conductivity decays with time (t) from an equilibrium value (σ_{eq}) after abruptly stopping radiation exposure. The photoconductivity decay is characterized to good approximation by $\sigma(t) = \sigma_{eq} [Ae^{-t/\tau_1} + Be^{-t/\tau_2}]$ when τ_1 and τ_2 are two distinct decay constants. Conductivity was observed to vary with temperature under both dark and radiation-induced conductivity conditions according to the relationship $\sigma = \sigma_0 e^{-E/kT}$. The thermal activation energy (E) is lowered by irradiation except for Epoxy 1478-1 which has one intensity interval, within which E is unchanged.

460. EFFECT OF TEMPERATURE ON THE PHOTOCONDUCTIVITY OF SOLUTIONS OF CHLOROFORM, BROMOFORM, AND IODOFORM IN ETHYL ETHER

Mitskevich, P. K., Bobyl, V. G., Kopylov, Yu. A.
***Sbornik Nauchnykh Trudov Dnepropetrovskogo Inzhenerno-Stroitelnogo Instituta*, no. 9, pp. 139–142, 1960**
(See also *Referativnyi Zhurnal, Fizika*, 1961, #12D80)

An increase in temperature (-16 to $+16$°C) increased the photoconductivity. Confirmation was given an earlier theory of temperature dependence of photoconductivity: $\sigma = (A/T) \exp(-B/T)$, where A and B are constant coefficients for voltage of the electrical field and intensity of incident light.

461. DEPENDENCE OF THE PHOTOCONDUCTIVITY AND THE INTENSITY OF LUMINESCENCE OF ANTHRACENE CRYSTALS ON THE EXCITATION WAVELENGTH

Eremenko, V. V., Medvedev, V. S.
***Soviet Physics—Solid State*, v. 2, no. 7, pp. 1426–1428, January 1961**
(Translation of Entry #215, AI/LS 341)

462. THE RED BOUNDARY OF PHOTOCONDUCTIVITY OF ETHER SOLUTIONS

Romanets, R. G., Nemchenko, A. M., Bobyl, V. G.
***Ukrains'kii Fizichnii Zhurnal*, v. 6, pp. 803–806, 1961**

Solutions of bromoaniline, CH_2I_2, MeI, and CHI_3 in Et_2O were investigated. Electroconductivity and photoconductivity were studied in an electrical field (1000 v/cm) at room temperature. The current was allowed to reach a steady value in the dark. Then the sample was irradiated with monochromatic ultraviolet light, and the increase in the current strength was measured.

463. INCREASING PHOTOSENSITIVITY OF PHOTOCONDUCTIVE MATERIALS

Shely, B. L.
December 18, 1962 (patent application, June 3, 1960)
U.S. Department of Commerce, Washington, D.C.
U.S. Patent 3,069,365 (assigned to Minnesota Mining and Manufacturing Co.)

An organic solution of Eosin Y dye is used as a sensitizer for ZnO photoconductive material. The solvents EtOAc, BuOAc, PrOAc, MeCOEt, BuOH, and EtOH were more successful than MeOAc and the latter better than Me_2CO. Several still less successful solvents are noted. Dark conductivity was obtained from current measurements on the unilluminated sample; photoconductivity measurements were made after 5 sec of illumination from a 200-w tungsten bulb operating at 3100°K and placed to allow 0.0045 w/cm^2 of radiant energy to fall on the sample. For three samples using EtOH as solvent and treated as follows: dark-adapted ZnO and dyed in dark, nondark-adapted ZnO but dyed in dark, and a sample dyed in light. the sensitivities were, respectively, 580×10^{-9}, 210×10^{-9}, and 130×10^{-9} mhos.

464. INDUCED ELECTROMOTIVE FORCE AND ELECTRICAL STRENGTH OF IRRADIATED POLYVINYLCHLORIDE

Kuchin, V. D., Shastova, A. K.
***Vysokomolekulyarnye Soedineniya*, v. 4, no. 12, pp. 1863–1866, December 1962**

X-ray-induced EMF in polyvinylchloride increases exponentially with increase in radiation intensity, tending toward a saturation value. With increase in temperature the induced EMF decreases, independently of the radiation intensity. The electrical strength of PVC increases with increase in dosage, evidently due to decrease in size of the defects and to the action of the space charge generated by the radiation. An analysis of the experimental results is presented, and the mechanism of the processes in PVC caused by irradiation is discussed.

465. PHOTOCONDUCTIVITY IN ORGANIC MATERIALS

Pope, M.
In "Luminescence of Organic and Inorganic Materials."
International Conference Proceedings, New York University, N.Y., 1961, pp. 276–281
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N.Y., 1962

Two problems face workers in this field. The first is the apparent discrepancy between the energy requirements for ionization in the solid crystal and the much lower optical energy threshold at which conductivity starts. The second problem relates to the method by which the carriers move inside the crystal from one molecule to the other, from one side of the crystal to the other. Experiments are reported for the anthracene crystal. It is shown that photoexcitation is not necessary for the induction of high conductivity in organic crystals. By a suitable choice of the electrodes, considerable charge injection can be effected. When photoexcitation is involved, the excitation diffuses to the surface where dissociation takes place as a result of an interaction with the electrode, the electron passing preferentially into the electrode or being trapped there and the hole becoming free to move through the crystal. When the electrode is absent or blocking, dissociation may occur at an impurity at the surface. The mobility of the carriers as determined by Kepler is about 1 cm²/v-sec. In the case of anthracene the extent of the true negative electron current is not greater than about 0.3% of the hole conductivity, and there is also some trapping of holes.

466. RÖNTGEN-PHOTOLEITUNG, UV-PHOTOLEITUNG UND FLUORESZENZ IN ANTHRAZEN (X-RAY PHOTOCONDUCTION, UV PHOTOCONDUCTION AND FLUORESCENCE IN ANTHRACENE)

Hartmann, H. K.
***Zeitschrift für Angewandte Physik*, v. 14, no. 12, pp. 727–734, December 1962**

X-ray excitation produces a homogeneous distribution of electrons and holes. The X-ray-induced current shows linear dependence on applied voltage. The current decreases with accumulated X-ray dose but is still ohmic. Temperature dependence is complex-exponential, giving various activation energies in different ranges, all dependent on X-ray dose. UV-excited currents are not ohmic, but pure anthracene shows a single activation energy for temperature dependence, decreasing with previous X-ray dose. Fluorescence also decreases with dose. Specimens with tetrazene impurity are also studied. Theoretical interpretations are given. (*PA*, 1963, #6628)

467. ÜBER DEN MECHANISMUS DER DUNKEL- UND PHOTOLEITFÄHIGKEIT VON RHODAMIN B (MECHANISM OF DARK AND PHOTOCONDUCTIVITY OF RHODAMINE B)

Hauffe, K., Kaufhold, J.
***Zeitschrift für Elektrochemie*, v. 66, no. 4, pp. 316–325, April 30, 1962**

It was found that photoconductivity of films of rhodamine B showed no maximum at 0°C and decreased below a measurable value at −40°C, and that oxygen lowered photoconductivity though the effect was reversible. The conductivity seems to be caused by surface electronic charge carriers.

468. LIGHT ABSORPTION BY ELECTRONS OF NONMETALLIC CRYSTALS IN AN ELECTRIC FIELD

Yakovlev, V. A.
***Zhurnal Eksperimentalnoi i Teoreticheskoi Fiziki*, v. 40, no. 6, pp. 1695–1698, June 1961**
(Translated from the Russian in *Soviet Physics—JETP*, v. 13, no. 6, pp. 1194–1196, December 1961)

The effect is determined of a strong electric field on the optical absorption coefficient due to the conduction electrons of a nonmetallic crystal (semiconductor, insulator).

469. PHOTOIONIZATION OF ORGANIC VAPORS IN THE VACUUM REGION OF THE SPECTRUM

Vilesov, F. I.
***Zhurnal Fizicheskoi Khimii*, v. 35, no. 9, pp. 2010–2015, September 1961**
(Translated from the Russian in *Russian Journal of Physical Chemistry*, v. 35, no. 9, pp. 986–989, September 1961)

The photoionization potentials of aniline (I), *m*-tolidine (II), benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, mesitylene, durene, pentamethylbenzene, hexamethylbenzene, and *N*,*N*-dimethylaniline were shown to be 7.69, 7.50, 9.24 ± 0.02, 8.81 ± 0.02, 8.56 ± 0.02, 8.59 ± 0.02, 8.44 ± 0.02, 8.41 ± 0.02, 8.05 ± 0.02, 7.92 ± 0.02, 7.85 ± 0.02, and 735 ev, respectively. Theoretical discussion of I and II is presented.

SYNTHESIS AND APPLICATION

470. GAMMA INDUCED PHOTOCONDUCTIVITY IN A POLYETHYLENE TEREPHTHALATE CAPACITOR

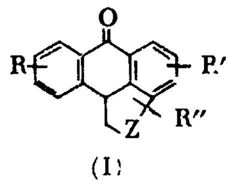
Conrad, E. E., Marcus, S. M.
May 4, 1962
Diamond Ordnance Fuze Laboratories, Washington, D.C.
DOFL-TR-1037

Results of photoconductivity measurements are presented for mylar capacitors at gamma radiation fluxes of 10^2 to 4×10^6 r/sec. The results are compared with a semiempirical relation. (*NSA*, 1962, #21,088)

471. PHOTOCONDUCTIVE LAYERS FOR ELECTROPHOTOGRAPHIC PROCESSES

Schaum, G., Haydn, H., Koenig, A. v., Seibert, H.
November 14, 1956 (application date)
U.S. Department of Commerce, Washington, D.C.
German Patent 1,102,556 (assigned to Agfa A.-G.)

The materials claimed contain derivatives of polycyclic condensed hydrocarbons of the form:



(I)

Z represents atoms to complete a benzene, pyridine, pyridone, pyrimidine, or pyrimidone ring; R and R′ are CN, NO_2, H, a halogen, alkyl or aryl groups, or alkyl- or arylamino groups. R″ depends on the ring completed by Z. These compounds are more light sensitive than usual organic conductors, and are sensitive to visible light as well as ultraviolet. An example is detailed.

472. PHOTOCONDUCTING FILMS FOR ELECTROPHOTOGRAPHIC PROCESSES

Schaum, G., Haydn, H., Koenig, A. v., Seibert, H.
November 14, 1956 (application date)
U.S. Department of Commerce, Washington, D.C.
German Patent 1,104,823 (assigned to Agfa A.-G.)

Condensates of the type $YN(R')(X)CH{:}CHC_6H_4R$ are claimed, in which Y is the residue of a heterocyclic ring to which may be fused a Ph or naphthyl ring, which may also bear substituents; R and R′ are substituent groups; and X is an anion. These condensates are prepared from aromatic aldehydes and salts of quinaldine, benzoquinaldine, or picoline. When they are incorporated into film-forming resins, such as cellulose, poly(vinyl chloride), polyurethans, polyesters, polyamides, polycarbonates, or silicones, the films obtained are sensitive to visible light and can be used in copying apparatus. Examples are given.

473. PHOTOCONDUCTIVE FILMS FOR ELECTROPHOTOGRAPHY

Schaum, G., Haydn, H., Koenig, A. v., Seibert, H.
November 14, 1956 (application date)
U.S. Department of Commerce, Washington, D.C.
German Patent 1,105,273 (assigned to Agfa A.-G.)

A product is claimed of crystalline aromatic nitriles, such as 1,4- and 1,5-dicyanonaphthalene, aminophthalonitrile, and nitrophthalodinitrile, embedded in a film by adding to a solution of the nitrile and film matrix another solvent which dissolves only the latter. A high level of charge is produced, and a smaller dark conductivity than usual with organic photoconductors results.

474. POLYACRYLONITRILE CONTAINING SILVER OR INSOLUBLE SILVER SALTS

Hendricks, R. W.
October 2, 1962 (patent application, September 28, 1959)
U.S. Department of Commerce, Washington, D.C.
U.S. Patent 3,056,169 (assigned to E. I. du Pont de Nemours & Co.)

A claim is made for the preparation and use of the material. Acrylonitrile monomer (15–70 mole %) is mixed with $AgNO_3$ (5–35 mole %) and H_2O (17–73 mole %), polymerized with catalysts and heat or radiation, and subsequently shaped, or if film, oriented. Light sensitizers may be added to film. The $AgNO_3$ is converted to Ag, AgS, or Ag halide, and the polymer is dried. The material exhibits low surface resistivities. It is usable for electrical apparatus, wave guides, and radiant heating unit parts, as well as seat covers, decorated surfaces, etc.

475. PHOTOCONDUCTIVE LAYERS

Miller, A., Haydn, H.
May 29, 1958 (patent application, December 14, 1956)
U.S. Department of Commerce, Washington, D.C.
German Patent 1,031,127 (assigned to Agfa A.-G.)

Photoconductive layers are claimed, which are composed of binders of polycarbonates of 4,4′-bis(4-hydroxyaryl) alkanes, and of photoconductors of either inorganic material or organic (anthracene, anthraquinone, *p*-diphenylbenzene, benzanthrone, 1,5-dicyanonaphthalene, or aminophthalodinitrile). Advantages of the layers are pointed out, the preparation is explained, and an example is detailed.

476. PHOTOELECTRIC CELLS CONTAINING LIGHT-SENSITIVE DYES

Kostelec, J.
March 12, 1959 (application date)
U.S. Department of Commerce, Washington, D.C.
U.S. Patent 3,009,006 (assigned to General Aniline and Film Corp.)

A continuous film of a light-sensitive dye (phthalein or rose bengal) is used to extend the spectral sensitivity of photoconductive ZnO. The cell using such a film is claimed in the patent.

477. PHOTOSENSITIVE POLYPHTHALOCYANINE COMPOUNDS FOR PHOTOELECTRIC DEVICES AND SOLAR CELLS

Wildi, B. S., Epstein, A. S.
June 1, 1959 (application date)
U.S. Department of Commerce, Washington, D.C.
U.S. Patent 3,009,981 (assigned to Monsanto Chemical Co.)

The use of photosensitive polyphthalocyanines in photoelectric and solar devices is claimed. The example of Cu polyphthalocyanine is explained; a *p*-type conductivity is produced with stoichiometric excess of Cu, *n*-type with less than stoichiometric amount of Cu, the degree of *n*- or *p*-type varying with deficiency or excess of Cu. Similar results are found with other metals. Doping techniques are explained.

478. ELECTROPHOTOGRAPHIC MATERIAL CONTAINING ORGANIC COMPOUNDS

Gevaert Photo-Producten N.V.
April 1, 1960 (British patent application, February 5, 1959)
U.S. Department of Commerce, Washington, D.C.
Belgian Patent 585,507

Organic compounds of the formula $R(A)_nR'$ are claimed as photoconductive layers. R and R′ represent aryl or substituted aryl radicals; A is CH:CH; and *n* is 1 or 2. Several suitable compounds and their preparation are presented.

479. ELECTROPHOTOGRAPHIC MATERIAL CONTAINING ORGANIC COMPOUNDS

Gevaert Photo-Producten N.V.
April 1, 1960 (patent application, December 9, 1959)
U S. Department of Commerce, Washington, D.C.
Belgian Patent 585,450

Benzofuran derivatives are claimed as photoconductors for electrophotographic material. Preparation of 6-hydroxy-2,3-bis(*p*-dimethyl-aminophenyl)benzofuran is described and several other furans (similarly prepared) are named.

480. PHOTOCONDUCTORS WITH OPTIMAL DARK RESISTIVITY

Cassiers, P. M., Nys, J. M., Willems, J. F.
August 5, 1960 (British patent application, February 5, 1959)
U.S. Department of Commerce, Washington, D.C.
Belgian Patent 587,300 (assigned to Gevaert Photo-Producten N.V.)

An improved photoconductive layer in close surface contact with conductive foil is claimed. The substance is purified by recrystallization, and a concentrated solution prepared by dissolving in a strong organic solvent which is easily evaporated; the warm solution is spread on the foil and quickly dried. Vacuum coating of the organic photoconductive substance onto the foil is also recommended.

481. ELECTROPHOTOGRAPHIC MATERIAL CONTAINING ORGANIC COMPOUNDS

Gevaert Photo-Producten N.V.
August 5, 1960 (British patent application, February 5, 1959)
U.S. Department of Commerce, Washington, D.C.
Belgian Patent 587,301

Organic compounds of the 1,2-dihydropyridine, 4-selenazoline, 4-thiazoline, 4-oxazoline, or 4-pyrroline series are claimed as photoconductors for an electrophotographic material.

482. ELECTROPHOTOGRAPHIC MATERIAL

Gevaert Photo-Producten N.V.
August 19, 1960 (patent application, February 19, 1960)
U.S. Department of Commerce, Washington, D.C.
Belgian Patent 587,794

Diphenylmethanes and phenothiazines are claimed as constituents of the photoconductive layer. Several specific compounds are mentioned.

483. ELECTROPHOTOGRAPHIC PROCESS

Cassiers, P. M., Hart, R. M., Conix, A. J., Nys, J. M., Willems, J. F.
August 26, 1960 (British patent application, February 26, 1959, April 22, 1959, January 29, 1960)
U.S. Department of Commerce, Washington, D.C.
Belgian Patent 588, 049 (assigned to Gevaert Photo-Producten N.V.)

A polymeric substance, with dark resistivity of 10^{12}–10^{19} ohm-cm which can be reduced by electromagnetic radiation such as ultraviolet or visible light, is claimed as material for a photoconductive layer in close surface contact with a conductive substrate. Among the suitable substances are polyesters, polyethers, and polymerized or copolymerized vinyl acetals, vinyl esters, vinyl derivatives of heterocyclic compounds, acrylic acid derivatives, and styrene derivatives.

484. ELECTROPHOTOGRAPHIC MATERIAL CONTAINING PHOTOCONDUCTIVE VINYL POLYMERS

Cassiers, P. M., Hart, R. M., Nys, J. M., Willems, J. F.
August 26, 1960 (British patent application, February 26, 1959, April 22, 1959, January 29, 1960)
U.S. Department of Commerce, Washington, D.C.
Belgian Patent 588,050 (assigned to Gevaert Photo-Producten N.V.)

The photoconductive layer of the claimed electrophotographic material contains vinyl polymers or copolymers. The following subsequent patents increase sensitivity of this photoconductor: Belgian Patent 589,994, by addition of nitrobenzene derivatives; Belgian Patent 589,995, by addition of a triazole derivative; and Belgian Patent 590,299, by addition of a hydrazine derivative.

485. ELECTROPHOTOGRAPHIC MATERIAL CONTAINING ORGANIC COMPOUNDS

Gevaert Photo-Producten N.V.
September 30, 1960 (patent application, March 31, 1960)
U.S. Department of Commerce, Washington, D.C.
Belgian Patent 589,239

A pyrrole or indole derivative is claimed as a constituent of the photoconductive layer of an electrophotographic material. An example is given of the use of an indole.

486. ELECTROPHOTOGRAPHIC PROCESS

Cassiers, P. M., Nys, J. M., Willems, J. F., Hart, R. M.
October 24, 1960 (British patent application, April 22, 1959)
U. S. Department of Commerce, Washington, D.C.
Belgian Patent 589,996 (assigned to Gevaert Photo-Producten N.V.)

The conductivity of organic polymers used in the photoconductive layer of the material is given a lasting increase by addition of a small amount of radiation-sensitive compound. Suitable organic polymeric photoconductors include acetals, vinyls with unsaturated groups or heterocyclic or aromatic polycyclic rings in the side chain, polyesters, cellulose derivatives, and amylose acetate. The radiation-sensitive compounds include benzenediazonium salts or complexes with amino or azo groups, stilbene derivatives, organic halides, chloranil, and organic peroxides.

487. POLYMERIC ACRYLONITRILES IN ELECTROPHOTOGRAPHY

Hoegl, H., Schlesinger, H.
June 20, 1962 (application date, May 30, 1959)
U.S. Department of Commerce, Washington, D.C.
German Patent 1,131,988 (assigned to Kalle A.-G.)

A claim is made for *N*-substituted acrylonitriles of the formula $[C(R^1)[CON(R^2)R^3]CH_2]_n$ to be used in photoconductive layers. R^1 is an alkyl group; R^2 and R^3 are H or a simple or substituted aryl group or heterocyclic group (or N, R^2, and R^3 together may be part of a heterocyclic group); and *n* is an integer > 1. When *n* is large, the materials are resinous and can be used without a binder. Mixed polymers are also useful. Optimum irradiation frequencies and methods of further sensitization of the layers are mentioned.

488. ORGANIC PHOTOCONDUCTING MATERIALS

Renker-Belipa G.m.b.H.
August 15, 1962 (German patent application, April 29, 1961)
U.S. Department of Commerce, Washington, D.C.
Belgian Patent 617,032

Sheets for xerographic printing were made by coating electrically conducting foil or paper with a film containing photoconductive conjugated ketones or thio-ketones of the types $(XA)_2C(:Y)$, $XAC(:Y)(CH:CH)_nAX$, and $XA(CH:CH)_mC(:Y)(CH:CH)_pAX$, where Y is O or S, X is a group which may contain active hydrogen, and A is an aromatic or unsaturated heterocyclic nucleus. Some of the photoconductive agents were treated with epoxy or isocyanate prepolymers and integrally bonded to the base sheet.

An example of the procedure is detailed, using 4-diethylamino-2-hydroxy-2′-carboxybenzophenone as the photoconductor, rhodamine B as sensitizer, and cyclohexanone as primary solvent.

489. PHOTOCONDUCTOGRAPHIC PRODUCTS

Graniza, E. P., Knox, W. J., Jr.
August 15, 1962 (U.S. patent application, May 1, 1961)
U.S. Department of Commerce, Washington, D.C.
Belgian Patent 617,025 (assigned to Kodak)

Amines (NR_3) or ammonium salts (R_4NX) in amounts of 0.01–4% of ZnO in a photoconducting coating are claimed to increase sensitivity, γ, and D_{max}. The R's may be the same or different, and may be H; alkyls of 1 to 22 C atoms, saturated or unsaturated; $(CH_2)_nNH_2$, where *n* is 2–22; or $(CH_2CH_2NH)_nH$, where *n* is 1–11. X is a halogen.

490. PHOTOELECTRIC CELL USING ORGANIC MATERIALS

Calvin, M., Kearns, D. R.
October 9, 1962 (patent application, October 1, 1959)
U.S. Department of Commerce, Washington, D.C.
U.S. Patent 3,057,947

Photoelectric cells responsive to visible, ultraviolet, and infrared radiation were constructed from (1) a polynuclear homo- or heterocyclic condensed ring compound having large, flat planar molecular configuration with primarily π-electron system, and (2) an organic material that could act as either an oxidizing agent or a reducing agent with respect to the first component. Examples are detailed. In the first, Mg phthalocyanine (I) and an acetone solution of air-oxidized tetramethyl-*p*-phenylenediamine were used to develop voltage of 200 mv with light from a 500-w lamp. In other examples, I was used with β-carotene; I was used with dibrominated tetramethylphenylenediamine (II); Ni phthalocyanine was used with II; decacylene was used with II; perylene was used with *p*-chloranil; and coronene was used with *o*-chloranil. The potential set up on light absorption depended on the nature of the electron donor, electron acceptor, and the matrix containing them. The organic photocells could be more economical than the inorganic and elemental semiconductors because there is a wider variety of starting materials, the manufacture of organic semiconductors is not dependent on the delicate crystal growth conditions of the inorganic, and photosensitivity is achieved without predetermined impurity dispersions.

491. ELECTROPHOTOGRAPHIC MATERIAL

Renker-Belipa G.m.b.H.
December 28, 1962 (German patent application,
September 13, 1961)
U.S. Department of Commerce, Washington, D.C.
Belgian Patent 622,409

Materials are claimed for application to an Al foil having a porous 1–8 μ film of Al_2O_3. Thus, 250 g Me 4-diethylamino-2-hydroxybenzophenone-2′-carboxylate, 500 g synthetic resin (styrene + Et maleate), and 7.5 g Safranine T are dissolved in 2 liters hot cyclohexanone and diluted with 3–6 liters EtOH. This solution is applied to an Al foil having a 2–4 μ film of Al_2O_3 deposited by anodization, to give, after drying, a 0.004–0.01 mm film of electrophotographic material. The production and development of an image are outlined.

492. COMPOSITION FOR ELECTROPHOTOGRAPHIC REPRODUCTION

Societa per Azioni Ferrania
March 14, 1963 (Italian patent application,
December 4, 1961)
U.S. Department of Commerce, Washington, D.C.
Belgian Patent 625,567

Condensation products of polymers, having free OH or NH_2 groups, with SO_2Cl or COCl derivatives of 1,2-naphthoquinone 1-diazide, 1,2-naphthoquinone 2-diazide, and *o*-benzoquinone diazide, are claimed as suitable compositions. These photosensitive compounds change in conductivity when exposed to radiations of adequate wavelength. The phototransformation is irreversible and permits prolongation of the time between exposure and developing.

EXCITED STATES

GENERAL REFERENCES

493. THE ELECTRONIC SPECTRA OF AROMATIC MOLECULAR CRYSTALS

Wolf, H. C.
In "Solid State Physics—Advances in Research and Applications," Volume 9, pp. 1–81
Seitz, F., Turnbull, D., Editors
Academic Press, Inc., New York, N.Y., 1959

A brief survey of the spectra of organic molecules, particularly those of the aromatic type, is given. The π-electrons of the rings are responsible for the essential form of the spectra. In the region where the electron excitation spectra are observed, their intensities can be described in terms of two selection rules: (1) In the allowed transitions the totally symmetrical molecular vibrations are excited most intensely. (2) Forbidden transitions can be made "allowed" as a result of the presence of vibrations which are not totally symmetric. Experimental investigation of the spectra of aromatic molecular crystals is presented. The methods developed to undertake the quantitative measurements of absorption, fluorescence, and reflection spectra are described, and the results are discussed for several types of organic molecular crystals. The theory of spectra of molecular crystals is presented and a comparison with experiments is made. (*SSA*, #9392)

494. ORIGIN AND EVOLUTION OF BIOLUMINESCENCE

McElroy, W. D., Seliger, H. H.
In "Horizons in Biochemistry," pp. 91–101
Kasha, M., Pullman, B., Editors
Academic Press, Inc., New York, N.Y., and London, England, 1962

Bioluminescence is randomly distributed throughout the animal, plant, and microbial world. The chemical reaction which creates the excited state in all forms is oxidative in nature, making use as it does of molecular oxygen as the ultimate electron acceptor. Except for two species, none of the oxidizable substrates (luciferins) from these various organisms will react with any but its own enzyme (luciferase), leading to the suggestion that luminescence is not uniquely associated with any single organic substance. It has been suggested, however, that despite the apparent diversity of the various luciferins they are part of a chemical reaction that is fundamental to all organisms.

It is proposed here that in the evolution of organisms from an anaerobic to an aerobic form of life there was, initially, a struggle for anaerobic existence. Because of the toxic nature of oxygen to anaerobes, it is suggested that the organisms that survived initially were those that were able to reduce molecular oxygen directly and quickly. This struggle for anaerobic conditions led to the selection of organisms having specific oxidases (luciferase) which catalyzed the rapid removal of oxygen; all primitive forms were therefore potentially luminescent. The gradual selection and evolution of electron transport processes in which oxygen was reduced stepwise to form water gave rise finally to the aerobic forms. With the appearance of the latter the luminescent, oxidative reaction was no longer of selective advantage. Thus, it is argued that bioluminescence is a vestigial system of organic evolution, but that through secondary evolutionary processes the luminescent system has been preserved in various and unrelated organisms by virtue of the fact that it has been adapted for other useful purposes.

495. INTERNATIONAL SYMPOSIUM ON LUMINESCENCE, BALATONVILAGOS, JUNE, 1961

Akademiai Kiado (Publishing House of the Hungarian Academy of Sciences), Budapest, Hungary, 1962

This volume reprints the 26 papers presented at the conference (held by the Hungarian Academy of Sciences) which have already been published in *Acta Physica Hungarica*, v. 14, no. 2–3, 1962. The 27th paper is given in abstract only, as its full text has not yet been published. (*PA*, 1963, #13,194)

496. ZUR PHYSIK UND CHEMIE DER KRISTALLPHOSPHORE (PHYSICS AND CHEMISTRY OF CRYSTALLINE PHOSPHORS)

Ortmann, H., Witzmann, H., Editors
Akademie Verlag, Berlin, Germany, 1960

Thirty-five papers were presented at the session of the Physikalische Gesellschaft in der Deutschen Demokratischen Republik (Physical Society in the GDR), held at Greifswald, April 26–29, 1959. (*PA*, 1962, #4163)

497. TRANSACTIONS [IN PART] OF THE EIGHTH CONFERENCE ON LUMINESCENCE (MOLECULAR LUMINESCENCE AND LUMINESCENCE ANALYSIS)

Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,
v. 24, no. 5, pp. 488–630; no. 6, pp. 724–783, 1960
(Translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 5, pp. 495–630; no. 6, pp. 727–786, 1960)

This conference was held at Minsk on October 19–24, 1959. Some of the transactions are cited in the above literature; the remaining transactions on molecular luminescence are published in *Uspekhi Fizicheskikh Nauk* (translation available in *Soviet Physics—Uspekhi*) and in *Optika i Spektroskopiya* (translation available in *Optics and Spectroscopy*). The transactions concerned with luminescence analysis appear as "Metody Lyuminestsentnogo Analiza, Materialy VIII Soveshchaniya po Lyuminestsentsii," published by Akademiya Nauk Belorusskoi SSR, Institut Fiziki, 1960.

498. **TRANSACTIONS OF THE NINTH ALL-UNION CONFERENCE ON LUMINESCENCE (CRYSTAL PHOSPHORS)**
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,
v. 25, no. 1, pp. 2–50; no. 3, pp. 314–439; no. 4, pp. 442–584, 1961
(Translated from the Russian in _Bulletin of the Academy of Sciences of the USSR, Physical Series,_ v. 25, no. 1, pp. 3–50; no. 3, pp. 303–427; no. 4, pp. 435–561, 1961)

Papers presented at a conference held at Kiev, June 20–25, 1960 included those on the following topics: luminescence of semiconductor crystals with excitation in the discrete structure region of the absorption spectrum; role of impurities in the luminescence of molecular crystals at low temperatures; piezospectroscopic effect in anisotropic centers in cubic crystals; mechanism of energy storage by crystal phosphors; effect of isostructure on the spectra of activated mixed crystals. (*PA*, 1962, #12,614)

499. **ROLE OF IMPURITIES IN THE LUMINESCENCE OF MOLECULAR CRYSTALS AT LOW TEMPERATURES**
Shpak, M. T.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,
v. 25, no. 1, pp. 13–19, January 1961
(Paper presented at the Ninth Conference on Luminescence—Entry #498; translated from the Russian in _Bulletin of the Academy of Sciences of the USSR, Physical Series,_ v. 25, no. 1, pp. 13–19, January 1961)

A review is presented of work performed in the Institute of Physics of the Ukrainian SSR Academy of Sciences on the luminescence of a variety of organic molecules dissolved in single crystal matrices and measured at liquid nitrogen or liquid hydrogen temperatures. Simple polynuclear aromatic compounds, compounds with benzene groups linked by carbon atoms extraneous to the benzene rings, compounds with condensed benzene groups as well as derivatives and deuterated forms of some of these substances have all been studied. The results are discussed under the following headings: (1) General Characteristics of Molecular Crystal Spectra; (2) Nature of Impurity Centers; (3) Role of Defects; (4) Mirror Symmetry and Lattice Vibrations; (5) Polarization of the Absorption Bands; (6) Effect of Mutual Interactions of Impurities and (7) Nature of the Luminescence of Molecular Crystals. It is concluded that few of the observed effects can be explained in detail at the present time, mainly because of the inherent difficulty of the crystal field problem. However, the experimental results can be useful in the practical applications (organic scintillators, etc.). (*PA*, 1962, #14,742)

500. **TRANSACTIONS OF THE TENTH CONFERENCE ON LUMINESCENCE, DEDICATED TO THE MEMORY OF S. I. VAVILOV**
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,
v. 26, no. 1, pp. 2–113, January 1962; no. 4, pp. 435–538, April 1962
(Translated from the Russian in _Bulletin of the Academy of Sciences of the USSR, Physical Series,_ v. 26, no. 1, pp. 3–111, January 1962; no. 4, April 1962)

The conference was held in Moscow in June and July 1961. Among topics discussed were: life and work of S. I. Vavilov, Cherenkov radiation and its use in high-energy physics; luminescence of complex molecules; luminescence of gadolinium salts; uses of luminescence in biological research; and photoluminescence of halide salts of heavy metals and semiconductors. (*PA*, 1963, #8612)

501. **NINTH AMPERE COLLOQUIUM (PISA, 12–16 SEPTEMBER, 1960)**
Archives des Sciences, Geneva, v. 13, Special Number, 1960

At this conference a total of 124 papers was presented in the following groups: (1) dielectric relaxation, paramagnetic relaxation, radiofrequency and microwave molecular spectra; (2) paramagnetic resonance; and (3) nuclear and quadrupole magnetic resonance.

502. **EFFECTS OF THE ENVIRONMENT ON THE FLUORESCENCE OF AROMATIC COMPOUNDS IN SOLUTION**
Van Duuren, B. L.
Chemical Reviews, v. 63, no. 4, pp. 325–354, 1963

A review with 187 references is presented.

503. **LUMINESCENCE AND ITS APPLICATIONS**
Patrovsky, V.
Chemicke Listy, v. 56, pp. 795–803, 1962

A review with 47 references is given.

504. **SYMPOSIUM ON LUMINESCENCE, PRAGUE 1962**
Czechoslovak Journal of Physics, Section B, v. 13, no. 2, pp. 85–171, 1963

The symposium was organized under the auspices of the Institute of Solid State Physics of the Institute of Physics of the Czechoslovak Academy of Sciences and of the Union of Czechoslovak Mathematicians and Physicists. There were 65 participants from nine countries. Eighteen papers were presented. (*PA*, 1963, #10,977)

505. **HUNGARIAN CONFERENCE ON LUMINESCENCE**
Froelich, H. C.
October 31, 1961
Office of Naval Research, London, England
TR-ORNL-C-17-61

This report contains summaries of papers presented at this conference. The program encompassed three main areas of interest: zinc sulphide (crystals and powders) and electroluminescence; luminescence of organics; and lamp phosphors and miscellaneous subjects.

506. SPECIAL LECTURES PRESENTED AT THE INTERNATIONAL SYMPOSIUM ON MOLECULAR STRUCTURE AND SPECTROSCOPY, TOKYO, JAPAN, SEPTEMBER 10–15, 1962

***Pure and Applied Chemistry*, v. 7, no. 1, 1962**

The entire issue is devoted to the lectures.

507. FORMATION AND DISSOCIATION OF EXCITED DIMERS

Förster, T.
***Pure and Applied Chemistry*, v. 7, no. 1, pp. 73–78, 1962**
(Paper presented at the International Symposium on Molecular Structure and Spectroscopy, Tokyo, Japan, September 10–15, 1962)

A review is presented of fluorescence and fluorescence quenching in acridine orange; crystalline pyrene, both pure and containing perylene; pure liquid pyrene; pyrene in heptane, liquid paraffin, nonane, and hexadecane; pyrene derivatives such as 4-methyl-, 3-cyano-, and 3-bromopyrene in organic solvents; pyrene-sulphonates in aqueous solution; concentrated naphthalene solutions and crystalline naphthalene; naphthalene in toluene; derivatives of naphthalene such as 1-methyl- and 1,6-dimethylnaphthalene; 1,2-benzanthracene; phenanthrene; and 2,5-diphenyloxazole. Some explanation is presented of the variation in phenomena exhibited.

508. LUMINESCENCE OF ORGANIC AND INORGANIC SYSTEMS

Spruch, G. M., Brown, F. H.
***Physics Today*, v. 15, no. 3, pp. 24–27, March 1962**
(See also Entry #514)

This is the report of an international conference held at the University of New York from October 9–13, 1961 under the sponsorship of the Air Force Aeronautical Research Laboratory, the Army Research Office, the Office of Naval Research, and New York University. (*PA*, 1962, #10,613)

509. MOLECULAR ELECTRONIC ABSORPTION SPECTRA

Mason, S. F.
***Quarterly Reviews*, London, v. 15, pp. 287–371, 1961**

The sections of this long review article are: Introduction, Factors Determining the Absorption of Light, Selection Rules, Saturated Compounds, Olefins and Dienes, Triple-Bonded and Cumulative Systems, Carbonyl Compounds, Unsaturated Sulphur and Nitrogen Compounds, Aromatic Systems, Non-alternant Hydrocarbons, Heteroaromatic Systems, Carbanions and Carbonium Ions, Linear and Cyclic Conjugated Systems, Charge Transfer Spectra, Steric Effects, and Environmental Effects.

510. ENERGY TRANSFER IN NONAROMATIC CHEMICAL SYSTEMS

Allen, A. O.
***Radiation Research*, Supplement 2, pp. 471–479, 1960**
(Proceedings of Bioenergetics Symposium, Brookhaven National Laboratory, Upton, N.Y., October 12–16, 1959, sponsored by the U.S. Atomic Energy Commission)

In aliphatic compounds, which constitute the bulk of the organic matter present in living cells, the excited states lie at higher energies than in the aromatic and their lifetime is very short. These compounds absorb light only in the far ultraviolet and the excited state then formed is likely to undergo chemical decomposition very quickly. Whether or not time is available for energy to be transferred from one molecule to another before the breakup of the molecule occurs is questionable. This paper reviews such scanty information as is available.

511. FINAL DISCUSSION

Platt, J. R.
***Radiation Research*, Supplement 2, pp. 639–672, 1960**
(Proceedings of Bioenergetics Symposium, Brookhaven National Laboratory, Upton, N.Y., October 12–16, 1959, sponsored by the U.S. Atomic Energy Commission)

In addition to the introduction (The Straight and Narrow Borderline), and a table of questions, experiments, and tools for molecular biology, the following sections are included:

Is There Any Real Biological Evidence for Energy Migration?
- Genetic Inversion Experiment
- Quantum Yield Problem

Are Mutations Random?
- The Two-Hit Argument
- Heat Transfer ESR Experiment
- Energy Reflection at Broken Ends
- Crystalline Protein Action Spectrum
- Reality of Double-Layer Structures
- Ultrasonic Microscope
- X-ray Diffraction From Oriented Layers *In Vivo*
- Multi-layers *In Vitro*
- Reason for Long-Wavelength Low Quantum Yield in Photosynthesis

Are Triplet States Important in Biology?
- Criteria of Triplet States
- Reflection Spectra for Detecting Binding of Water
- Hydrogen-Bond Spectra in the Far-Infrared
- Experiments and Theory on Mechanisms of Bio- and Chemiluminescence
- Theory and Measurements on Purines and Pyrimidines
- Need for Homogeneity and Known Sequence in Experiments
- Nuclear Magnetic Resonance Measurements of Deuterated Proteins

Models of Energy-Transfer
- Supersensitizers

- Non-observability of Sensitizers and Acceptors; The Collective Model
- Discriminative Photosensitization by Dyes
- Phototaxis
- Electrotaxis
- Electric Field Detection
- Interaction Effects in Radiation Sensitivity
- Changes in Spectra of Colored Haptens When Bound

Discrimination Between Hydrogen-Bond and Charge-Transfer Complexes

Other New Tools
- Fluorescence and Carcinogenicity
- Low-Energy Excitation by Neutrons
- Vacuum-Ultraviolet Techniques
- Time-Resolution Phosphorescence
- Enhancement of Optical Rotation Using Absorbed Dyes
- Probes for Configurations in 10^{-9} Seconds

512. PROCEEDINGS OF THE UNIVERSITY OF NEW MEXICO CONFERENCE ON ORGANIC SCINTILLATION DETECTORS, AUGUST 15–17, 1960

Daub, G. H., Hayes, F. N., Sullivan, E., Editors
U.S. Atomic Energy Commission, Office of Technical Information, Oak Ridge, Tenn.
(Available as TID-7612, U.S. Dept. of Commerce, Office of Technical Services, Washington, D.C.)

Twenty-three papers are included which were presented at the Conference on Organic Scintillation Detectors. The topics treated range from measurements of organic phosphor properties to liquid and plastic scintillation detectors. (*NSA*, 1961, #29,402)

513. PROGRESS IN PLASTIC SCINTILLATORS

Basile, L. J.
In "Proceedings of the University of New Mexico Conference on Organic Scintillation Detectors. August 15–17, 1960," pp. 161–176
U.S. Atomic Energy Commission, Office of Technical Information, Oak Ridge, Tenn.
(Available in TID-7612, U.S. Dept. of Commerce, Office of Technical Services, Washington, D.C.)

A review of plastic scintillators is presented which treats preparation, luminescence properties, mechanism of energy transfer, and applications of these scintillators. (*NSA*, 1961, #29,411)

514. LUMINESCENCE OF ORGANIC AND INORGANIC MATERIALS

Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N.Y., 1962

Contained in this book are proceedings of an international conference (New York University, N. Y., 1961) sponsored by the Air Force Aeronautical Research Laboratory, U.S. Air Force; Army Research Office at Durham, N. C.; Office of Naval Research, U.S Navy; and New York University, N.Y.

515. GENERAL DISCUSSION OF ORGANIC SYSTEMS

In "Luminescence of Organic and Inorganic Materials," International Conference Proceedings, New York University, N.Y., 1961, pp. 282–301
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N.Y., 1962

Communications, triplet states, lifetimes, and energy transfer are discussed.

THEORY

516. NONRADIATIVE TRANSITIONS AND LUMINESCENCE OF MOLECULES. DERIVATIVES OF THE DIPHENYLMETHYL CATION AND OTHER TORSIONABLE AROMATIC SYSTEMS

Simon, Z.
***Academia Republicii Populare Romine, Studii şi Cercetări de Chimie*, v. 9, pp. 667–672, 1961**

The absence of the fluorescence in molecular ions of the type diphenylmethyl is noted in contrast with the fluorescence of diphenylamine, diphenyl polyenes, biphenyl, and diphenylmethyl. An approximate calculation of the energy variations of the states of the diphenylmethyl ion in relation to the torsion of the phenyl nuclei is used in an attempt to explain this absence. It is demonstrated that the difference in fluorescence behavior in these cases is due to the fact that in the diphenylmethyl cation the electron deficiency configurations of one of the phenyl nuclei are more stable than those deficiency configurations on the central CH group (in the absence of the interaction, the groups C_6H_5 and CH). This leads through torsion of the molecule to a degeneration between the fundamental state and the first excited state. Such degeneration does not occur in the other molecules, and so the fluorescence is permitted.

517. ON THE QUESTION OF THE SPHERE OF ACTION IN THEORIES RELATING TO CONCENTRATION DEPOLARIZATION OF FLUORESCENCE LIGHT

Szalay, L., Sarkány, B.
***Acta Physica et Chemica*, v. 8, no. 1–2, pp. 25–29, 1962**
(in German)

Jablonski gave the relation $R' = 1.327\ R_0$ for the radius R' of the sphere of action of the dye molecule during quenching by foreign additives, and R_0 the critical separation of the molecules defined by Förster. The theory of concentration depolarization leads to R (radius in this case) $= 1.367R_0$.

Previous measurements on Na fluorescein in aqueous glycerol gave $R = 70.8$Å, while absorption and emission spectra led to the value $R_0 = 51.66$Å, agreeing well with the second equation. Hence $R' = 68.55$Å from Jablonski's equation. The discrepancy between R and R' is considered to be greater than that arising from experimental error. (*PA*, 1963, #3808)

518. FLUORESCENCE, ABSORPTION AND TEMPERATURE RADIATION OF SOLUTIONS

Ketskeméty, I., Dombi, J., Horvai, R.
***Acta Physica Hungarica*, v. 14, no. 2–3, pp. 165–166, 1962**
(in English)
(Paper presented at the International Symposium on Luminescence—Entry #495)

A comparatively simple expression connecting the absorption spectrum and the emission energy spectrum of fluorescent solutions obtained by Stepanov was generalized using some new fairly evident conditions relating to the process of fluorescence. The new expression, which contains the fluorescence yield, also renders possible the calculation of the yield as a function of the exciting wavelength when the above-mentioned spectra have been determined. The generalized formula is well supported by the experimental data obtained on several dye solutions. (*PA*, 1963, #1695)

519. ENERGY TRANSPORT PHENOMENA IN THE CASE OF MOLECULAR FLUORESCENCE

Budó, A., Ketskeméty, I.
***Acta Physica Hungarica*, v. 14, no. 2–3, pp. 167–176, 1962**
(in German)
(Paper presented at the International Symposium on Luminescence—Entry #495)

Secondary fluorescence is examined with regard to its theoretical effect on direct measurements of emission spectrum, yield, decay time, and degree of polarization in a solution. Agreement with experiments on fluorescein is shown for yield and polarization. The case of sensitized fluorescence is considered, where two materials are in solution. Using results for a solution with one solute, the overall emission spectrum can be derived by a linear combination of the two component spectra, the coefficients in the combination being in agreement with previous theories of energy transfer. (*PA*, 1963, #3806)

520. THEORETICAL INVESTIGATIONS OF THE SPECTRA OF FLUORESCEIN

Hoffmann, T. A.
***Acta Physica Hungarica*, v. 14, no. 2–3, pp. 177–185, 1962**
(in English)
(Paper presented at the International Symposium on Luminescence—Entry #495)

The near ultraviolet, visible, and near infrared spectra of fluorescein were calculated theoretically by the LCAO-MO method of quantum chemistry. Conclusions were drawn regarding the interpretation of the observed spectra of adsorbed and solute fluorescein. (*PA*, 1963, #2647)

521. THEORY OF FLUORESCEIN-ACTIVATED $Al_2O_3 \times H_2O$ LAYER PHOSPHORS

Lendvay, E.
***Acta Physica Hungarica*, v. 14, no. 2–3, pp. 187–210, 1962**
(in English)
(Paper presented at the International Symposium on Luminescence—Entry #495)

The luminescent spectra of $Al_2O_3 \times H_2O$–fluorescein layer phosphors depend on the duration of the adsorption time and the chemical treatment of the oxide film. The change of the luminescent intensity and the shift of the maximum emissivity are connected with the rate of generation of adsorbing centers with respect to the alteration of the rate of adsorption. The measured luminescent band contains some elementary luminescent bands, which are characteristic for the luminescence of different kinds of adsorption centers. From analysis of the measured spectra, the quality of the surface and the adsorption can be concluded. (*PA*, 1963, #3036)

522. MAGNETIC AND DIELECTRIC PROPERTIES OF HIGHLY ORDERED MACROMOLECULAR STRUCTURES

Blyumenfeld, L. A., Benderskii, V. A.
***Akademiya Nauk SSSR, Doklady*, v. 133, no. 6, pp. 1451–1454, August 11, 1960**
(Translated from the Russian in *Soviet Physics—Doklady*, v. 5, no. 4, pp. 919–921, February 1961)

Past use of electromagnetic resonance and static susceptibility techniques has opened the study of the magnetic properties of nucleic acids, nucleoproteins, and certain classes of synthetic polymers with conjugated bonds. Observations in the latter case have been made only on the solid phase. The width and form of the resonance curves, their thermal behavior, and the attainment of permanent magnetization in very low fields in experiments on static magnetism, indicate that the investigated compounds do not appear to be of the ordinary paramagnetic type and that their magnetic properties are determined by collective spin interaction. The absence, however, of initial moments in conjunction with each and every experimental value precludes classifying these compounds as ferro- or antiferromagnetic.

It has previously been shown that the anomalous magnetic properties of biopolymers are closely connected with the conservation of native highly ordered structures, and that the anomalous magnetic properties of synthetic polymers are related to the normal packing of planes of conjugated structures (even of relatively low molecular weight) in the solid lattice. In this paper, these properties will be provisionally termed "pseudoferromagnetism" of highly ordered organic structures. Any adequate interpretation of the observed effects must explain the appearance of unpaired valence electrons in saturated organic structures of this type, and also provide a mechanism of collective spin interaction leading to the above stated properties. An attempt is made to formulate a qualitative basis for such a theory.

Besides the investigated anomalous dielectric properties, the indicated systems should possess unusual magnetic characteristics. Polarized structures represent essentially one-dimensional spin chains, since unpaired π-electrons on the surface of aromatic rings cannot influence exchange interactions in a perpendicular direction along the axes of the chains. The estimated value of J for 2 p_z-electrons with an interval of 3.4 Å is $J = +0.030$. This does not contradict experimental values for the migrating charge complex. Obviously, with increased chain length the number of interacting unpaired electrons increases, creating total-molecular orbits extending the entire length of the chain; this leads to some decrease in the energy of the system, or to an increase in the effective value of J in connection with estimates at one pair. Calculation shows that J_{eff} increases relatively slowly down to $N = 20$, and thereafter remains practically constant. One can assume that for sufficiently lengthy chains $J_{eff} > kT$ throughout the investigated temperature interval.

The presence of strong spin-orbital coupling in individual nitrogenous bases in conjunction with anisotropy of the internal electric field must lead to strong magnetic anisotropy, developing in great breadth, and to asymmetry of magnetic resonance lines, and, more specifically, to splitting of Zeeman planes in a zero magnetic field. Thus, under certain conditions affecting the value of the ionization potential, electron affinity, and exchange interaction, highly ordered and essentially linear organic structures (individual macromolecules, polymer "crystallites," crystalline monomers) must possess surprising electrical and magnetic properties. Evidently, cases can be realized where, with an increase in N, such chains will change over from a diamagnetic to a paramagnetic state, and thereupon to a pseudoferromagnetic state. The magnitude of the magnetic effect is due to the increase in the exterior electrical field.

It is possible that the biological specificity of nucleic acids and nucleoproteins is connected not as much with the sequence of nucleotides in the chain, as with the dimensions and reciprocal interaction of regions with electrical and magnetic anomalies. The clouds of unpaired electrons in these regions probably play a substantial role in the catalytic activity of these compounds.

523. INTERNAL CONVERSION FROM THE FLUORESCENCE TO THE PHOSPHORESCENCE LEVEL IN NAPHTHALENE DERIVATIVES

Ermolaev, V. L., Kotlyar, I. P., Svitashev, K. K.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,
v. 24, no. 5, pp. 492–495, 1960
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 24, no. 5, pp. 499–502, 1960)

Internal conversion of organic molecules from the fluorescent (singlet) to the phosphorescent (triplet) state is interpreted as a process of excitation energy transfer operating by the exchange-resonance mechanism. The probability for internal conversion in naphthalene derivatives increases greatly with halogen substitution. The change in the spin–orbit interaction in the singlet state, responsible for the increased conversion probability, is greater than the corresponding change in the spin–orbit interaction in the triplet state. The spin–orbit coupling is much greater in quinoline than in naphthalene, but decreases when the N atom of quinoline enters into a hydrogen bond. (*PA*, 1962, #14,746)

524. ON THE POSSIBLE ROLE OF TEMPERATURE QUENCHING IN SCINTILLATION OF ORGANIC SUBSTANCES

Rozman, I. M.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya
v. 24, no. 5, pp. 567–571, 1960
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 24, no. 5, pp. 573–577, 1960)

In order to explain the reduced scintillation efficiency for slow α-particles accompanied with fast β-particles, an attempt is made to correlate it with the temperature dependence of luminescent efficiency for the bulk materials. Localized temperature sources along the α-particle track are assumed with the instantaneous thermal energy/cm taken as ½ the specific energy loss/cm of the α-particle, giving rise to an initial gaussian temperature distribution with adjustable mean radius. The theory does not yet explain the experimental data. (*PA*, 1962, #14,739)

525. DIELECTRIC EFFECTS AND THE ELECTRONIC SPECTRA OF POLYATOMIC ORGANIC MOLECULES IN SOLUTIONS

Bakhshiev, N. G.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,
v. 24, no. 5, pp. 587–590, 1960
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 24, no. 5, pp. 593–596, 1960)

The purpose of the paper is to consider the universal interactions, methods of investigating them, and ways of isolating them from the total effect observed experimentally.

In accord with modern views, molecular interactions in solutions can be divided into two basic types: (1) universal interactions connected with the influence of the aggregate (collective) of the surrounding solvent molecules on the solute molecule, and (2) specific (individual) interactions between the solute molecule and one or more of the surrounding particles. This terminology is meaningful inasmuch as the indicated types of interaction are obviously not equivalent: systems can be imagined in which there are no specific interactions, whereas collective interactions obtain in all cases.

In this paper, the theory is advanced that a complete description of an actual system can be realized only by considering both the collective (macroscopic description) and the individual (microscopic description) effect of the molecules of the surrounding medium on the spectrum of the solute molecule. In actual systems specific interactions are always present to some degree. Therefore, the molecule of the dissolved substance, linked by specific interactions with a molecule of the solvent or an extraneous particle, must be regarded as a new center of absorption or emission subject, in turn, to the universal action of the aggregate of the surrounding particles, which are described by the internal field in the solution. In view of this, the first stage in elucidating the influence of the solvent must consist in investigating the general, universal effects and clarifying their contribution to the phenomenon as a whole. Taking into account this universal interaction is particularly important precisely from the standpoint of investigation of specific interactions, which always and inevitably are evinced against the "background" of the universal influence of the medium.

In view of the above, the question of the influence of molecular interactions on the spectra of solutions must be approached in the following manner. First, the influence of universal interactions on the spectrum of the absorption or emission centers must be taken into account, and after analyzing the spectrum of the centers, the nature and strength of the specific interactions must be judged. Then the divergence between experiment and the theory describing the universal influence of solvents will be a measure of the specific interactions.

526. PRESENT VIEWS REGARDING THE INFLUENCE OF THE SOLVENT ON THE SPECTRA OF COMPLEX ORGANIC MOLECULES (SUMMARY OF REPORT)

Zhmyreva, I. A., Zelinskii, V. V., Kolobkov, V. P.
Kochemirovskii, A. S., Rezuikova, I. I.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,
v. 24, no. 5, pp. 596–600, 1960
(Paper presented at the Eighth Conference on Luminescence
—Entry #497; translated from the Russian in *Bulletin of*
the Academy of Sciences of the USSR, Physical Series,
v. 24, no. 5, pp. 602–606, 1960)

The action of solvents on the electronic spectra of organic compounds is considered from three viewpoints. The effects of the macroscopic characteristics of the solvent on the dipole-dipole interactions are considered, and also the influence of microinteraction of the solvent and solute. A further mechanism is proposed for the differences in the variation of absorption and fluorescence spectra. This is based on a more detailed discussion of the energy levels involved in the optical transitions and the equilibrium separations of the various states. (*PA*, 1962, #15,595)

527. LUMINESCENCE OF SYSTEMS WITH HYDROGEN BONDS

Zadorozhnyi, B. A., Naboikin, Yu. V.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,
v. 24, no. 6, pp. 758–762, 1960
(Paper presented at the Eighth Conference on Luminescence
—Entry #497; translated from the Russian in *Bulletin of*
the Academy of Sciences of the USSR, Physical Series,
v. 24, no. 6, pp. 761–764, 1960)

Both theory and experiment have shown that the hydrogen bond is evinced in the luminescence of substances in a manner similar to its manifestation in absorption spectra. Further consideration of the question has led the authors to the following conclusions: (1) the formation of hydrogen bonds (intermolecular or intramolecular) leads to increase of the Stokes drift; (2) the hydrogen bonds may be ruptured incident to electronic transitions (absorption or emission); this leads to the appearance of fluorescence bands strongly displaced to the long-wavelength side; and (3) in many cases there may be present simultaneously two luminescence bands in the spectra of substances with hydrogen bonds. (*PA*, 1962, #14,703)

528. PRESENT STATE OF THE THEORY OF LUMINESCENCE OF COMPLEX MOLECULES

Stepanov, B. I.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,
v. 26, no. 1, pp. 32–41, January 1962
(Paper presented at the Tenth Conference on Luminescence
—Entry #500; translated from the Russian in *Bulletin of*
the Academy of Sciences of the USSR, Physical Series,
v. 26, no. 1, pp. 32–42, January 1962; published 1963)

The various approaches include (1) universal relationships obtained from thermodynamic considerations, (2) classical dipole theory, (3) the probability method for describing the redistribution of vibrational energy, (4) the method of moments for characterizing the spectra, (5) entropy considerations, (6) Fourier representation of vibronic bands, (7) quantum-mechanical theory of predissociation, and (8) the vector-parametric method for the consideration of anisotropy. The following aspects of luminescence theory are discussed: one-dimensional models; nonlinear luminescence; systems of four electronic levels; and luminescence quenching. (*PA*, 1963, #10,488)

529. CONTRIBUTION TO THE THEORY OF LUMINESCENCE QUENCHING BY EXTRANEOUS SUBSTANCES [COMMENTARY ON THE REPORT OF B. I. STEPANOV]

Samson, A. M.
Akademiya Nauk SSSR, Izvestia, Seriya Fizicheskaya,
v. 26, no. 1, pp. 41–42, January 1962
(Paper presented at the Tenth Conference on Luminescence
—Entry #500; translated from the Russian in *Bulletin of*
the Academy of Sciences of the USSR, Physical Series,
v. 26, no. 1, pp. 42–43, January 1962; published 1963)

In an attempt to generalize the theory of impurity quenching, an expression is obtained for the luminescence decay law which may be applied to either resonance or diffusion quenching. The concentration dependence of the relative luminescence yield and decay time is evaluated for typical parameter values. (*PA*, 1963, #9465)

530. ENERGY MIGRATION IN SOLUTIONS AND THE ASSOCIATION THEORY OF LUMINESCENCE QUENCHING

Levshin, V. L.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,
v. 26, no. 1, pp. 43–52, January 1962
(Paper presented at the Tenth Conference on Luminescence —Entry #500; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 26, no. 1, pp. 44–53, January 1962; published 1963)

Studies of concentration quenching of luminescence and of molecular aggregation (dimer formation) in dye solutions (rhodamine 3B, S, 6G, magdala red, etc.) are reviewed. It is concluded that in these systems the quenching reduces to two processes: (1) internal quenching, and (2) migration of energy from excited monomer molecules to the nonluminescent aggregates. The heat of dissociation of the aggregates is greater than 5 kcal/mole for rhodamines, magdala red and other dyes, consistent with hydrogen bonding, but the lower values obtained for fluorescein dyes and the porphyrins suggest that the aggregates are held together by van der Waals forces in these cases. (*PA*, 1963, #9466)

531. CONCENTRATION QUENCHING OF LUMINESCENCE

Levshin, V. L.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,
v. 27, no. 4, pp. 540–550, April 1963

Luminescence quenching by associated molecules in solution can be achieved by (1) nonactive direct absorption of energy by the associated molecules, (2) resonant energy transfer to the associated molecules, (3) diffusion of excited molecules plus resonance, and (4) energy migration through monomer molecules plus resonance. There are 10^5–10^7 quenching particles for one excited particle. The influence of energy migration in 4 can be obtained from the depolarization of luminescence, which, as shown by calculation, is practically complete after the first to third energy transfer. In H_2O, mechanisms 1 and 3 are predominant, and formulas are derived for quenching in thick and thin layers as a function of concentration. Comparison with experimental results is reported.

532. FLUORESCENCE OF VAPORS OF COMPLEX MOLECULES

Borisevich, N. A.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,
v. 27, no. 4, pp. 562–569, April 1963

The fluorescence yield γ is given by the formula $\gamma = (\bar{E}_d^* - \bar{E}^*)/(\bar{E}_d^* - \bar{E}_{fl}^*)$ (the ratio of the difference between energies of all molecules having nonradiative transitions from the excited state, $\bar{E}_d^*$, and all molecules having the excited state, $\bar{E}^*$, to the difference between $\bar{E}_d^*$ and the energy of molecules emitting fluorescence, $\bar{E}_{fl}^*$). Activation energy and the two differences are given for tetramethyldiamino-, 3-dimethylamino-6-amino-, 3-amino-, and 3,6-diaminophthalimide, 1-aminoanthraquinone, β-naphthylamine, perylene, and anthracene. The ratio $\gamma/\tau = f$ (probability of radiative transition) is tabulated for four of the compounds.

533. APPLICATION OF A UNIVERSAL RELATION TO STRUCTURED FLUORESCENCE AND ABSORPTION SPECTRA OF VAPORS OF AROMATIC MOLECULES

Gruzinskii, V. V.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,
v. 27, no. 4, pp. 580–583, April 1963

The formula $c_{\mathrm{vibr}} \Delta T = h(\nu_{\mathrm{exc}} - \nu_{\mathrm{el}})$, where c_{vibr} is the vibrational heat capacity and ΔT the difference between the temperature of molecular excitation, T^*, and the experimental temperature, T, is applied to determination of c_{vibr} for β-naphthylamine and perylene.

534. INTERPRETATION OF MOLECULAR ELECTRONIC SPECTRA

Kasha, M.
American Chemical Society, Washington, D.C.
Paper 136. Division of Physical Chemistry, presented at the 140th Meeting, ACS, Chicago, Ill., September 3–8, 1961

One of the fundamental classifications of molecular electronic spectra distinguishes between electronic absorption bands which arise from the promotion of π-electrons to available π-orbitals, and the promotion of lone-pair electrons of either bonding or nonbonding type to available π-orbitals.

The various orbital types involved in molecular electronic transitions can often be identified by use of chemical techniques such as protonation, or in many cases polarized light could be used to separate electronic transitions. Further experimental techniques are available.

However, among the most powerful methods for identifying electronic transitions are those using differential solvent effects on the absorption band analysis. A number of different phenomena are observed, such as blue shifts or high frequency displacements of bands for transitions involving lone-pair electrons, as contrasted with the normal dispersion red shift. In more subtle cases, differences in absorption spectra are too small to be definitive, but the emission spectra of the molecule often permit a clear resolution of bands.

The use of the diverse techniques available to the electronic spectroscopist today permits the study of molecules of considerable complexity, from simple ring compounds, such as pyridine and pyrimidine, to relatively complex molecules, such as chlorophyll, polynucleotides, and nucleic acids.

535. THE THEORY OF CARBON-13 SPLITTING IN ELECTRON SPIN RESONANCE SPECTRA

Fraenkel, G. K.
American Chemical Society, Washington, D. C.
Paper 139, Division of Physical Chemistry, presented at the 140th Meeting, ACS, Chicago, Ill., September 3–8, 1961

A quantitative theory of the isotropic C^{13} splitting in the electron spin resonance spectra of organic free radicals is presented and applied to a number of π-electron radicals. The splittings arise from sigma-pi (*sp*) interactions which polarize both the 1*s* and 2*s* electrons. The 1*s*-orbital spin polarization is shown to contribute a term of negative sign with a magnitude comparable to that from the 2*s* electrons.

For an sp_2 hybridized carbon atom that is bonded to three atoms, X_i ($i = 1, 2, 3$), the hyperfine constant a^C has the form

$$a^C = \left(S^C + \sum_{i=1}^{3} Q^C_{CX_i}\right)\rho^{\pi} + \sum_{i=1}^{3} Q^C_{X_iC}\rho_i^{\pi}$$

where ρ^{π} and ρ_i^{π} ($i = 1, 2, 3$) are the π-electron spin densities on atoms C and X_i, respectively. The contribution of the 1*s* electrons is determined by S^C and that of the 2*s* electrons by the Q's, where Q^A_{BC} is the sigma-pi parameter for the nucleus of atom A resulting from the interaction between the bond BC and the π-electron spin density on atom B. Calculations for a planar CHC_2 fragment model yield $S^C = -12.7$ gauss, $Q^C_{CH} = 19.5$ gauss, $Q^C_{CC'} = 14.4$ gauss, and $Q^C_{C'C} = -13.9$ gauss.

The theory predicts both the magnitude and sign of the hyperfine splittings and is readily applied to a variety of compounds. Comparisons with the available experimental data indicate excellent agreement. The theory shows that the calculated C^{13} interactions depend on the π-electron spin densities in a very sensitive way, and therefore measurements of C^{13} splittings provide a useful criterion of the validity of approximate molecular wave functions.

536. OPEN SHELL SELF-CONSISTENT FIELD MOLECULAR ORBITAL DESCRIPTIONS OF ORGANIC π-ELECTRON RADICALS

Snyder, L. C.
American Chemical Society, Washington, D. C.
Paper 126, Division of Physical Chemistry, presented at the 144th Meeting, ACS, Los Angeles, Calif., March 31–April 5, 1963

Spin-polarized open shell self-consistent field molecular orbital calculations have been made to describe a large number of organic π-electron radicals. The present calculations include the single annihilation techniques recently developed by Hall and Amos. Computed π-electron spin densities are related to empirical values derived from isotropic hyperfine structure in the electron spin resonance spectra of several radicals. A qualitatively good agreement between calculated and empirical spin densities is found when semi-empirical integral values, similar to those used by Pariser and Parr, are employed. It is found that "theoretical" integral values give less satisfactory predictions. The computations have been made for even alternant, odd alternant, and nonalternant hydrocarbon π-electron radicals.

537. HYPOCHROMISM AND OTHER SPECTRAL PROPERTIES OF HELICAL POLYNUCLEOTIDES

Rhodes, W.
***American Chemical Society, Journal of the,* v. 83, no. 17, pp. 3609–3617, September 5, 1961**

Exciton interaction in a double-stranded helical polymer, such as a homogeneous polynucleotide, leads to a splitting of each excited electronic energy level of the monomer into two exciton bands of energy levels. Consideration of the selection rules derived from zeroth-order functions shows that for double-stranded polynucleotides $\pi \rightarrow \pi^*$ transitions are allowed to, at most, one exciton level of each band, both polarized perpendicularly to the helix axis; whereas $n \rightarrow \pi^*$ transitions are allowed only to one level of the upper band, that being polarized parallel to the helix axis. Examination of the spectral properties of the four constituents of deoxyribonucleic acid (DNA) reveals that although exciton bands probably exist in regions of spectral overlap, there should be isolated energy levels lying below the main exciton bands. These levels may act as localized energy traps during excitation propagation through the helix. In order to treat the problem of hypochromism, it is necessary to use first-order functions. An equation (similar to one derived by Tinoco) is developed which takes into account the effect of exciton interaction and dispersion-force interaction on the oscillator strength of the helix. Application of this equation to a helical, double-stranded polyadenylic acid having the configuration of DNA indicates that perturbation resulting from dispersion-force interaction among the bases can account for the observed hypochromism.

538. ZWISCHENMOLEKULARE ENERGIEWANDERUNG UND KONZENTRATIONSDEPOLARISATION DER FLUORESZENZ (INTERMOLECULAR ENERGY TRANSFER AND CONCENTRATION DEPOLARIZATION OF FLUORESCENCE)

Kawski, A.
***Annalen der Physik,* v. 8, no. 1–2, pp. 116–119, June 14, 1961**

R_0, the critical molecular separation when the probability of emission is equal to the probability of transfer of excitation energy, has previously been calculated for fluorescein in glycerol and anthracene in perspex. The corresponding critical concentrations C_0 for these solutions are 2.4×10^{-3} and 1.2×10^{-2} mole/l. Former experimental data on concentration depolarization in these solutions are plotted for the above values of C_0 as relative fluorescence polarization against γ, where γ is the (concentration) $\times$ $(1/C_0)$ $\times$ (relative fluorescence yield)$^{1/2}$. The experimental results are shown to agree well with Förster's theory of concentration depolarization as modified by Ore. (*PA*, 1961, #15,888)

539. ÜBER DEN EINFLUSS DER SELBSTAUSLÖSCHUNG AUF DIE KONZENTRATIONSDEPOLARISATION DER PHOTOLUMINESZENZ BESTÄNDIGER LÖSUNGEN (THE INFLUENCE OF SELF-QUENCHING ON THE CONCENTRATION DEPOLARIZATION OF THE PHOTOLUMINESCENCE OF STABLE SOLUTIONS)

Bojarski, C.
***Annalen der Physik*, v. 8, no. 7–8, pp. 402–411,**
September 4, 1961

A formula is developed for the dependence of the polarization on dyestuff concentration, based on Jablonski's theory of concentration depolarization and also taking account of self-quenching effects. It is assumed that no chemical reactions occur. Data for fluorescein and rhodamine B in glycerol given by Feofilov and Sveshnikov are shown to disagree with Jablonski's formula but to be reasonably well represented by the new formula. The emission probabilities in these two solutions are calculated. They agree roughly with the same constants calculated from the work of several other authors. (*PA*, 1962, #55)

540. MOLECULAR VIBRATIONS IN THE EXCITON THEORY FOR MOLECULAR AGGREGATES. I. GENERAL THEORY

McRae, E. G.
***Australian Journal of Chemistry*, v. 14, no. 3, pp. 329–343,**
August 1961

A molecular aggregate is defined as an ordered array of identical molecules. This definition includes molecular crystals, dimers, and certain polymeric aggregates of dye molecules. The vibronic states of an electrically excited molecular aggregate are studied theoretically. The aggregate is treated as an array of non-rigid molecules in a rigid lattice. The simplest form of the excitron theory is assumed to be correct except with regard to intramolecular vibrations. The molecules in the aggregate are considered as harmonic oscillators with one vibrational degree of freedom, whose individual wave functions are Born–Oppenheimer separable. The molecules are assumed to interact by a purely electronic mechanism.

Born–Oppenheimer separable wave functions for the whole aggregate, here called *E-V* functions, are defined. It is shown that the interaction integrals between *E-V* functions may be expressed in terms of integrals which depend only on the properties of individual molecules. Explicit expressions are given for the latter integrals.

The resonance interactions between *E-V* functions are described. On this basis, the limiting conditions under which the *E-V* functions steadily approach exact vibronic state functions of the aggregate are specified.

The vibrational overlap integrals between *E-V* and electronic ground-state wave functions are studied. These integrals may be expressed as sums of products of vibrational overlap integrals for individual molecules. Explicit expressions for the latter integrals are obtained through an approximation to Hutchisson's theory.

541. MOLECULAR VIBRATIONS IN THE EXCITON THEORY FOR MOLECULAR AGGREGATES. II. DIMERIC SYSTEMS

McRae, E. G.
***Australian Journal of Chemistry*, v. 14, no. 3, pp. 344–353,**
August 1961

The theory of Part I of this series is developed in detail for dimeric systems. The simplest possible theory of the exciton states for a system of two non-rigid molecules is obtained through the use of perturbation theory. The theory makes possible the prediction of electronic band structures in absorption and fluorescence spectra as functions of the theoretical Davydov splitting for two rigid molecules.

Numerical calculations are made for a dimer of a typical dye, and the results are compared with the observed absorption spectrum of the 1,1′-diethyl-2,2′-pyridocyanine iodide dimer.

542. MOLECULAR VIBRATIONS IN THE EXCITON THEORY FOR MOLECULAR AGGREGATES. III. POLYMERIC SYSTEMS

McRae, E. G.
***Australian Journal of Chemistry*, v. 14, no. 3, pp. 354–371,**
August 1961

The theory of Part I of this series is developed for aggregates of many molecules. The low-energy exciton states are considered on the basis of perturbation theory. The conditions for applicability of perturbation theory based on *E-V* wave functions are examined. It is shown that perturbation theory is valid where the intermolecular interaction in the exciton state is strong and/or the vibronic progression in the monomer spectrum is short.

Expressions relating to the vibrational structure in electronic absorption and emission spectra and the vibrational inhibition of intermolecular interaction are derived. A formula connecting the polarization ratios in absorption and fluorescence is given. The formula is shown to be relatively free from uncertainties arising from the use of perturbation theory, and offers a new method of calculating the theoretical Davydov splitting for a system of rigid molecules from experimental data.

Numerical calculations are made for a linear aggregate, and the results are compared with the observed electronic spectra of the *N*,*N*′-diethyl-ψ-cyanine dye polymer.

It is shown that the rigid-lattice model is an adequate representation of the cyanine dye polymer, but not of the anthracene crystal.

543. MOLECULAR VIBRATIONS IN THE EXCITON THEORY FOR MOLECULAR AGGREGATES. IV. EXCITED STATES OF WEAKLY-COUPLED SYSTEMS

McRae, E. G.
***Australian Journal of Chemistry*, v. 16, no. 3, pp. 295–314, June 1963**

The theory of the vibronic states of an electronically excited molecular aggregate is developed for the case of weak intermolecular interaction. The resulting description is complementary to that derived for the case of strong intermolecular interaction in Parts I–III of this series.

The intermolecular interaction term in the Hamiltonian is treated as a small perturbation. A particular set of zeroth-order functions for the problem, here called *m-m* functions, is defined. The interaction integrals between *m-m* functions are studied and certain of the *m-m* functions are corrected to the first order of perturbation theory. A criterion for the validity of the perturbation treatment is given.

The effect of molecular vibrations in exciton theory is to inhibit intermolecular interaction. Expressions are obtained for the vibrational inhibition factors, and their properties are related to the molecular distortion in the vicinity of the electronically excited molecule.

All theoretical results are discussed in comparison with those of Parts I–III. The results of the two methods of treatment are combined to give a general description of the excited states of molecular aggregates. It is shown that an exciton together with the associated molecular distortion in polymeric aggregates may be regarded as a quasiparticle analogous to the polaron in a molecular crystal.

544. DIFFERENT POSSIBLE EXPLANATIONS OF ANOMALOUS MAGNETIC PROPERTIES OF MACROMOLECULAR COMPOUNDS

Blyumenfeld, L. A., Benderskii, V. A., Kalmanson, A. E.
***Biofizika*, v. 6, pp. 631–637, 1961**

A review with 22 references is presented.

545. ESTIMATION OF THE INFLUENCE OF FOREIGN ATOMS IN THE CORE OF CONJUGATED BONDS ON THE SPECTRUM AND THE CHARGE DISTRIBUTION IN THE MOLECULE

Woźnicki, W., Kwiatkowski, S.
***Bulletin de l'Académie Polonaise des Sciences, Série des Sciences, Mathématiques, Astronomiques et Physiques*, v. 9, no. 1, pp. 39–42, 1961**

FEMO calculations, taking into account the influence of foreign atoms in the core, were carried out for pyridine and pyrimidine. Theoretical estimates for the absorption bands and bond orders are given. (*PA*, 1961, #9936)

546. EXCITED STATES OF ACETYLENE

Woźnicki, W.
***Bulletin de l'Académie Polonaise des Sciences, Série des Sciences, Mathématiques, Astronomiques et Physiques*, v. 9, no. 4, pp. 273–279, 1961**

A 10-electron calculation using the ASMO method is reported. The 1*s* electrons on the carbon atoms are not included. The calculations are carried through assuming an *sp* carbon valence state and for states with increasing *p* character up to sp_2. It is found that the linear state (*sp* hybrids) forms the most stable ground state, while the most stable form for the first excited (electronic) state is that formed from carbon atoms in a pure sp_2 hybrid state. (*PA*, 1961, #14,062)

547. BIO-ORGANIC CHEMISTRY QUARTERLY REPORT, DECEMBER 1962 THROUGH FEBRUARY 1963

March 29, 1963
California, University of, Lawrence Radiation Lab., Berkeley
UCRL-10743, W-7405-eng-48

Among the topics considered are: (1) studies on the quantum-conversion process in photosynthesis using photo-induced electron spin resonance in solutions of organic electron donors and acceptors; and (2) a theoretical study of the fluorescence of oriented dye-macromolecule complexes using a planar dye molecule that can be bound with its plane either parallel or perpendicular to the polymer axis.

548. THE NEAR-ULTRAVIOLET SPECTRA OF SOME 9-ALKYLPHENANTHRENES

Anet, F. A. L., Bavin, P. M. G.
***Canadian Journal of Chemistry*, v. 41, no. 9, pp. 2160–2164, September 1963**

Hyperconjugation does not seem to explain the bathochromic shifts relative to phenanthrene of the α-band. The rotameric forms of the alkyl substituents influence the band envelope.

549. THE ELECTRONIC SPECTRA OF N-HETEROAROMATIC SYSTEMS. PART X. FIVE-MEMBERED RING SYSTEMS

Mason, S. F.
***Chemical Society, Journal of the*, London, v. 1963, pp. 3999–4002, August 1963**

(For others in series, see Entries #842–850.) The electronic absorption spectra of the aza derivatives of indolizine, indole, and 1-methyl-1-pyrindine are analyzed in terms of a common energy-level scheme, given by the Hückel theory for the indenyl anion, and first-order perturbation theory. It is concluded that π-electron delocalization is the more extensive in the azaindolizine series than in the azaindoles.

550. A SEMI-EMPIRICAL THEORY OF THE π-ELECTRONIC SPECTRA OF AROMATIC DERIVATIVES

Nishimoto, K., Fujishiro, R.
***Chemical Society of Japan, Bulletin of the,* v. 35, no. 6,**
pp. 905–910, June 1962

551. ELECTRONIC STRUCTURES AND SPECTRA OF NON-BENZENOID HYDROCARBONS: FULVENE, HEPTAFULVENE, FULVALENE, HEPTAFULVALENE AND SESQUIFULVALENE

Nakajima, T., Katagiri, S.
***Chemical Society of Japan, Bulletin of the,* v. 35, no. 6,**
pp. 910–916, June 1962

552. σ ELECTRONIC STRUCTURES AND SOME PHYSICOCHEMICAL PROPERTIES OF HALOGENATED-CONJUGATED HYDROCARBONS

Morokuma, K., Fukui, K., Yonezawa, T., Kato, H.
***Chemical Society of Japan, Bulletin of the,* v. 36, no. 1,**
pp. 47–53, January 1963

553. THE INTERPRETATION OF ABSORPTION SPECTRA OF CONDENSED POLYCYCLIC AROMATIC HYDROCARBONS BY USING A SIMPLE RESONANCE THEORY. I. THE RESONANCE STRUCTURE OF THE EXCITED STATE IN CORRELATION WITH PLATT'S THEORY

Handa, T.
***Chemical Society of Japan, Bulletin of the,* v. 36, no. 3,**
pp. 235–247, March 1963

554. THE ELECTRONIC SPECTRUM AND STRUCTURE OF THE *s*-TRIAMINOBENZENIUM ION

Mataga, N.
***Chemical Society of Japan, Bulletin of the,* v. 36, no. 3,**
pp. 357–358, March 1963

Theoretical calculations are reported on the electronic spectra of *s*-triaminobenzene and *s*-triaminobenzenium ion and on the stabilities of the protonation products of aminobenzenes, which give a basis for interpretation of the absorbed results. The calculated spectra are in satisfactory agreement with the observed values. Although the hyperconjugation was excluded in this calculation, it may be taken into account by some approximate method. Tables are presented of (1) calculated electronic spectra in comparison with the observed values and (2) localization energies of some aminobenzenes.

555. THE ELECTRONIC SPECTRA AND STRUCTURES OF *s*-TRIAMINOBENZENIUM AND SOME RELATED IONS

Mataga, N.
***Chemical Society of Japan, Bulletin of the,* v. 36, no. 9,**
pp. 1109–1118, September 1963

556. PHYSICAL PROPERTIES AND CHEMICAL REACTIVITY OF ALTERNANT HYDROCARBONS AND RELATED COMPOUNDS. II. STUDY OF THE DERIVATIVES OF BENZENOID HYDROCARBONS BY THE SIMPLE M.O.-L.C.A.O. METHOD

Zahradník, R., Koutecký, J.
Collection of Czechoslovak Chemical Communications,
v. 28, pp. 904–934, 1963

The energies of MO of 97 models of compounds derived from benzene, naphthalene, phenanthrene, anthracene, triphenylene, benz(*c*)phenanthrene, pyrene, chrysene, benz(*a*)-anthracene, naphthacene, picene, perylene, pentaphene, benz-(*a*)pyrene, dibenz(*a,c*)anthracene, dibenz(*a,h*)anthracene, dibenz(*a,j*)anthracene, pentacene, anthanthrene, dibenz(*a,h*) pyrene, and coronene by attaching one substituent were calculated. The group of compounds consisted of 44 members and included amino, hydroxy, chloro, and bromo derivatives. The values of the total π-electron energies, the highest occupied and lowest free MO, and the $N \rightarrow V_1$ energies are tabulated. Relations between various theoretical quantities were studied, and the importance of the value $\nu\,(\nu = \rho^2_{ij}/\delta_i)$ for the extraction of various theoretical indexes was stressed. Fairly close parallelism between theoretical $(\bar{\nu}_t)$ and experimental $(\bar{\nu}_e)$ excitation energies was found. Equations of the type $\bar{\nu}_e = a\,\bar{\nu}_t + b$ satisfy the dependence for L_b, L_a, and B_b bands in electronic spectra.

557. NOUVELLE INTERPRÉTATION DU SPECTRE D'ABSORPTION DU NAPHTALÈNE CRISTALLISÉ À BASSE TEMPÉRATURE (A NEW INTERPRETATION OF THE ABSORPTION SPECTRUM OF SOLID NAPHTHALENE AT LOW TEMPERATURES)

Ciais, A., Pesteil, P.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences,* v. 254, no. 5, pp. 849–851,**
January 29, 1962

Numerous very weak lines have been observed by earlier workers. The authors attribute them to the effect of the crystalline Stark field lifting the degeneracy of exciton states of the same quantum number. The frequencies of many of these lines are recorded together with their polarizations. (*PA*, 1962, #12,595)

558. CINÉTIQUE DE LA COMPOSANTE RAPIDE DE LA SCINTILLATION DANS UN MILIEU ORGANIQUE PUR. APPLICATION AU CAS DE L'ANTHRACÈNE (KINETICS OF THE FAST COMPONENT OF SCINTILLATION IN A PURE ORGANIC MEDIUM. APPLICATION TO THE CASE OF ANTHRACENE)

Blanc, D., Cambou, F., Gervais de Lafond, Y.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences,* v. 254, no. 18, pp. 3187–3189,**
April 30, 1962

A formula is presented for specific intensity of fluorescence. An application of the formula to anthracene is made, and the results are confirmed by experiment. An exponential decrease in fluorescence with the same time constant as that for electron excitation is noted.

559. ON THE DIFFUSION MODEL OF LOCALIZED EXCITON IN THE PHOTOSYNTHETIC SYSTEM

Takeyama, N.
***Experientia*, v. 18, no. 6, pp. 289–291, 1962**

In a system such as chlorophyll-*a*, in the photosynthetic apparatus there exists a short-range molecular order, but no long-range order as for example in a crystal. It is possible therefore to have localized excited states and consequently the transfer of energy by the movement of the excited state from one molecule to a neighboring one. From a consideration of the absorption and fluorescence bands, calculations are carried out of the diffusion constant, and the diffusion distance of a localized exciton in the chlorophyll-*a* system; in addition, the frequency of energy transfer is calculated. Figures are given showing the relation between (1) diffusion constant and (2) transfer frequency and chlorophyll concentration. For a system with chlorophyll concentration of 0.1 mole/l the transfer frequency is calculated to be 4.07×10^{11} sec^{-1}. An experimental value of 1×10^{11} sec^{-1} has been reported by Teale (Entry #815) from the measurement of the fluorescence dipolarization of chlorella. (PA, 1962, #16,633)

560. ELECTRONIC STATES OF LONG POLYENES WITH ALTERNATING BOND LENGTHS

Pople, J. A., Walmsley, S. H.
***Faraday Society, Transactions of the*, v. 58, no. 471, pt. 3, pp. 441–448, March 1962**

A description of the electronic states of long polyenes is given in which the basic functions correspond to the extreme case of localization of the π-electrons to double bonds in the chain. Two types of electronic excited states are found: (1) those at higher energies in which the excited electron and hole are dissociated, corresponding to conduction states; and (2) energy states falling below the conduction band in which the electron and hole are bound.

Calculations, using the semi-empirical LCAO molecular orbital theory of Pariser and Parr, are made for a case of weak and strong alternation. The lowest excited state predicted for the former agrees fairly well with the observed limit of the lowest absorption band as the chain length tends to infinity. An estimate of the effects of polarization on the states predicted by this model is made.

561. CONTRIBUTION TO THE EXCITON ABSORPTION BAND EDGE THEORY

Agranovich, V. M., Konobeev, Yu. V.
***Fizika Tverdogo Tela*, v. 3, no. 2, pp. 360–369, February 1961**
(Translated from the Russian in *Soviet Physics—Solid State*, v. 3, no. 2, pp. 260–268, August 1961)

The retarding interaction between electrons in a crystal leads to the creation of new elementary excitations, termed polaritons, in place of excitons and transverse photons. It is shown that this effect leads to the occurrence of long-wave absorprion which, for positive effective exciton mass and high oscillator powers, determines the form of the long-wave edge of the exciton absorption band. The benzene molecular parameters are used as an illustrative example.

562. EXCITON ABSORPTION IN MIXED MOLECULAR CRYSTALS

Broude, V. L., Rashba, E. I.
***Fizika Tverdogo Tela*, v. 3, no. 7, pp. 1941–1949, July 1961**
(Translated from the Russian in *Soviet Physics—Solid State*, v. 3, no. 7, pp. 1415–1420, January 1962)

A simplified theory was developed for the exciton absorption of light in mixed molecular crystals. A preliminary comparison was made between theory and experiment, showing that the main regularities observed in experiments are correctly described by the theory and are connected with the simultaneous excitation of molecules of different kinds.

563. THE ROLE OF DEFECTS IN EXCITON LUMINESCENCE OF MOLECULAR CRYSTALS

Konobeev, Yu. V.
***Fizika Tverdogo Tela*, v. 4, no. 12, pp. 3634–3639, December 1962**
(Translated from the Russian in *Soviet Physics—Solid State*, v. 4, no. 12, pp. 2658–2661, June 1963)

A calculation is made for the probability of an exciton being converted into light by a defect in the crystal structure without accompanying localization of the electron excitation energy at the defect. It is shown that this process actually occurs in a number of favorable cases and can compete with exciton capture by an impurity.

564. THE LOCALIZED CHARGE IN THE AVERAGE FIELDS OF ATOMS IN ORGANIC MOLECULES

Sparatore, E.
***Gazzetta Chimica Italiana*, v. 90, pp. 1348–1364, 1960**

Equations are developed which define the atomic charge q_r of an atom r as the integral to the region Vr (i.e., a sphere of the radius 0.6 A, as defined for this purpose) of the global electronic density. The effect on q_r of the σ-electrons localized on the various linking orbits of the molecule, and the displacement of these orbits, as well as the effects of the π-electrons, are expressed in equations. The integrals of partial superimposition or displacement for the $1s$, $2s$, $2p_x$, and $2p_z$ orbits of H, C, and N atoms (useful in calculating q_r) are tabulated.

565. RECHERCHES SUR LE STRUCTURE ÉLECTRONIQUE DU NAPHTALÈNE PAR LA MÉTHODE L.C.A.O. ANMÉLIORÉE (INVESTIGATION OF THE ELECTRONIC STRUCTURE OF NAPHTHALENE BY A MODIFIED L.C.A.O. METHOD)

Julg, A., Francois, P., Mourre, R.

***Journal de Chimie Physique et de Physicochimie Biologique*, v. 59, no. 4, pp. 363–366, April 1962**

The electronic structure of naphthalene was studied by a modified LCAO method. The calculations were performed for three different geometries. The resultant electronic charges, although always close to unity, showed significant variations. The determination of transition energies led to a new interpretation of the absorption spectrum. The calculated ionization potential is in good agreement with experiment. (*PA*, 1962, #22,992)

566. ÉTUDE THÉORIQUE DE LA POLARISATION DE FLUORESCENCE DES MACROMOLECULES PORTANT UN GROUPE EMETTEUR MOBILE AUTOUR D'UN AXE ROTATION (THEORETICAL STUDY OF THE POLARIZATION OF THE FLUORESCENCE OF MACROMOLECULES CARRYING A MOBILE EMITTER GROUP AROUND THE AXIS OF ROTATION)

Gotlib, Yu. Ya., Wahl, P.

***Journal de Chimie Physique et de Physicochimie Biologique*, v. 60, no. 7–8, pp. 849–856, July–August 1963**

A simple model can be used to explain the polarization of fluorescence of a solution of macromolecules carrying a fluorescent group fixed by covalent bonds; the fluorescent group is assumed mobile around a rotational axis linked to a spherical macromolecule. The calculation is directed first to the case in which the rotation is entirely free, then to that in which the rotation takes place by discontinuous jumps between determined positions. Finally, the theory is applied to experiments carried out on poly-*p*-aminostyrene.

567. PROCESSUS EXCITONIQUES DANS LES CRISTAUX MOLÉCULAIRES. I. EXCITON PERTURBEÉ PAR LES VIBRATIONS (EXCITON PROCESSES IN MOLECULAR CRYSTALS. I. VIBRATIONALLY PERTURBED EXCITONS)

Iguchi, K.

***Journal de Physique et le Radium*, v. 23, no. 7, pp. 433–445, July 1962**

The general theory of vibrationally perturbed excitons is developed, and the expression of the electric dipole transition moment by the inclusion of the vibrational interaction is obtained. It is shown that a non-radiative transition occurs from S_2^+ to S_1^- in naphthalene with a probability of about 10^{11} sec^{-1} at 300°K. The first terms of the multi-phonon transition are obtained by expanding the perturbed vibrational functions into series. The correction factor f for the energy transfer is computed. This explains the Davydov splitting of the spectrum of naphthalene. In naphthalene the radiation is absorbed to the S_2^+ free exciton state; then it degrades to the S_1^- perturbed exciton which plays the principal role in long-range transfer of energy. The energy is emitted spontaneously as fluorescence or may be captured by imperfections, or a part is transferred to the lowest triplet state where phosphorescence occurs. In anthracene and diphenyl the situation is simpler. (*PA*, 1962, #23,122)

568 COLOR AND CHEMICAL CONSTITUTION

Juster, N. J.

***Journal of Chemical Education*, v. 39, no. 11, pp. 596–601, November 1962**

A general discussion of light and its reception, and a history of work in the field of color and chemical constitution are followed by a section on the principles of color production. The following explanation is taken from that section.

Early spectrographic work led to the conclusion that when energy (heat, light, or other wave forms) is absorbed by matter the energy gain is directly proportional to the frequency. Thus, $E_2 - E_1 = h\nu$, where E_1 and E_2 are quantum energy levels (usually ground state and excited state, respectively), h = Planck's constant and ν is the frequency. The energy absorbed causes a quantum jump from E_1 to E_2 by electrons when the frequency of the impinging energy matches that described by Planck's equation for one or more "allowable" quantum jump(s), as determined by the nature of the substance involved; this frequency has been termed the "natural" or "resonant" frequency of the electron wave. The mechanism involved is simply an addition of electrical and magnetic vectors of the resonant light frequency with the molecular electron system. A widely supported thesis which is derived from wave mechanics pictures conjugated unsaturation in a molecule as consisting of a delocalized electron wave pattern arising from the overlap of parallel *p*-orbital electrons to form a single polarizable π-cloud (a molecular orbital). When the adjoining *p*-orbitals cannot be aligned in parallel fashion, such overlap does not occur and there can be no delocalization. In order to have the vector addition mentioned above, the impinging electromagnetic radiation must encounter electromagnetic vector forces in the molecule at the "natural" or "resonant" frequency. This occurs primarily when the molecule possesses a permanent dipole and/or a delocalized electron system that is polarizable by the interacting electromagnetic vectors.

Subsequently the excited state returns to the ground state and the energy is relatively rapidly reradiated as heat (via collisions with other molecules), fluorescence and/or phosphorescence. Thus, the frequencies that may be absorbed depend on the number and types of transitions possible for the molecule, including especially electron transitions. The electron delocalization leaves the system at a lower quantum energy level, so that quantum jumps to the close-lying more localized excited states involve a greater number of smaller energy transitions. Due to vibrational and rotational energies, the number of energy differences or quantum jumps (and hence frequencies) are increased by small amounts near the electronic state transitions. Because of the close spacing of the quantum level transitions there is also a fairly wide, but closely spaced, band of frequencies which can be absorbed. For gases and for liquids and solids at very low temperatures the frequencies may still be separated as individual absorption bands. At normal temperatures for liquids and solids the frequency bands merge and there results a region of continuous absorption. Thus, a substance will appear colored only if selective absorption occurs in the visible region of the spectrum: this is related to the resonant frequency of the molecular electron wave. At ordinary temperatures most of the molecules are at an essentially zero-point of vibrational energy and in their lowest electronic state. As energy is absorbed they go to a higher electronic state, but not necessarily to the zero-point of vibrational energy for this state. This excess vibrational energy is quickly lost in collisions. In ordinary nonfluorescent and nonphosphorescent substances, the transition to the lower electronic state is bridged by going from a low vibrational energy in the excited state to a high vibrational energy in the ground state (E_1). The result is a complete return without the emission of visible radiation (light is converted to kinetic energy at various stages).

When the energy level available in the ground state is very much lower than the zero vibrational energy level in the excited state, visible radiation (fluorescence) results. Because of the initial loss of vibrational energy before the transition involving radiation, the frequency of the emitted radiation is lower than that of the absorbed radiation and nearly independent of it. If the molecule in the ground state has a high vibrational energy when absorption occurs, the frequency of the emitted radiation may be higher than that of the absorbed radiation. In phosphorescence, the molecule in the excited state loses vibrational energy and reaches a semistable level from which a transition to a lower level does not occur readily. It ordinarily leaves this level by first absorbing energy from outside, usually from molecular collisions, then going to a slightly higher energy level, and finally emitting radiant energy to return to the ground state. The length of time it remains in the semistable level determines the time lag between absorption and emission. Examples of color-producing organics are cited.

569. ZERO-FIELD SPLITTING OF MOLECULAR ZEEMAN LEVELS

McWeeny, R.
***Journal of Chemical Physics*, v. 34, no. 2, pp. 399–401,**
February 1961

This paper deals with the general theory of electron spin–spin coupling by means of a "coupling anisotropy function" defined in terms of the two-electron density matrix, and involves approximations which lead from the general results to simple (orbital) approximations. The theory is applied to the phosphorescent triplet state of naphthalene; some correlation with experiment is noted.

In reply to J. H. van der Waals' subsequent comment that more rigorous treatment would be difficult because of singularities encountered, McWeeny considers the calculations again (ibid., no. 3, pp. 1065–1066, March 1961).

570. QUANTUM MECHANICS OF MOBILE ELECTRONS IN CONJUGATED BOND SYSTEMS. I. GENERAL ANALYSIS IN THE TIGHT-BINDING FORMULATION

Ruedenberg, K.
***Journal of Chemical Physics*, v. 34, no. 6, pp. 1861–1877,**
June 1961

The quantum-mechanical treatment is carried through for a set of electrons in a homonuclear conjugated bond system of arbitrary size, including electronic interaction and all overlap effects between neighbors. All framework contributions are obtained by explicit integration over the framework Hamiltonian, including the effect of nonconjugated neighbor atoms and differentiating between different types of conjugated atoms (joint, nonjoints, etc.). Expressions are given for the ground-state energy, ionization potential, electron affinity, electronegativity, and for the configuration interaction matrix for the calculation of excited states, assuming singly excited configurations. The results take simple forms permitting instructive interpretations. The partial additivity of one-electron binding-energy contributions, obtained as eigenvalues of topological molecular orbitals, and the approximate validity of the "neglect of differential overlap" are proved. (*PA*, 1961, #9940)

571. QUANTUM MECHANICS OF MOBILE ELECTRONS IN CONJUGATED BOND SYSTEMS. II. AUGMENTED TIGHT-BINDING FORMULATION

Ruedenberg, K.
***Journal of Chemical Physics*, v. 34, no. 6, pp. 1878–1883,**
June 1961

The analysis of homonuclear conjugated systems, which is given within the limits of the tight-binding approximation in Part I, is extended to include the interactions between nonneighbor atoms and the variation in the interactions between neighbor atoms. Both kinds of interactions are included as perturbation effects on the tight-binding approximation. As a consequence, the formalism developed for the latter is not being complicated and the interpretations remain unchanged. Application to benzene and naphthalene illustrates the approach. (*PA*, 1961, #9941)

572. QUANTUM MECHANICS OF MOBILE ELECTRONS IN CONJUGATED BOND SYSTEMS. III. TOPOLOGICAL MATRIX AS GENERATRIX OF BOND ORDERS

Ruedenberg, K.
***Journal of Chemical Physics*, v. 34, no. 6, pp. 1884–1891,**
June 1961

It is shown that in homonuclear conjugated systems the various bond orders and similar quantities can be written as matrix functions of the topological incidence matrix. This entails the existence of a number of useful general relations between these various quantities. The relations include as special cases: Coulson and Rushbrooke's theorem on charge orders in alternants; Hall's theorem on bond orders in alternants; McWeeny's theorem on the formal charges; Ham and Ruedenberg's correlation between Coulson and Mulliken bond orders for neighbors in alternants. The Ham–Ruedenberg–Platt relation between valence-bond bond orders and molecular orbital theory is closely related. A number of new relations between bond orders are derived and discussed. The generalization from alternants to nonalternants is given particular attention. (*PA*, 1961, #9942)

573. QUANTUM MECHANICS OF MOBILE ELECTRONS IN CONJUGATED BOND SYSTEMS.
IV. INTEGRAL FORMULAS

Ruedenberg, K.
***Journal of Chemical Physics*, v. 34, no. 6, pp. 1892–1896, June 1961**

Formulae are established for all carbon and hydrogen penetration integrals occurring in the tight-binding approximation of the theory of mobile electrons. The orbital exponents of the penetrated shielding orbitals may differ from the orbital exponent of the penetrating $2p\pi$-electrons. A simple correlation between kinetic energy integral and overlap integral is found. (*PA*, 1961, #9943)

574. QUANTUM MECHANICS OF MOBILE ELECTRONS IN CONJUGATED BOND SYSTEMS. V. EMPIRICAL DETERMINATION OF INTEGRALS BETWEEN CARBON ATOMIC ORBITALS FROM EXPERIMENTAL DATA ON BENZENE

Ruedenberg, K., Layton, E. M., Jr.
***Journal of Chemical Physics*, v. 34, no. 6, pp. 1897–1907, June 1961**

It is shown that the experimental information given in the ultraviolet spectrum of benzene uniquely determines the two-center coulomb integrals between the $2p\pi$ atomic orbitals of carbon as a function of the internuclear distance. The calculations are carried out including all terms involving neighbor overlap. For the many-center electron-interaction integrals, the Mulliken approximation and the London approximation are both considered with little difference in the results. Some peculiar properties of the empirically determined distance dependence are compared with the theoretical behavior of two-center coulomb integrals. The empirical values for the resonance integral and the coulomb integral are also found. The investigation differs from similar work of Pariser by the inclusion of overlap effects. (*PA*, 1961, #9944)

575. QUANTUM MECHANICS OF MOBILE ELECTRONS IN CONJUGATED BOND SYSTEMS.
VI. THEORETICAL EVALUATION OF ENERGY CONTRIBUTIONS

Ruedenberg, K.
***Journal of Chemical Physics*, v. 34, no. 6, pp. 1907–1913, June 1961**

The general formulae of Part I are used to analyze the energy contributions of the molecular framework of a π-electron system in detail, without use of additional assumptions. The valence-state potential of carbon, used in the framework potential, and the $2p\pi$ atomic orbitals are determined by a minimum principle. The coulomb integral and resonance integral are evaluated from their constituent integrals in the tight-binding approximation. The agreement with the empirical values is unsatisfactory for the coulomb integral but very good for the resonance integral The approximate proportionality between energy matrix elements and overlap integrals is proven for a variation of the internuclear distance between 1.26 and 1.54 A. (*PA*, 1961, #9945)

576. COHERENT STIMULATED EMISSION FROM ORGANIC MOLECULAR CRYSTALS

Brock, E. G., Csavinszky, P., Hormats, E., Nedderman, H. C., Stirpe, D., Unterleitner, F.
***Journal of Chemical Physics*, v. 35, no. 2, pp. 759–760, August 1961**

The properties of conjugated molecules strongly suggest several methods in which maser action may be obtained. At microwave frequencies, the population of the Zeeman levels of the first triplet state may be used, and this maser action would occur only when optical excitation was applied. Stimulated emission at optical wavelengths is proposed using radiative transitions from metastable triplet states. Factors affecting the feasibility of these experiments are discussed. (*PA*, 1961, #12,489)

577. PARAMAGNETIC EXCITONS IN MOLECULAR CRYSTALS

Sternlicht, H., McConnell, H. M
***Journal of Chemical Physics*, v. 35, no. 5, pp. 1793–1800, November 1961**

The possibility of using ESR to study paramagnetic excited electronic states of aromatic crystals is explored. Two limiting cases are considered: on the one hand the excitation energy moves from molecule to molecule by a diffusion process; on the other the triplet excitation is described by a Frenkel exciton. In either case intermolecular propagation of the triplet excitation is assumed to proceed through virtual triplet ionization states. The theory of the spin resonance of triplet excitons is developed in some detail. It is shown that there is only a weak dependence of the spectra on the **k** vector of the exciton wave, except when **k** is near regions or band degeneracies. Band degeneracies arise from time-reversal symmetry in benzene, naphthalene, and coronene crystals and occur on boundary planes of the first Brillouin zone. A spin Hamiltonian is calculated for these three aromatic crystals for most k vectors which are far removed from regions of band degeneracy. Two-line spectra (with no hyperfine structure), representing an average over the molecular sites in the unit cell, are obtained. Scattering of the exciton wave by lattice vibrations can cause line broadening and also can serve as a mechanism for spin lattice relaxation.

578. STRUCTURAL REQUIREMENTS OF ORGANIC LIQUID SCINTILLATORS

Heller, A.
***Journal of Chemical Physics*, v. 35, no 6, pp. 1980–1986,**
December 1961

A theory is proposed to explain the relationship between the structure and the scintillation efficiency of organic liquid scintillators. The requirements for good scintillation properties in given solvent–solute systems are found to be (1) the existence of pairs of energy levels in the solute which are identical with those involved in the excitation of the solvent, and (2) a nonrigid structure in the solute, capable of undergoing conformational changes in the excited state. It was found that the behavior of liquid scintillators satisfied these requirements. Good scintillation properties were predicted for some hitherto unknown scintillators. (*PA*, 1962, #1157)

579. DYNAMIC ASPECTS OF BOND ALTERNATION IN CYCLIC POLYENES

Gouterman, M., Wagnière, G.
***Journal of Chemical Physics*, v. 36, no. 5, pp. 1188–1196,**
March 1, 1962

The theoretical shapes of the potential curves for bond alternation in ground and excited states in cyclic polyenes are given. It is shown that the current MO model tends to give a rather small barrier to tunneling between the two alternating nuclear configurations, and that the barrier disappears in the excited states. If the potential curves do differ between ground and excited states, peculiar progressions should appear in the spectrum. An analysis is presented of the low-temperature spectrum of $C_{18}H_{12}$ that shows no such effect. It is suggested that the success that bond alternation has had in interpreting various phenomena is due to the fact that it makes the electrons less free than current models would, but that this effect may stem from other subtler causes. (*PA*, 1962, #8121)

580. EXCITATION OF MOLECULAR VIBRATION BY SLOW-ELECTRON IMPACT

Chen, J. C. Y., Magee, J. L.
***Journal of Chemical Physics*, v. 36, no. 6, pp. 1407–1411,**
March 15, 1962

A mechanism for excitation of molecular vibration by slow electron impact involving negative-ion states as intermediates is proposed and discussed. It is believed that this mechanism is the most important energy loss mechanism for slow electrons for energy regions in which it occurs. Calculation of the vibrational excitation cross section using the proposed mechanism has been carried out for hydrogen molecules, and the result is compared with the experimental observations. The estimated cross section is in the order of 1 $Å^2$.

581. PARAMAGNETIC EXCITONS IN SOLID FREE RADICALS

McConnell, H. M., Lynden-Bell, R.
***Journal of Chemical Physics*, v. 36, no. 9, pp. 2393–2397,**
May 1, 1962

It is suggested that the low-temperature paramagnetism of many aromatic free-radical solids may be due to triplet excitons, and that the formation of these exciton states rather than other low-temperature magnetic states is due to low-temperature crystal lattice structures that favor a single pairing of electrons on neighboring molecules. As an example, it is shown that the paramagnetic resonance spectra of certain TCNQ charge-transfer complexes observed by Chestnut and Phillips may be interpreted in terms of triplet excitons.

582. COMPARISON OF LOCALIZED AND DELOCALIZED MODELS FOR $n \rightarrow \pi^*$ TRANSITIONS: A POSSIBLE INTERPRETATION OF THE OBSERVED *SYM*-TETRAZINE FLUORESCENCE

El-Bayoumi, M. A., Kearns, D. R.
***Journal of Chemical Physics*, v. 36, no. 9, pp. 2516–2517,**
May 1, 1962

Different theories of $n \rightarrow \pi^*$ transitions in monocyclic azines have been examined in detail in order to explain recent experimental results; in particular, the observed fluorescence from the lowest n,π^* singlet state of *sym*-tetrazine. Two essentially different theoretical models for $n \rightarrow \pi^*$ transitions have been suggested. In the "delocalized model" which has been used by Mason and by Goodman and Harrell, an electron is promoted from a nonbonding MO (formed by taking the proper linear combination of the nitrogen nonbonding AOs) to the lowest unfilled π^* MO. El-Sayed and Robinson suggested an independent systems model, i.e., a "localized model," in order to explain certain features of the spectra of diazines trapped in rare-gas matrices at liquid-helium temperatures (4.2°K). In this model $n \rightarrow \pi^*$ transitions are assumed to be highly localized due to the coulomb attraction of the excited electron and the hole it leaves behind, and involve excitation of a nitrogen nonbonding electron to a p-orbital localized on the same nitrogen atom. In the diazines two orbitally degenerate singlet n,π^* states result. The degeneracy is removed by taking into account electron–electron interaction, and this gives rise to two nondegenerate n,π^* singlet states.

The semiempirical theory for $n \rightarrow \pi^*$ transitions of monocyclic azines presented in this paper seems to account for most experimental observations much more satisfactorily. The treatment may be summarized as follows:

(1) The form and energy of the lowest unfilled MO may be determined from the benzene orbitals by the use of a perturbation scheme suggested by Coulson and Longuet-Higgins.

(2) The singlet–triplet splittings of n,π^* states will vary according to the coefficients of the π^*-p AO on the nitrogen atoms for different azines.

(3) The treatment starts with a zero-order approximation in which each $n \rightarrow \pi^*$ transition involves the lone-pair electrons of a single nitrogen atom. Depending on the number of nitrogen atoms in the azine there are degenerate n,π^* states for each multiplicity. By applying first-order configuration interaction the orbital degeneracy is removed. The splitting of the orbitally degenerate states increases with a decrease in the N–N distance and is larger for the singlet states than for the corresponding triplet states.

This treatment accounts for the variation of the center of gravity of the singlet components and correctly predicts the selection rules. For pyrazine the low-energy component is predicted to be forbidden, in agreement with the predictions and observations of El-Sayed and Robinson. For the other azines which have been studied (e.g., pyridazine and sym-tetrazine) the low-energy component is predicted to be allowed, corresponding to what is observed. An explanation is offered for the n,π^* fluorescence of *sym*-tetrazine which has been observed, although it is not usual for fluorescence to occur if a triplet n,π^* state is the lowest excited state. By this theory the lowest singlet n,π^* state is predicted to be slightly lower in energy than the lowest triplet state of *sym*-tetrazine, and the only radiative path is fluorescence since no competing intersystem crossing exists.

583. VIBRATIONAL STRUCTURE OF MOLECULAR EXCITON STATES

Merrifield, R. E.
***Journal of Chemical Physics*, v. 36, no. 9, pp. 2519–2520,**
May 1, 1962

The Born–Oppenheimer separation of nuclear and electronic motion is not valid for molecular exciton states; however, if the Born–Oppenheimer approximation is valid for the individual molecules, such a separation can be obtained, and an effective Hamiltonian derived for the nuclear motion. (*PA*, 1962, #16,635)

584. ORGANIC LIQUID SCINTILLATORS. III. ON THE QUANTUM YIELD OF FLUORESCENCE AND THE QUENCHING OF FLUORESCENCE BY OXYGEN

Heller, A.
***Journal of Chemical Physics*, v. 36, no. 11, pp. 2858–2861,**
June 1. 1962

Expressions for the quantum yield of fluorescence of aromatic hydrocarbons in benzene and alkylbenzenes are derived assuming zero internal quenching. These expressions indicate that the molecular quantum yield of fluorescence increases with (1) the lifetime of the first excited singlet state of the solvent, (2) the transition probabilities from the levels of the solute that correspond to the levels involved in the excitation of the solvent, and (3) the increase in the degree of degeneracy in the solute levels corresponding to those involved in the excitation of the solvent. Minimum values of the molecular quantum yield of fluorescence of a group of aromatic hydrocarbons are computed at different concentrations of the solutes. The compounds with the highest values are *p*-divinylanthracene, perylene, *p*-quaterphenyl and *p*-terphenyl. The dimensions of the excited aggregates that are formed by the exchange interaction between the molecules in liquid or plastic scintillators are estimated from Basile's data for solutions of PBD in polyvinyltoluene. The number of monomer units per aggregate is about 1.2×10^3 and the radius of interaction about 18 A. The quenching of fluorescence by oxygen is explained by the existence of π-electron level pairs of almost similar energy difference in the solvent and the solvent–oxygen complex (Tsubomura and Mulliken, 1960), and by the short lifetime of the complex compared with that of the solvent. The latter results from the lower order of symmetry of the complex in comparison with that of the π-electron system in benzene. (*PA*, 1962, #13,347)

585. RELATIONSHIP BETWEEN ABSORPTION INTENSITY AND FLUORESCENCE LIFETIME OF MOLECULES

Strickler, S. J., Berg, R. A.
***Journal of Chemical Physics*, v. 37, no. 4, pp. 814–822,**
August 15, 1962

The equations usually given relating fluorescence lifetime to absorption intensity are strictly applicable only to atomic systems, whose transitions are sharp lines. This paper gives the derivation of a modified formula

$$1/\tau_0 = 2.880 \times 10^{-9}\, n^2 < \tilde{\nu}_f^{-3} > A\nu^{-1}\, (g_l/g_u) \int \epsilon d \ln \tilde{\nu},$$

which should be valid for broad molecular bands when the transition is strongly allowed. Lifetimes calculated by this formula are compared with measured lifetimes for a number of organic molecules in solution. In most cases the values agree within experimental error, indicating that the formula is valid for such systems. The limitations of the formula and the results expected for weak or forbidden transitions are also discussed. (*PA*, 1962, #20,782)

586. STUDY OF THE ELECTRON DENSITY DISTRIBUTION IN THE SIMPLER HYDROCARBONS

Roux, M., Cornille, M., Burnelle, L.
***Journal of Chemical Physics*, v. 37, no. 5, pp. 933–936,**
September 1, 1962

The electronic charge distribution is calculated in the molecules of acetylene and ethylene by making use of a function which characterizes the effect of bond formation on the electronic density. In agreement with earlier results on methane, the effect is found to consist in a charge removal from the vicinity of the nuclei and a buildup of electron density in the regions of the bonds. In acetylene the calculation of the charge drifts subsequent to the bonding indicates that these are fairly small, as had been found earlier in simpler molecules. It is also observed that the electrons associated with the C–C bond tend to accumulate, in ethylene, above and below the molecular plane, and in acetylene, at some distance from the C–C axis. This point is in favor of the Pauling picture of bent multiple bonds. (*PA*, 1962, #20,849)

587. ANGULAR DISTRIBUTION OF INTENSITY AND POLARIZATION IN THE TRIPLET-SINGLET EMISSION OF BENZENE

Hameka, H. F.

***Journal of Chemical Physics*, v. 37, no. 5, pp. 1085–1087, September 1, 1962**

The angular distribution of intensity and polarization in the triplet-singlet emission of benzene is calculated for the following mechanisms: (1) a magnetic quadrupole transition caused by the interaction between the electron spins and the radiation field; (2a) an electric dipole transition where the wave functions are first corrected for spin orbit coupling and then for vibronic interactions; (2b) an electric dipole transition where the triplet functions are first corrected for vibronic interactions and then for spin orbit coupling. (*PA*, 1962, #20,843)

588. EFFECT OF WEAK COUPLING ON THE ABSORPTION SPECTRUM OF AN AGGREGATE OF CHROMOPHORES

DeVoe, H.

***Journal of Chemical Physics*, v. 37, no. 7, pp. 1534–1540, October 1, 1962**

A theory is developed for the absorption spectrum of chromophores in a molecular aggregate with weak coupling in which they interact through their vibronic transition moments while vibrating independently. The change upon aggregation of the oscillator strength of a vibronic line, due to interaction with other vibronic lines of the same electronic band or other bands, is treated by first-order perturbation theory. Equations are derived which relate the aggregate extinction coefficient of a band, as a function of wave number, to the monomer chromophore spectra and certain factors for the interaction of electronic transition moments in the aggregate. The interaction of degenerate electronic transition moments can be evaluated from the experimental monomer and aggregate spectra, and used in cases of simple aggregate geometry to determine whether weak coupling applies to the aggregate. The effects of weak coupling upon the shapes and oscillator strengths of bands are illustrated by an example which shows that weak coupling of two overlapping bands in the spectrum of a planar dye molecule may explain the hypsochromic shift of the wave number of maximum absorption observed upon aggregation of the dye. (*PA*, 1962, #22,985)

589. PROPOSED EFFECT OF HIGH PRESSURES ON THE RADIATIONLESS PROCESSES

El-Sayed, M. A.

***Journal of Chemical Physics*, v. 37, no. 7, pp. 1568–1569, October 1, 1962**

Gregg and Drickamer found that for two organic compounds, for increasing pressures, the phosphorescence lifetime decreases and the fluorescence and absorption bands show a red shift. These authors' explanation is criticized and an alternative explanation proposed: namely, the decreased lifetime of the excited triplet state (T_1) is due to an increase of the rate constant of the $T_1 \rightarrow S_0$ radiationless process, probably caused by an increase in vibrational overlap. (*PA*, 1963, #3059)

590. SYMMETRY OF HELICAL POLYMERS. ELECTRONIC STATES OF DOUBLE-STRANDED POLYNUCLEOTIDES

Rhodes, W.

***Journal of Chemical Physics*, v. 37, no. 10, pp. 2433–2439, November 15, 1962**

The symmetry properties of a model double-stranded polynucleotide, containing only one type of monomer unit, are investigated by the application of the theory of space groups. The rotational parts of the symmetry operations of such a helix form a group which is isomorphic to the point group D_{∞}, indicating that there is sufficiently high symmetry to make formal treatment by group theory profitable for applications to the molecular dynamics of related helical polymers. A method of developing the irreducible representations of the space group is discussed, and some features of the irreducible representations so obtained are described. Electronic spectral properties related specifically to π,π^* and n,π^* states are then discussed within the framework of the group theoretical results, particular emphasis being placed on the nature of the exciton bands produced by excitation resonance interaction among the monomer units, selection rules restricting the mixing of states, selection rules for electric-dipole transitions between the ground state and states of the various exciton bands, and the expected effects of state mixing on the electronic spectral intensities of transitions to π,π^* and n,π^* exciton bands. (*PA*, 1963, #2682)

591. VIBRONIC-SPIN-ORBIT PERTURBATIONS AND THE ASSIGNMENT OF THE LOWEST TRIPLET STATE OF BENZENE

Albrecht, A. C.

***Journal of Chemical Physics*, v. 38, no. 2, pp. 354–365, January 15, 1963**

Second-order perturbation theory in electron configuration and spin space using both vibronic and spin-orbit perturbations reveals a number of routes for bringing dipole allowed character into a spin-forbidden transition. Apart from direct spin-orbit interaction, there are three additional mechanisms: (1) direct spin-vibronic coupling (a very weak, though first-order term), (2) spin-orbit coupling with vibronic coupling in the singlet manifold, and (3) vibronic coupling in the triplet manifold with spin-orbit coupling. In the case of benzene, vibrational analysis alone of the phosphorescence spectrum can neither discern the route for bringing allowed singlet character into the triplet state nor can it lead to an assignment of that state. It happens that polarized luminescence data are able to show that route 3 is dominant, and, given this, vibrational analysis leads to a ${}^3B_{1u}$ assignment. The vibronic characteristics of the various routes are discussed. Estimates are made of the relative importance of the various routes based on energy considerations within the framework of second-order perturbation theory. Approximate oscillator strengths are obtained and compared with the experimental value showing, independently, that route 3 is dominant and that the assignment must be ${}^3B_{1u}$. Other possible examples where mixed vibronic-spin-orbit terms are important to phosphorescence are mentioned suggesting the fruitfulness of detailed polarized phosphorescence experiments, both to aid in assigning excited states and to test vibronic theories. (*PA*, 1963, #8289)

592. EXCITON IMPURITY LEVELS IN MOLECULAR CRYSTALS

Merrifield, R. E.
***Journal of Chemical Physics*, v. 38, no. 4, pp. 920–924,**
February 15, 1963

Impurity levels for excitons in molecular crystals are discussed in terms of the wave functions and energy levels of a crystal containing a single substitutional impurity molecule. The problem is formulated in general terms and found to be solvable in the special case in which the transition dipole moment of the impurity molecule is parallel to those of the host molecules. A simple criterion for the existence of localized bound states is derived, from which it is concluded that such states should be of widespread occurrence. In particular, it is found that bound states can arise even where the impurity molecule has a higher excitation energy than the molecules of the host crystal if its transition moment is sufficiently large. Bound states can also arise where the "impurity" is a host molecule at a site of localized strain. The specific case of a one-dimensional crystal with nearest-neighbor interactions is treated in some detail as a numerical example.

593. PHOTON-INDUCED ELECTRONIC TRANSITIONS IN MOLECULAR CRYSTALS

Sage, M. L.
***Journal of Chemical Physics*, v. 38, no. 5, pp. 1083–1085,**
March 1, 1963

The electric dipole transition matrix element of a molecular crystal in the presence of an electric field is calculated. It is found to be proportional to the matrix element of the zero-field Hamiltonian between nearest neighbors and inversely proportional to the electric field strength for the limit of strong fields.

594. ELECTRONIC EXCITATION TRANSFER AND RELAXATION

Robinson, G. W., Frosch, R. P.
***Journal of Chemical Physics*, v. 38, no. 5, pp. 1187–1203,**
March 1, 1963

One purpose of this paper is to point out that so-called intermolecular resonance transfer, intermolecular nonresonance transfer, and intramolecular electronic relaxation in solid media are simply all special cases of radiationless transitions between nonstationary states of the entire system of molecules plus environment. Intermolecular resonance transfer is also a special case of the pure crystal exciton problem. The theoretical results from a previous paper are applied to radiationless transitions in π-electron systems, and the importance of the Franck–Condon factors is emphasized. One role which the vibrational factors play in these processes is illustrated by the large isotope effects which can arise when the radiationless transition converts a large amount of electronic energy into vibrational energy of the system. Quantitative calculations are made of the radiationless transition probability for ${}^1B_{2u}\rightarrow{}^3E_{1u}$ $(S_1\rightarrow T_2)$ and ${}^1B_{2u}\rightarrow{}^3B_{1u}(S_1\rightarrow T_1)$ "intersystem crossing" in C_6H_6. It is further shown that the ${}^3B_{1u}\rightarrow{}^1A_{1g}(T_1\rightarrow S_0)$ and ${}^1B_{2u}\rightarrow{}^1A_{1g}(S_1\rightarrow S_0)$ processes and other similar processes are slow because of the small vibrational factors which accompany the large energy gap between initial and final electronic states. Calculations cannot rule out the relative importance of the $S_1\rightarrow S_0$ radiationless transition compared with fluorescence and singlet–triplet nonradiative processes. An empirical method by which the Franck–Condon factors may be ascertained from the electronic-energy gaps in π-electron molecules is presented, and the results are used to estimate radiationless transition probabilities for a number of systems. The enhancement of multiplicity forbidden radiationless transitions by a heavy-atom environment is treated, and, in the case where the environment is a solid rare gas, a third-order mechanism accounts for the observed effect. Temperature effects and other kinds of environmental effects upon nonradiative transitions are also dealt with. It is shown that the use of high-energy excitation may increase, but never decrease, Q_P/Q_F, the relative quantum yields of phosphorescence to fluorescence. Radiationless transitions for the interesting case of azulene and the enhancement by a heavy-atom environment of the triplet–triplet emission spectrum of this molecule are discussed. Many needed experiments are suggested.

595. VIBRATIONAL EFFECTS IN MOLECULAR EXCITON MOTION ALONG A POLYMER

Goad, W.
***Journal of Chemical Physics*, v. 38, no. 5, pp. 1245–1250,**
March 1, 1963

Two aspects of the effects of molecular vibrations on exciton motion are considered: First is the reversible evolution of an electronically excited state of a system of molecules, in each of which many vibrational excitations are possible upon electronic excitation. Vibrational structure of the ground state is ignored. The reversible, or coherent, propagation is found to depend on the parameter $2\pi v^2\delta^{-1}$, where v^2 is the intermolecular coupling energy of individual vibronic levels, and δ is the spacing of vibrational levels. Second is the irreversible effect of vibrational relaxation in individual molecules through interaction with the solvent. The result of a heuristic treatment is that simple diffusive motion occurs if the relaxation time is much smaller than $2\pi h\delta^{-1}$; the diffusion coefficient is calculated. Throughout, an infinite, linear array of molecules is dealt with.

596. TRIPLET-TRIPLET ANNIHILATION AND DELAYED FLUORESCENCE IN MOLECULAR AGGREGATES

Sternlicht, H., Nieman, G. C., Robinson, G. W.
***Journal of Chemical Physics*, v. 38, no. 6, pp. 1326–1335, March 15, 1963**

This paper deals with triplet–triplet annihilation in pure and mixed organic crystals. In crystals containing a small concentration of impurity traps, triplet excitation migration may proceed from trap to trap on a time scale which is short compared with the long triplet state lifetime but which is long compared with the normal fluorescence lifetime. Nearest-neighbor and long-range mutual annihilation of two triplets may then take place giving rise to delayed fluorescence. The rates of long-range triplet excitation migration and annihilation show a concentration dependence, a temperature dependence, and a solvent dependence. Providing the triplet–triplet annihilation rate is not too fast, the intensity of the delayed fluorescence can be shown to depend upon the square of the intensity of the exciting light. This expectation is borne out by experiments, briefly reported here, on delayed fluorescence in dilute isotopic mixed crystals. In crystals containing high concentrations of such impurity traps, or in pure crystals, the annihilation rate becomes extremely rapid, and this mechanism effectively quenches phosphorescence in many, but not all, classes of pure organic crystals. The kinetics of the overall process is discussed within the limits of fast and slow annihilation rates. A theoretical investigation of the origin of the annihilation matrix element is carried out, and it is shown that exchange interactions play the largest role in determining annihilation rates. Past work (by H. Sponer, Y. Kanda, and L. A. Blackwell and by N. W. Blake and D. S. McClure) on delayed fluorescence of assumed pure naphthalene crystals containing very small amounts of β-methyl naphthalene (traps) can be understood within the framework of this paper. The need in organic crystals for the major delayed fluorescence mechanism to be based upon ionization and electron trapping seems now to be considerably lessened.

597. RESONANCE FLUORESCENCE IN GASES AND MOLECULAR CRYSTALS

Hameka, H. F.
***Journal of Chemical Physics*, v. 38, no. 9, pp. 2090–2100, May 1, 1963**

A general theoretical description is derived for the resonance fluorescence of dilute gases and molecular single crystals, with special emphasis on optical rotation spectra. The validity of previous theoretical work on dilute gases is confirmed by proving that the damping constants connecting excited states on different molecules are zero. It is shown that the intensities of optical rotation spectra of molecular crystals are much larger than the corresponding quantities for gases. An important theoretical prediction is that the natural line breadth of a resonance fluorescence emission band belonging to an exciton state in a molecular crystal should be larger than the width of the corresponding optical absorption line. The dependence of the intensity of the optical rotation spectrum on the relative orientation of the crystal with respect to the incident beam of light is discussed.

598. PI ELECTRONIC STRUCTURE OF THE BENZENE MOLECULE

Moskowitz, J. W., Barnett, M. P.
***Journal of Chemical Physics*, v. 39, no. 6, pp. 1557–1560, September 15, 1963**

An understanding of the electronic structure of the benzene molecule is of central importance to much of theoretical organic chemistry. For this reason, and because certain formal simplifications follow from the molecule's symmetry, numerous theoretical calculations have previously been made of the electronic structure of benzene.

This paper presents some results that were obtained using (1) accurate values for the three- and four-center integrals which hitherto have been ignored or approximated, and (2) rather more configurations than have been used by earlier workers. The calculations can be compared with those of Parr, Craig, and Ross, which are here extended in the two ways mentioned. Previous theoretical work is reviewed and these new calculations are presented and discussed.

599. MAGNETIC DIPOLE TRANSITION IN THE ELECTRONIC SPECTRUM OF FORMALDEHYDE

Callomon, J. H., Innes, K. K.
***Journal of Molecular Spectroscopy*, v. 10, no. 3, pp. 166–181, March 1963**

Explanations that have been advanced for the appearance of the weak 0–0 band of the 3500-A system of H_2CO are reviewed. The entirely similar $2\nu_4'$–0 band is analyzed as a type-A band of normal intensity distribution. The established symmetries of the combining states are then compatible only with a magnetic transition moment parallel to the carbon-oxygen bond, the first example to be established in a polyatomic molecule.

600. ON THE ESR SINGLET SPECTRA FREQUENTLY OBSERVED IN IRRADIATED POLYMERS AT A LARGE DOSE

Ohnishi, S.-I., Ikeda, Y., Sugimoto, S.-I., Nitta, I.
***Journal of Polymer Science*, v. 47, no. 149, pp. 503–507, November 1960**

Irradiated polymers have been known to give a variety of ESR spectra. Recently it has been found that many polymers such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), rubber (smoked sheet), polymethyl methacrylate (PMMA), and polyvinyl alcohol (PVA) give singlet spectra when they are highly irradiated or heated after irradiation. For example, PE gives the sextet spectrum when lightly irradiated ($\sim 10^6$ rad) and, when irradiated more (10^7–10^8 rad), the spectrum becomes a complex one involving a septet. At higher doses ($\sim 10^9$ rad) PE gives only a singlet spectrum.

The singlet spectra can be interpreted as arising from the unpaired electron in some conjugated double bond systems; for example, in the case of PE and PVC, the radical might be of the polyenyl type:

$$-CH_2-\dot{C}H-(-CH=CH-)_n-CH_2-.$$

In radicals of such a type, the unpaired electron delocalizes and is stabilized by bond resonance. If $n = 0$, however, the electron localizes on the central carbon and, as a result of the well-known hyperfine interaction (hyperconjugation and configurational interaction) with the adjacent five protons, the radical gives the sextet spectrum, the hyperfine separation (ΔH_{hfs}) being 30 gauss, and the ΔH_{msl} of each peak being 13 gauss. When $n = 1$, the unpaired electron delocalizes, and two resonance forms are possible.

If the interpretation is correct, it might be concluded that radiation produces double bonds in carbon-chain polymers and, as the dose increases, the conjugation region of the double bonds extends. This proceeds, it might be added, asymptotically toward that containing more or less 11 double bonds. The ease with which the conjugation proceeds differs from polymer to polymer, of the polymers investigated, conjugation proceeds most easily in PVC, less easily in polypropylene, and with more difficulty in polyethylene. When the polymers are heated after irradiation, double bonds of shorter conjugations decay faster, those of the longer conjugation region, i.e., of narrower singlet spectra, remaining, as shown in the cases of polyethylene and polyvinyl chloride.

601. THE DETERMINATION OF NUMBER-AVERAGE MOLECULAR WEIGHTS OF POLYMERS USING FLUORESCENCE SPECTROSCOPY

Journal of Polymer Science, Part B: Polymer Letters,
v. 1, no. 12, pp. 669–670, December 1963

A more generalized expression is derived for M_N to increase the applicability of Heintz' study on determination of M_N for polystyrene and polyisobutylene by means of fluorescence spectroscopy.

602. SUR LA NATURE DES CENTRES PARAMAGNÉTIQUES DÉTECTÉS PAR RPE DANS LES POLYMÈRES CONJUGUÉS (ON THE NATURE OF PARAMAGNETIC CENTERS DETECTED BY EPR IN CONJUGATED POLYMERS)

Nechtschein, M.
Preprint 73, presented at the International Symposium on Macromolecular Chemistry, Paris, France, July 1–6, 1963, sponsored by the International Union of Pure and Applied Chemistry, under the patronage of Monsieur le Ministre d'État chargé de la Recherche Scientifique, under the auspices of the Délégation Générale à la Recherche Scientifique et Technique, and the National Committee for Chemistry
(To be published in *Journal of Polymer Science, Part C: Polymer Symposia*)

The nature of the paramagnetic centers which give an electron paramagnetic resonance signal in conjugated polymers is not yet quite clear. Are they conduction electrons transferred in the conduction band by thermal excitation, or triplets in the ground state corresponding to macrobiradicals, or free bonds giving macroradicals stabilized by the high energy resonance of the conjugated polymers, or simply defects in the periodicity of the alternant bonds? After showing how the free spins observed seem to correspond to ground states, these various models are reviewed and discussed.

603. SUR LE RÔLE ÉVENTUEL DES "DOUBLETS ÉLECTRONIQUES" DANS LE COMPORTEMENT QUANTIQUE DES BIOPOLYMÈRES (ON THE POSSIBLE ROLE OF ELECTRONIC DOUBLETS ON THE QUANTUM BEHAVIOR OF BIOPOLYMERS)

Douzou, P., Francq, J. C., Ptak, M., Sadron, C.
Preprint 79, presented at the International Symposium on Macromolecular Chemistry, Paris, France, July 1–6, 1963, sponsored by the International Union of Pure and Applied Chemistry, under the patronage of Monsieur le Ministre d'État chargé de la Recherche Scientifique, under the auspices of the Délégation Générale à la Recherche Scientifique et Technique, and the National Committee for Chemistry
(To be published in *Journal of Polymer Science, Part C: Polymer Symposia*)

Biopolymers, especially spherical proteins, indicate transfer of chemical energy. The polypeptide lattice is assumed. Attention is drawn to electrons of the "free doublets" which do not stay with one role in their original molecule but establish liaisons with partners in other polymer chains. Optical emission experiments permit determination of the transitional characteristics for the doublets and discussion of their effect on the conceptions of quantum behavior of both free molecules and polymers. A logical result of these experiments is research, by EPR studies, on the metastable radicals possibly formed from the optical excitation. A summary of these works is presented, and an attempt is made to show the perspectives of the problem of quantum behavior of biopolymers.

604. THEORY OF MOLECULAR EXCITONS

Davydov, A. S.
Kasha, M., Oppenheimer, M., Jr., Translators
McGraw-Hill Book Company, Inc., New York, N.Y., 1962

Davydov's book summarizes the use of the exciton model in many electronic and optical problems, and its perceptive treatment suggests many starting points for further extensions. The book was published originally in 1951 by the Ukranian Academy of Sciences, Kiev, Ukranian SSR, under the title "Theory of the Absorption of Light in Molecular Crystals." The rephrased title stresses the principal theme of the book – the resonance interaction of excited states of weakly coupled molecular systems. To bring this edition more up to date, two appendixes are included which cover principal literature on related topics to December 1961. The future publication of this book in English was noted in Entry #776, AI/LS 341.

In addition to an introduction, the book comprises the following chapters:

"Translations and Rotational Vibrations of Molecules in a Molecular Lattice"

"Influence of the Interaction Forces Between Molecules of a Molecular Lattice on the Intramolecular Vibrations"

"Quantum Theory of Absorption and Combinational Scattering (Raman) Spectra in Molecular Crystals (Zeroth Approximation)"

"General Equations Determining the Energy States of Molecular Crystals"

"Free Excitons in a Molecular Lattice"

"Excitation of Free Excitons Simultaneously With the Excitation of Lattice Vibrations"

"Localized Excitons in a Molecular Lattice"

"Transformation of Absorbed Energy Into Heat and Radiation"

"Comparison of Theory With Experiment"

"Application of Exciton Concepts to the Calculation of the Energy States of Several Polyatomic Molecules"

"Conclusion."

The publications of Davydov and a supplementary bibliography of publications are appended to the text.

605. SELF-CONSISTENT FIELD THEORY OF THE ELECTRON SPIN DISTRIBUTION IN π-ELECTRON RADICALS

McLachlan, A. D.

***Molecular Physics*, v. 3, no. 3, pp. 233–252, May 1960**

In a radical the single determinant wave function which gives the lowest electronic energy is one where electrons of opposite spins occupy different sets of molecular orbitals and thereby lower the "exchange" part of the energy. The unpaired spin density may be negative in a wave function of this type and is easily found by perturbation theory if certain exchange integrals are small. It is shown that the spin density is then almost the same as is found by combining the usual single determinant function (with one unpaired electron, and $2n$ paired ones in n orbitals) with its singly excited doublet configurations. In alternant hydrocarbons the Pariser and Parr theory leads to a simple formula for the spin density: $\rho_r = c_{ro}^2 - \lambda \Sigma_s \pi_{rs} c_{so}^2$, where c_{ro} is the Hückel coefficient of the odd orbital on atom r, π_{rs} is the mutual polarizability of atoms r and s, and λ is a constant derived from the theory. The observed hyperfine structure in the electron resonance spectra of naphthalene, anthracene, perylene, diphenyl, phenanthrene, and pyrene negative ions agrees well with this formula, provided the constant Q defined by McConnell is about −24.2 gauss. The non-alternant negative ions of acenaphthylene and fluoranthene also agree; acepleiadylene does not. The theory predicts identical spin densities in corresponding positive and negative ions. In neutral alternant radicals negative spin densities are found on all the unstarred atoms of triphenylmethyl, perinaphthenyl, allyl, and benzyl. The calculated negative densities are a little too small to fit the spectra of the first two radicals, but fit just as well as the valence bonds. (*PA*, 1961, #14,108)

606. THE EFFECT OF BOND LENGTH VARIATIONS IN MOLECULAR ORBITAL CALCULATIONS OF π ELECTRON SPECTRA—ANILINE

Peacock, T. E.

***Molecular Physics*, v. 3, no. 5, pp. 453–456, September 1960**

The effect of bond-length changes on ground and excited state energies is examined. The results are applied to aniline. (*PA*, 1961, #14,085)

607. THE CRYSTAL SPECTRA OF VERY WEAK TRANSITIONS. II. THEORETICAL

Craig, D. P., Walmsley, S. H.

***Molecular Physics*, v. 4, no. 2, pp. 113–124, March 1961**

(For Part I, see Entry #1000.) The theory of intermolecular resonance effects in the spectra of molecular crystals is extended to very weak systems in which the pure electronic transitions are either forbidden (as in the benzene 2600-A system) or comparable in intensity with accompanying vibrationally induced transitions (as in the naphthalene 3200-A system). For the pure electronic transitions the intermolecular coupling is through transition octupole moments, giving splittings and intensity transfers of the same type as, though smaller than, those familiar in the stronger, dipole-coupled systems. Values of octupole–octupole and octupole–dipole interaction sums are reported for naphthalene, and the crystal spectrum is calculated. For vibration-induced transitions it is shown that the intermolecular effects are due only to the small component of "stolen" character, thus allowing the lack of splitting and intensity transfer to be understood. The nature of such bands as arising from localized excitation can thus be explained in the framework of the simple rigid-lattice exciton theory. (*PA*, 1961, #14,593)

608. ELECTRONIC ABSORPTION SPECTRA OF CRYSTALS OF AROMATIC COMPOUNDS AT LOW TEMPERATURES

Sirkar, S. C.
National Institute of Sciences of India, Proceedings of the, Part A, Physical Sciences, **v. 27, no. 6, pp. 568–578, November 1961**

The experimental results of investigations on the near UV bsorption spectra of crystals of benzene at low temperatures up to −259°C reported by previous workers and the various heories put forward to explain these results are briefly reviewed. The application of Davydov's theory (1951) to the absorption spectra of crystals of anthracene and naphthalene made by some previous workers is critically examined, and it s pointed out that the experimental results do not concluively verify Davydov's theory and that in the case of absorption bands with low oscillator strengths the average value of transition moment derived from oscillator strength cannot be used to calculate the Davydov splitting. It is further pointed out that large splitting of the absorption bands was observed in the near UV absorption spectra of polycrystalline masses of a large number of aromatic compounds with polar molecules at −180°C, and that such splitting can be explained partly by modifying Davydov's theory and taking into account the interaction of the permanent electric moments of the nearest neighbors on the transition moment of the molecule in the crystal. (*PA*, 1962, #8525)

609. THE ELECTRONIC SPECTRA OF MIXED CRYSTALS [ABSTRACT]

Craig, D. P.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 7–8
National Research Council, Ottawa, Canada, 1962

The main phenomenon in the optical spectra of pure molecular crystals is the Davydov splitting of individual molecular energy levels according to the structure of the unit cell. Several examples are known in which the magnitude of the plitting has been calculated theoretically in quite good agreement with experiment. A second phenomenon in pure crystals is the mixing by crystal forces of different molecular excited states; this results in the transfer of intensity between molecular transitions and is observed as a departure of the ntensity ratio for absorption measured along different crystal axes from the value calculated from the oriented gas model. While the Davydov splitting is caused by a resonance beween the energy levels of identical molecules, the intensity ransfer is not a resonance phenomenon and can be expected o persist in mixed crystals (as a coupling between levels of different molecules, instead of coupling between different levels of identical molecules) as in a pure crystal.

A typical aromatic mixed crystal is that of tetracene contained as impurity in anthracene. Tetracene is the guest molecule present in very low concentration (in the order 10^{-4} *M*) in anthracene as host crystal. Experimental studies by Choudhury and Ganguly indicate a marked departure from oriented gas behavior. The absorption spectrum of the tetracene can be measured parallel to the *a* and *b* crystal axes of the anthracene crystal, leading to a polarization ratio *b*/*a* of about 1.9, compared with the oriented gas value of 7.7:1. This result, which indicates a substantial degree of interaction between guest and host, can be explained satisfactorily using the idea that the 4800-Å transition of tetracene steals some intensity from the anthracene transitions at 3800 Å and 2500 Å.

In the fluorescence spectrum of the same mixed crystal, the polarization ratio is again reduced from the oriented gas value, but not to the same extent as in the absorption spectrum. It is believed that several distinct causes operate to produce this lack of symmetry between the absorption and fluorescence behavior. One cause is a small change in equilibrium orientation of the guest in the host's lattice that occurs during the radiative lifetime; another is a local change in the lattice dimensions because of changed intermolecular forces in the excited state. The former cause seems more probable.

In mixed crystals in which the lowest level of the guest is below the lower limit of the host's exciton band, simple perturbation methods suffice to calculate spectral effects. In other cases, such as those of guest and host being isotopically related, more precise treatment is necessary. This shows that the polarization behavior still follows satisfactorily from elementary perturbation arguments. The energetics are more complicated. For example, at high guest concentrations one expects splitting arising from guest–guest interactions with a magnitude depending sensitively on the strength of intermolecular interaction in relation to the energy gap between host and guest levels.

610. EXCIMER FLUORESCENCE IN ORGANIC SOLUTIONS AND CRYSTALS [ABSTRACT]

Birks, J. B.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 9–12
National Research Council, Ottawa, Canada, 1962

The fluorescence of pyrene in solution is considered first. The ratio $(I_D/I_M)_{\text{soln.}}$ of the quantum yields of *D* and *M* is proportional to the concentration *c*. *M* is the normal monomer emission; *D* is the emission of excited dimers (excimers) formed by the diffusion-controlled association of excited and unexcited molecules. The excimers dissociate on emission. This interpretation of the origin of *M* and *D* has been confirmed by detailed studies of their rise and decay times, following excitation by a pulsed light source, as a function of concentration, viscosity, and temperature.

If k_{fM}, k_{iM} and $k_{D}c$ are the rate parameters (sec^{-1}) of monomer fluorescence, monomer internal quenching, and excimer formation, respectively, and q_D is the excimer fluorescence quantum efficiency, then

$$\left(\frac{I_D}{I_M}\right)_{\text{soln.}} = \frac{q_D k_D c}{k_{fM}} \quad (1)$$

The fluorescence decay time τ_M of M, in the absence of oxygen or other quenching impurities, is given by

$$1/\tau_M = k_{fM} + k_{iM} + k_D c \quad (2)$$

For a diffusion-controlled process at temperature T

$$k_D = \frac{8RT}{3000\,\eta}\,p \quad (3)$$

where η is the viscosity, and p is the probability that an encounter between excited and unexcited monomer molecules results in excimer formation. From an analysis of the measurements of τ_M as a function of c, η, and T from 290–340°K, it is found that

$$p = p_0 \exp(-W/kT) \quad (4)$$

where $W = -0.37$ ev, corresponding to a decrease in p with increase in T. This value may be compared with that of 0.76 ev obtained for the energy separation of the excited monomer and excimer emitting levels from the fluorescence spectra, and that of 0.39 ev = (0.76-0.37) ev calculated independently for the dissociation enthalpy of the pyrene excimer.

Förster has explained the fluorescence behavior of pyrene in the following manner. The two lowest excited singlet levels of the pyrene molecule are ^1L_b and ^1L_a. The fluorescence emission M occurs from the lower level ^1L_b, which has a very weak transition moment to the ground state. This is confirmed by the value of τ_M = 450 nsec observed at 20°C in oxygen-free solutions at low c. ^1L_a, which is adjacent to ^1L_b, has a strong transition moment to the ground state. Consequently the large splitting of the ^1L_a level in the excited dimer produces the lowest excited singlet level ^1L_a from which the excimer emission D occurs.

The fluorescence spectra of solution of 32 compounds which exhibit excimer fluorescence at room temperature have been studied.

611. INTERSYSTEM CROSSING AND DONOR-ACCEPTOR INTERACTION [ABSTRACT]

McGlynn, S. P., Christodouleas, N., Daigre, J.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 33–37
National Research Council, Ottawa, Canada, 1962

It has been shown that the phosphorescence to fluorescence quantum yield ratio, ϕ_p/ϕ_f, of anthracene in an ether-isopentane glass at 77°K is increased by a factor of 10 when complexation with *sym*-trinitrobenzene (TNB) is effected in the same matrix, and that the phosphorescence of the anthracene (to the exclusion of the fluorescence) may be excited by irradiation in the charge-transfer absorption region of the complex. No further work along these lines seems to have been carried out, although there does seem to exist a general feeling that charge-transfer complexation should sensitize phosphorescence of the donor partner of the complex. It is now accepted that oxygen effects on singlet ↔ triplet transition probabilities are due to increased spin-orbital coupling caused by complex formation with oxygen, and a complexed intermediate has been invoked to explain the external heavy atom spin-orbital coupling effect. In view of the above, and the recent results of Czekalla who showed that complexation caused a decrease in the phosphorescence lifetime of various aromatics, it seems necessary to discuss the effect of complexation on the ratio ϕ_p/ϕ_f. Such a discussion is presented in this paper; the subject is divided into three sections.

(1) The external heavy atom spin-orbital coupling effect is considered. A sampling of the results obtained with naphthalene in various media is tabulated, and a graphic illustration is given. It seems reasonable to conclude that the room-temperature quenching of fluorescence caused by various heavy-atom containing perturbers can be attributed to singlet depopulation via an enhanced intersystem crossing process. It also seems reasonable that one result of the heavy-atom perturbation is a mixing of the charge transfer singlet and donor triplet states.

(2) Charge transfer and heavy-atom spin-orbital coupling effects are also discussed. A sampling of the results obtained with naphthalene-acceptor systems of relatively large equilibrium constant is tabulated, and the effects of concentration variation for a typical case are shown. The results show the efficacy of a large equilibrium constant, a significant increase in ϕ_p/ϕ_f by a non-paramagnetic non-heavy atom containing acceptor (TNB) in a CT complex, the additional effectiveness of heavy atoms in the acceptor partner, and the effect of acceptor concentration.

(3) Discussion is given of both cases, although the first is simple. For case 2, discussion includes the CT state as an intermediate in an energy cascade process, and the loss of the validity of the spin concept. Two processes are suggested to account for the results, and the two mechanisms are generalized.

612. LOW FREQUENCY VIBRATIONS OF MOLECULAR CRYSTALS [ABSTRACT]

Pople, J. A.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 39–41
National Research Council, Ottawa, Canada, 1962

Such low-frequency (< 500 cm^{-1}) spectra generally involve relative motion of large groups of atoms and are related to mechanical and thermal – but not electrical – properties. However, it is pointed out that quanta of such vibrations are sometimes found in combination with electronic excitation and some have been observed in Raman spectra. This particular paper is concerned with observations (and their interpretation) in the far infrared.

613. THE ENERGIES OF IONIZED STATES IN MOLECULAR CRYSTALS; AND SOME RELATED PROPERTIES [ABSTRACT]

Lyons, L. E.

In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 42–45
National Research Council, Ottawa, Canada, 1962

The following subjects are included: the calculation of the crystal values, I_C (ionization potential) and A_C (electron affinity), of molecular crystals from the gas values I_G and A_G by evaluating charge–dipole and dipole–dipole interactions; calculation of α (average molecular polarizability) from I_C and I_G, and comparison with experimental results; polarization energy P; the temperature dependence of intrinsic dark conductivity in molecular crystals, including the theory behind observations and the possibility of further intrinsic conductivity as yet unobserved; the number of charges at thermal equilibrium in a molecular crystal (mobile charges of probable importance in biological systems) and the EPR signal; the threshold of intrinsic photoconductivity; and spectral maximum of photoemission.

614. THEORY OF THE VIBRATIONAL STRUCTURE OF MOLECULAR EXCITON STATES [ABSTRACT]

Merrifield, R. E.

In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 53–55
National Research Council, Ottawa, Canada, 1962

It has been recognized for some time that the Born–Oppenheimer separation of nuclear and electronic motion is not, in general, valid for molecular exciton states. However, whenever the Born–Oppenheimer approximation is valid for the individual molecules, such a separation can be obtained in the sense that an effective Hamiltonian for the nuclear motion can be derived.

The total vibronic wave function of a state of a molecular crystal in which the molecule at R_n is electronically excited may be written $\chi_n(r,Q) = \phi_n(r,Q)\Lambda_n(Q)$, where r and Q represent all of the electronic and internal vibrational coordinates, respectively, of the molecules in the crystal. The electronic part of the wave function $\phi_n(r,Q)$ may be written

$$\phi_n(r,Q) = u'(r_n,Q_n) \prod_{i \neq n} u(r_i,Q_i) \quad ,$$

where $u(r_i,Q_i)$ and $u'(r_i,Q_i)$ are the ground and excited state electronic wave functions, respectively, of the individual molecules. In the absence of intermolecular interactions, the vibrational wave function, $\Lambda_n(Q)$, can be factored similarly into molecular vibrational wave functions, but in general this will not be possible.

$E_n(Q)$, the total intramolecular vibrational potential energy in the absence of intermolecular interaction, is represented by

$$E_n(Q) = \sum_{i \neq n} V(Q_i) + V'(Q_n) \quad ,$$

where $V(Q_i)$ and $V'(Q_i)$ are the vibrational potential energy functions of the ground and excited electronic states, respectively, of an individual molecule.

Finally, a general equation is derived which represents the vibronic behavior:

$$[T_N + E_n(Q)]\Lambda_n(Q) + \sum_m{}' \exp(ik \cdot R_m)\, H_m\, \Lambda_{n-m}(Q)$$
$$= E_k\, \Lambda_n(Q) \; .$$

The first term on the left-hand side of the equation simply determines the molecular vibrations in the absence of any intermolecular interaction, while the summation represents the effect of the exciton motion on the vibrations. This represents a generalization to crystals of Witkowski and Moffitt's treatment of the vibronic states of dimers and is closely related to recent work of McConnell on the "self-trapping" of excitons through interaction with intramolecular vibrations.

Since a general method of solution for this equation has not been found, a simple exactly soluble example has been selected which allows numerical solution over the entire range of coupling strengths.

Preliminary calculations have been carried out which illustrate the simple behavior of the energy levels and spectra in the weak and strong coupling limits and the very complex behavior in the intermediate coupling region.

615. VIBRONIC POLARIZATION IN MOLECULAR CRYSTAL SPECTRA [ABSTRACT]

McRae, E. G.

In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 61–65
National Research Council, Ottawa, Canada, 1962

The object of this communication is to show how variations of polarization ratio within electronic band systems in molecular crystal spectra may be interpreted in terms of vibronic interactions. The vibronic states considered here correspond to the excitation of intramolecular vibrations only; as lattice vibrations are left out of the theory, the results refer to the gross vibrational structure in spectra.

The model and theoretical assumptions are the same as in the simplest form of the exciton theory, except that each molecule is allowed to vibrate in one normal mode. The vibration is assumed to be harmonic and the force constant is taken to be the same in the ground and excited electronic states.

The method of treatment is that of perturbation theory. The intermolecular interaction energy is considered as a small perturbation, so that the zeroth-order description of the crystal corresponds to the case of "weak coupling." The procedure followed here is to obtain a first-order correction to the wave functions, and then to calculate the transition moment integral involving the appropriate corrected wave function for a vibronic transition of arbitrary polarization. The vibronic polarization ratios may be obtained in general as ratios of squares of the relevant transition moments. The present discussion is limited for definiteness to a crystal with two molecules per unit cell.

The zeroth-order wave functions are built up from products of vibronic wave functions for the individual molecules. These products are characterized by two numbers, p and d, respectively designating the number of vibrational quanta excited and the number of molecules participating in vibronic excitation. In the derivations the basis set is limited to those wave functions which can be constructed from products characterized by $a = 1$; i.e., products representing vibronic excitation of one molecule only.

616. ELECTRON AFFINITIES OF ORGANIC MOLECULES

Batley, M., Lyons, L. E.

***Nature*, v. 196, no. 4854, pp. 573–574, November 10, 1962**

The simplest relationship between the E's of two acceptors depends on a number of assumptions and follows from the expression for the energy, $h\nu$, of the maximum of the charge-transfer band being given by the expression

$$h\nu = I(D) - E(A) + \phi_{AD} \qquad (1)$$

where $I(D)$ is the ionization potential of the donor molecule D; $E(A)$, the electron affinity of the acceptor, A.

The difference in E for two molecules, i and j, for a given donor is then:

$$E(A_i) - E(A_j) = h\nu_j - h\nu_i + \phi_{iD} - \phi_{jD} \qquad (2)$$

The assumption that the right-hand side of equation 2 is approximately equal to $h\nu_j - h\nu_i$ can be tested by determining $E(A_i) - E(A_j)$ for a series of donors. Using available data for various donors, it has been possible to compile a table of electron affinities for molecules which act as acceptors in charge-transfer spectra.

617. DELAYED FLUORESCENCE SPECTRUM OF PYRENE SOLUTIONS AT LOW TEMPERATURES

Tanaka, C., Tanaka, J., Hutton, E., Stevens, B.

***Nature*, v. 198, no. 4886, p. 1192, June 22, 1963**

Parker and Hatchard have convincingly demonstrated that delayed fluorescence exhibited by dissolved aromatic hydrocarbons A originates in the interaction of two triplet states, and that at low light intensities the overall process 1, followed by 2, is controlled by the first-order process 3 which is almost entirely responsible for triplet-state decay under these conditions.

$$^3A + {}^3A \rightarrow {}^1A^* + A \qquad (1)$$

$$^1A^* \rightarrow A + h\nu_M \qquad (2)$$

$$^3A \rightarrow A \qquad (3)$$

To account for the presence of the dimer band in the delayed fluorescence spectrum of pyrene, it has been suggested that process 1 involves Colpa's doubly excited state $^1A_2^{**}$ and the excimer $^1A_2^*$ as intermediates, that is:

$$^3A + {}^3A \xrightarrow{a} {}^1A_2^{**} \xrightarrow{b} {}^1A_2^* \xrightarrow{c} {}^1A^* + A \qquad (1)$$

where the energy-dependent process 1c competes with excimer fluorescence, process 4.

$$^1A_2^* \rightarrow (A_2) + h\nu_D \qquad (4)$$

This mechanism accounts for the observation that the ratio of intensities I_D/I_M of dimer to monomer bands in the delayed spectrum approaches a limiting non-zero value at zero concentration of A at room temperature; moreover, it requires a negative temperature coefficient of I_D/I_M which is indeed observed above 0°C.

At lower temperatures, however, the ratio I_D/I_M has a positive temperature coefficient and this ratio is higher at −72°C than at 71°C for a 10^{-3} M solution in ethanol. Since the singlet–triplet splitting in pyrene is some 10,000 cm^{-1}, this is unlikely to be due to a thermal repopulation of the fluorescent from the triplet states which in any event would lead to a negative temperature coefficient of I_D/I_M in this region.

The dominance of the monomer band in the delayed fluorescence spectrum at lower temperatures (and higher viscosities) may be understood if process 1 can occur directly at greater distances than those required for the formation of dimeric intermediates by processes 1a and 1b, and if the latter processes are suppressed under these conditions due to energy requirements. This mechanism would require that the ratio I_D/I_M approach zero at zero concentration since photoassociation would follow rather than precede the formation of the excited singlet state; this aspect is being currently investigated.

Long-range triplet–triplet state interaction has been suggested by Muel to account for the square-law intensity dependence of delayed fluorescence exhibited by 3,4-benzpyrene in rigid media, while Nieman and Robinson have recently demonstrated the occurrence of long-range energy migration between triplet state traps in C_6D_6-doped crystals of benzene at very low temperatures.

618. THE CALCULATION OF THE EFFECT OF THICKNESS OF ORGANIC SOLID SOLUTIONS ON THE TRANSFER OF ENERGY OF ELECTRON EXCITATION FROM A MAJOR COMPONENT TO THE IMPURITY

Faidish, O. M.

***Naukovi Zapiski, Kiivs'kii Derzhavnii Universitet*, v. 18, no. 3, pp. 64–69, 1959**

Literature on the transfer of energy of electron excitation in solid organic solutions is discussed (22 references), and the presence of excitons in molecular crystals is considered fully proved. In the case of anthracene crystals, the excitation energy transfer depended almost entirely on the excitons. An equation, applicable to thin films, is discussed. The ratio of quantum yield of the major component to that of the impurity (Y_m/Y_a) depends on the thickness of films, the concentration of the admixture, and the coefficient of the absorption of excited light. The calculated effect of the thickness, based on the equation, agreed well with the experimental data. In solid solutions of naphthalene in anthracene, a decrease in thickness from 10μ to 1μ increased the Y_m/Y_a ratio only by a few percent; a decrease from 1μ to 0.2μ had a much greater effect. The effects of impurity concentration and excitation wavelength are discussed.

619. DIFFÉRENCE DE FORME DES IMPULSIONS DE SCINTILLATIONS ORGANIQUES DUES AUX ÉLECTRONS ET AUX PARTICULES ALPHAS (DIFFERENCE OF THE FORM OF THE IMPULSES OF ORGANIC SCINTILLATIONS DUE TO ELECTRONS AND ALPHA PARTICLES)

Gervais de Lafond, Y., Bouyssou, J.
***Nuclear Instruments & Methods*, v. 22, no. 2, pp. 365–366, April 1963**

The curve of decreasing luminescence emission of an organic scintillator essentially includes two exponentials:

$$I(t) = A \cdot e^{-t/\tau_1} + B \cdot e^{-t/\tau_2}$$

For anthracene, the decay time τ_1 of the first component is 33 mμsec and that of the second component is 370 mμsec. The relative percentage of these two components depends on the nature of the incident particle. Knowing the value of this percentage for an electronic excitation ($\simeq 10\%$), an attempt is made to deduce the percentage which corresponds to excitation by α-particles. The method used consists of causing the RC time constant of the output circuit of the photomultiplier to change by means of the resistance of the charge; when the time constant is of the order of size of τ_1, the electrical impulse is practically limited to the rapid component of the scintillation; then, when the time constant is greater than τ_2, the impulse corresponds to the total scintillation (rapid component and slow component).

620. ELECTRONIC STRUCTURE AND SPECTRA OF CHLORANIL AND *p*-PHENYLENEDIAMINE

Giacometti, G., Nordio, P. L., Rigatti, G.
***Il Nuovo Cimento*, v. 23, no. 2, pp. 433–439, January 16, 1962**

The energy levels of π-electrons for chloranil, *p*-phenylenediamine and their ions, respectively positive and negative, were calculated by the semiempirical LCAO–MO–SCF method. The results are in good agreement with all known spectral data on these substances. (*PA*, 1962, #8115)

621. UNIVERSAL MOLECULAR INTERACTIONS AND THEIR EFFECT ON THE POSITION OF THE ELECTRONIC SPECTRA OF MOLECULES IN TWO-COMPONENT SOLUTIONS. I. THEORY (LIQUID SOLUTIONS)

Bakhshiev, N. G.
***Optika i Spektroskopiya*, v. 10, no. 5, pp. 717–720, May 1961**
(Translated from the Russian in *Optics and Spectroscopy*, v. 10, no. 5, pp. 379–384, May 1961)

Starting from the most general physical considerations, a simple theory was developed describing the effect of universal intermolecular interactions (orientation, induction, and dynamic effects) on the position of the electronic spectra of molecules in two-component liquid solutions. Using the Onsager–Böttcher model of the structure of solutions, new and simple expressions were found correlating the magnitude of the spectral shift with physical characteristics of the solvent and the molecules of the solute. The effect of dispersive interactions on the position of the spectra is reviewed. (For Part II, see Entry #1076.)

622. REABSORPTION IN CRYSTALS OF FINITE THICKNESS. II

Agranovich, V. M., Konobeev, Yu. V.
***Optika i Spektroskopiya*, v. 11, no. 3, pp. 369–384, September 1961**
(Translated from the Russian in *Optics and Spectroscopy*, v. 11, no. 3, pp. 199–206, September 1961)

(For Part I, see AI/LS 341, Entry #248.) This paper presents results which are derived from a theory of the reabsorption of light in crystals of finite thickness. Calculated values are listed for the stationary case, making it possible to to determine the shape of the luminescence spectrum and the quantum yield for phosphors of arbitrary thickness. Accurate new exact equations have been obtained for the nonstationary case (luminescence decay), from which formulas are derived for the average time of luminescence decay. Various asymptotic cases are studied in detail. The results obtained for nonstationary processes can be used in the theory of radiant energy transfer in planetary atmospheres and in the theory of neutron moderation.

623. REABSORPTION IN CRYSTALS OF FINITE THICKNESS. III

Konobeev, Yu. V.
***Optika i Spektroskopiya*, v. 11, no. 4, pp. 504–512, October 1961**
(Translated from the Russian in *Optics and Spectroscopy*, v. 11, no. 4, pp. 272–276, October 1961)

A theory of light reabsorption in molecular crystals is presented. Formulae are obtained for the average true luminescence decay and rise times in the nonstationary case (decay and rise of luminescence). Various asymptotic cases are investigated in detail. The results obtained in the present paper for nonstationary processes can be applied to the theory of radiation energy transfer in planetary atmospheres and to the theory of neutron moderation. (*PA*, 1962, #6559)

624. UNIVERSAL MOLECULAR INTERACTIONS AND THEIR EFFECT ON THE POSITION OF ELECTRONIC SPECTRA OF MOLECULES IN TWO-COMPONENT SOLUTIONS.

IV. DEPENDENCE ON THE MAGNITUDE OF THE STOKES SHIFT IN THE SOLVENT LUMINESCENCE SPECTRUM (LIQUID SOLUTIONS)

Bakhshiev, N. G.
***Optika i Spektroskopiya*, v. 12, no. 5, pp. 557–564, May 1962**
(Translated from the Russian in *Optics and Spectroscopy*,
v. 12, no. 5, pp. 309–313, May 1962)

(For Part III, see Entry #1077.) On the basis of a previously developed theory describing the influence of universal molecular interactions on the positions of electronic spectra of molecules in two-component liquid solutions (Entry #621), a new and more rigorous expression was obtained relating the magnitude of the Stokes shift in the luminescence spectrum to the physical characteristics of the solvent and of the dissolved substance. A general quantitative comparison was carried out of the previously described expression with experimental results, and its suitability was shown for interpreting all the experimental data on the spectra of solutions of large groups of aromatic compounds in a wide range of solvents. The considerations included that of the influence on the spectra of specific molecular interactions and, in particular, of hydrogen bonds. (*PA*, 1962, #21,913)

625. RELATION BETWEEN ABSORPTION AND LUMINESCENCE SPECTRA AND THE ANTI-STOKES LUMINESCENCE YIELD

Alentsev, M. N., Pakhomycheva, L. A.
***Optika i Spektroskopiya*, v. 12, no. 5, pp. 565–570, May 1962**
(Translated from the Russian in *Optics and Spectroscopy*,
v. 12, no. 5, pp. 314–317, May 1962)

It is shown that to satisfy the relationship between absorption and luminescence spectra proposed by Stepanov, the quantum yield of luminescence must be constant in all regions of excitation. As a supplement to the work of Antonov-Romanovskii, et al., this result confirms the fact that thermodynamic and statistical laws do not contradict the invariability of the luminescence quantum yield nor, as a consequence, the possibility of an energy yield greater than one for anti-Stokes excitation. It is confirmed experimentally that the luminescence spectrum of an aqueous solution of fluorescein is invariable under anti-Stokes excitation, and it is shown that experimentally observed reductions of yield in certain regions are associated with departure from the Stepanov relationship. Extrapolation of this relationship to anti-Stokes regions permits separating out the active absorption, and the quantum yield calculated for this absorption turns out to be constant. (*PA*, 1962, #22,941)

626. VARIATION OF THE MEAN LIFETIME AND YIELD OF LUMINESCENCE IN THE PROCESS OF QUENCHING AS A FUNCTION OF THE LAW OF MOLECULAR INTERACTION

Sveshnikov, B. Ya., Shirokov, V. I.
***Optika i Spektroskopiya*, v. 12, no. 5, pp. 576–581, May 1962**
(Translated from the Russian in *Optics and Spectroscopy*,
v. 12, no. 5, pp. 320–322, May 1962)

Formulae for the decay law of quenched solutions and the dependence of the lifetime and yield of luminescence on the concentration C of the quenching agent are obtained under the following assumptions: (1) the probability that a molecule be quenched by another between times t and $t + dt$ is $kr^{-n}\,dt$, where k and n are constants, and r is the intermolecular separation, and (2) the interactions between an excited molecule and all quenching molecules are algebraically additive. The ratio of the slopes of the curves describing the variation of the lifetime and yield of luminescence as a function of concentration C of the quenching agent is tabulated for $C \to 0$, together with the limiting value of the ratio $(\tau/\tau_0)/(B/B_0)$ for $C \to \infty$, where τ, τ_0, B and B_0 are the lifetimes and yields of the quenched and unquenched solutions, respectively. (*PA*, 1962, #21,914)

627. ENERGY TRANSFER IN RIGID SOLUTIONS

Maksimov, M. Z., Rozman, I. M.
***Optika i Spektroskopiya*, v. 12, no. 5, pp. 606–609, May 1962**
(Translated from the Russian in *Optics and Spectroscopy*,
v. 12, no. 5, pp. 337–338, May 1962)

An analytical expression is obtained for the luminescence decay law of a donor and for the quantum yield of energy transfer from donor to acceptor in the case of solid solutions with different degrees of correlation of the mutual orientation of dipole moments. An estimate is given of the upper concentration limit, at which the concept of point molecules is still applicable.

628. ON THE EXISTENCE OF SEVERAL METASTABLE STATES OF THE ACTIVATOR MOLECULE IN ORGANOLUMINORS

Aristov, A. V., Sveshnikov, B. Ya.
***Optika i Spektroskopiya*, v. 14, no. 5, pp. 732–733, May 1963**
(Translated from the Russian in *Optics and Spectroscopy*,
v. 14, no. 5, pp. 388–389, May 1963)

Certain results obtained in studies of the phosphorescence of solid solutions of organic substances cannot be directly explained within the framework of Jablonski's scheme with one metastable level. A number of authors have thus attempted to generalize this scheme by taking into consideration additional metastable states. Many of the above-mentioned experimental data can, however, be explained equally well if the existence of luminescent, physically inhomogeneous centers in the solution (including among them chemical admixtures) is assumed. In this communication an experiment is proposed which should permit a decision in favor of one or the other of these hypotheses in a number of cases.

The experiment proposed here, which permits a choice between the two hypotheses, can also be applied to substances with coincident spectra of different phosphorescent centers. In this case, the evaluation of the quantum intensities of each one of the phosphorescences becomes rather difficult, but a choice can be made based on the dependence of the decay law upon the degree of illumination by the exciting light in the domain where Bouger's law is violated. If the decay factors turn out to be different for the phosphorescent centers, the general curve representing delayed emission in the case of saturation will show no variation only in the case where the ratio of the intensities of the phosphorescences of these centers is independent of the degree of illumination by the exciting light. In the case of physically inhomogeneous centers, an increase of the illumination by the exciting light leads to an acceleration of the luminescent emission, in particular during the first stages of the decay process. This happens because of the relative increase of the number of centers of phosphorescence for which the decay factor (decrement) is large: the long-lived centers are more easily saturated at lower intensities of illumination by the exciting light. Thus, the possibility should be considered that the acceleration of the phosphorescent emission in solid solutions of fluorescein at saturation which has been observed by Sveshnikov, and which was later studied in detail, could be explained in terms of one of the hypotheses considered above. In conclusion, it should be said that in performing the proposed experiment optically thin samples ($D\lambda_{\max\,abs} \leqslant 0.05$) should be used so as to exclude the possibility of errors resulting from irregularities of the excitation and of the reabsorption of the luminescent light by activator molecules in the ground state and in metastable states.

629. NEGATIVE ABSORPTION BY CERTAIN ORGANIC COMPOUNDS

Derkacheva, L. D.
***Optika i Spektroskopiya*, v. 15, no. 1, pp. 138–139, July 1963**
(Translated from the Russian in *Optics and Spectroscopy*, v. 15, no. 1, pp. 73–74, July 1963)

Until recently, investigations into the production of liquid lasers were carried out on systems having solutions of either rare-earth salts or their complexes as the working substance. Luminescent solutions of organic substances did not appear to be suited to such applications because of the diffuseness of their spectra and the short lifetime of the excited state, thus preventing the attainment of a sufficient degree of population inversion. In the present investigation the possibility is considered of producing a population inversion in solutions of organic substances whose dissociation constants exhibit a strong shift in the excited state as compared with the ground state.

630. INTRAMOLECULAR QUENCHING OF FLUORESCENCE IN SOLUTIONS OF ORGANIC COMPOUNDS

Aristov, A. V., Sveshnikov, B. Ya.
Optika i Spektroskopiya, Akademiya Nauk SSSR, Otdelenie Fiziko-Matematicheskikh Nauk, Sbornik Statei,
v. 1, pp. 58–60, 1963

The devising of experiments to indicate the states involved in radiationless deactivation is discussed.

631. EFFECT OF EXCITON DIFFUSION ON THE KINETICS OF LUMINESCENCE

Konobeev, Yu. V.
Optika i Spektroskopiya, Akademiya Nauk SSSR, Otdelenie Fiziko-Matematicheskikh Nauk, Sbornik Statei,
v. 1, pp. 135–147, 1963

The effect of the reabsorption and excitonic mechanisms of transfer of electronic energy of excitation on quantum yield and mean life luminescence of molecular crystals was studied theoretically. In some cases approximate formulas are obtained. Only luminophores with negligible reflection of luminescent light on the sample surface are considered. The method could be used in the case of crystals with finite thickness. Anthracene is discussed as an example.

632. APPLICATION OF THE ADDITIVE STATISTICAL METHOD FOR THE STUDY OF FLUORESCENT AND ABSORPTION SPECTRA

Maslov, P. G.
In "Advances in Molecular Spectroscopy. Proceedings of the IVth International Meeting on Molecular Spectroscopy, Bologna, Italy, 1959," Volume 1, pp. 266–287
Mangini, A., Editor
Pergamon Press, Ltd., London, England, and
The Macmillan Co., New York, 1962

The method was applied to ionization potential, dipole moment, bond length, and molecular refraction of simple and halogenated hydrocarbons, as well as to fluorescent and absorption spectra of substituted anthracenes, naphthalenes, and diphenylpolyenes. Tables of calculated and experimental values are presented.

633. DECAY OF PHOSPHORESCENCE FROM A DISTRIBUTION OF TRAPPING LEVELS

Medlin, W. L.
***Physical Review*, v. 123, no. 2, pp. 502–509, July 15, 1961**

In a previous paper it was shown that the usual model for second-order decay predicted the correct form for the decay in many thermoluminescent crystals but gave the wrong behavior for the parameters involved. Specifically, it was shown that b and m in the decay expression, $I = I_0[b/(b+t)]^m$, should behave differently as functions of the decay temperature and the degree of trap filling than is observed experimentally at temperatures near or below the glow peak. In the present paper it is shown that the discrepancies can be accounted for by assuming a first-order decay from a distribution of trapping levels. Most of the results are based on a gaussian distribution, but it is shown that other distributions can produce similar results. The first-order mechanism is justified by considering the relative magnitudes of the rate constants for trap emptying, retrapping, and recombination. At temperatures well above the glow peak this assumption is no longer justified, but in this range the second-order decay predicts the observed results for b and m. The effects of retrapping and of crystal dimensions are considered. Also, the effect on the glow peak of having a distribution of levels rather than a set of discrete levels is worked out, and it is shown that the peak is broadened appreciably even for relatively narrow distributions.

634. HALL EFFECT IN IMPURITY CONDUCTION

Holstein, T.
***Physical Review*, v. 124, no. 5, pp. 1329–1347,**
December 1, 1961

Existence of a nonvanishing Hall effect in the impurity-conduction regime (prevalent at low temperatures and at low impurity concentrations) is demonstrated. The dominant electron transport mechanism is the phonon-induced hopping of charge carriers from occupied to unoccupied majority sites. The basic element of the theory is the existence of a (magnetic) field-dependent contribution to the jump probability between two sites. This contribution is computed and is shown to arise from interference between the amplitude for a direct transition between initial and final sites and the amplitude for an indirect, second-order transition, involving intermediate occupancy of a third site. The case of an ac applied electric field is considered.

635. BOSE–EINSTEIN CONDENSATION OF EXCITONS

Blatt, J. M., Böer, K. W., Brandt, W.
***Physical Review*, v. 126, no. 5, pp. 1691–1692,**
June 1, 1962

This note discusses the question whether quasi particles, such as excitons, i.e., nonlocalized excited states of solids, can fulfill necessary conditions for a Bose–Einstein condensation, and whether such condensation can be observed. Although uncertainties of present data on excitons preclude precise numerical predictions, it is concluded that under certain experimentally attainable circumstances excitons fulfill the necessary conditions; i.e., condensation is possible. Ways of detecting the condensation are considered, and a specific experiment is proposed.

636. COLOR AND POLARIZABILITY OF CONJUGATED CHAIN-MOLECULE

Murai, T.
***Progress of Theoretical Physics*, Kyoto, v. 27, no. 5,**
pp. 899–935, May 1962

The electronic excitation of long conjugated chain molecules is studied by Tomonaga's method of collective motion. One of the most elementary modes of collective motion is the dipole oscillation. Assuming the occurrence of this oscillation for π-electrons in the conjugated chain, it is found that, for cyanine dyes which contain C–C bonds of equal length, the wavelength of absorption increases nearly in proportion to their chain length, while for carotenoids which contain alternating bond lengths, the wavelength of absorption approaches a finite value with increasing chain lengths of carotenoids. When the classical polarizability is introduced, the energies of excitation are reduced by a small amount. It is found that the introduction of the classical polarizability or the effect of depolarization corresponds to the mixing of configurations. (*PA*, 1962, #14,345)

637. ELECTRONIC SPECTRA AND ELECTRON-TRANSFER INTERACTION BETWEEN ELECTRON DONOR AND ACCEPTOR

Nagakura, S.
***Pure and Applied Chemistry*, v. 7, no. 1, pp. 79–92, 1962**
(Paper presented at the International Symposium on Molecular Structure and Spectroscopy, Tokyo, Japan, September 10–15, 1962)

The concept of intramolecular charge-transfer absorption band was developed by the author and Tanaka, and also by Longuet-Higgins and Murrell, by analogy with Mulliken's theory for intermolecular cases. A dominant characteristic of this concept is that systems where electron donating and accepting groups are combined with each other directly, or through a bridge of conjugated double bonds, generally show additional absorption bands characteristic of the interaction between electron donor (D) and acceptor (A). In other words, it may be said that absorption bands of this kind appear additionally as the result of the contribution of so-called charge-transfer (CT) structures $A^{-}-D^{+}$ to the resonance hybrid. It is suggested that the appearance of CT bands be regarded as evidence for the existence of electron transfer interaction between D and A. In reality the situation generally becomes more complicated, since locally excited configurations, which contain electron excitation within each component, take part in the configuration interaction.

During the past few years, various investigations have been carried out on the nature of intra- and intermolecular CT absorption bands from both the theoretical and experimental points of view. In this paper some important results, mainly concerning intramolecular cases, are reported. Discussion is given concerning acetic acid, formamide, and nitrobenzene. Data for thioacetamide, thiourea, nitromesitylene, and benzoic acid are also presented.

638. THE THEORY OF CHARGE-TRANSFER SPECTRA

Murrell, J. N.
***Quarterly Reviews*, London, v. 15, no. 2, pp. 191–206, 1961**

The term charge-transfer absorption may be used whenever there is a large electron displacement in going from the ground to the excited state. The energy and intensity of the charge-transfer bands are discussed. A mathematical treatment is presented. It is impossible in general, to separate the electronic states of the system into those which have and those which do not have a charge-transfer character.

639. A CONSIDERATION ON THE TRAPPING REGION OF FREE RADICALS IN IRRADIATED POLYETHYLENE

Kashiwabara, H.
***Reports on Progress in Polymer Physics in Japan*, v. 6, pp. 257–260, 1963 (in English)**
(Available through Kobayasi Institute of Physical Research, Kokubunji, Tokyo, Japan)

In the present note, several features of the stable free radical of allyl type are summarized, and the part of the polymer in which the radicals may be trapped is discussed in connection with the morphological knowledge of polymer crystals.

640. THE LUMINESCENCE OF ORGANIC MOLECULAR CRYSTALS

Hochstrasser, R. M.
***Reviews of Modern Physics*, v. 34, no. 3, pp. 531–550, July 1962**

An attempt is made to relate the chemical approach to spectroscopy of molecular crystals to theoretical explanations in terms of solid-state physics. The first section considers exciton theory applied to the luminescence of organic substances, also molecular vibrations, polarization effects, the influence of lattice defects, nonradiative degradation of excitation energy, and the importance of triplet states. The second section describes fluorescence spectra classified as sharp, broad, and diffuse. The final section deals with the relationship of theory to experiment. In most cases it is difficult to identify mechanisms derived from theory in the experimental results, and in particular to explain the occurrence of slow fluorescence. (*PA*, 1962, #23,608)

641. RING CURRENTS AND THEIR EFFECTS IN AROMATIC MOLECULES

Hall, G. G., Hardisson, A.
***Royal Society of London, Proceedings of the, Series A—Mathematical and Physical Sciences*, v. 268, no. 1334, pp. 328–338, July 24, 1962**

The form of the localized orbitals needed to describe the properties of an aromatic molecule in the presence of a magnetic field is discussed using the standard excited state. The ring currents induced by an external field give rise to contributions to the diamagnetic anisotropy and to the shielding of the nuclear dipole of an attached proton. Both of these effects are calculated on the basis of the self-consistent form of molecular orbital theory. For this purpose the perturbation equations are solved iteratively, and results are given for some hydrocarbon molecules.

642. STATIC JAHN–TELLER DISTORTIONS IN THE SMALL MOLECULES: CH_4^+, CF_4^+, NH_3^+ (EXCITED STATE) AND NH_3 (EXCITED STATE)

Coulson, C. A., Strauss, H. L.
***Royal Society of London, Proceedings of the, Series A—Mathematical and Physical Sciences*, v. 269, no. 1339, pp. 443–455, October 9, 1962**

The potential-energy curves corresponding to arbitrary displacements of the atoms in the four small molecules concerned were estimated by the use of the Hellmann–Feynman theorem and some simple assumptions about the location and distribution of the total electronic charge. Some necessary values of the relevant force constants are taken from spectroscopic work. It is shown that in CH_4^+ and the excited state of NH_3^+, where the electron has been taken from a bonding orbital, the static Jahn–Teller displacement in the equilibrium configuration is large, and in CH_4^+ the important normal coordinate increases by as much as 0.23 Å. In CF_4^+ and the excited state of NH_3, where the bonding electrons are almost unaffected, the static distortion is much less, and is of the order of 0.02 Å for the important coordinate in CF_4^+. (*PA*, 1962, #22,983)

643. THE COUPLING BETWEEN ELECTROMAGNETIC WAVES AND EXCITATION WAVES IN A MOLECULAR CRYSTAL

Hall, G. G.
***Royal Society of London, Proceedings of the, Series A—Mathematical and Physical Sciences*, v. 270, no. 1341, pp. 285–294, November 13, 1962**

Analysis is given of some of the approximations involved in the electrostatic calculation of the dipole–dipole forces between molecules in an excited state of a molecular crystal. It is shown that there is a close analogy between the quantum mechanical theory of these excited states and the classical theory of the vibrations of an ionic crystal. The theory of long waves developed by Born and Huang for an ionic crystal is adapted for a molecular crystal which has one molecule in each unit cell. This enables the effects due to the coupling of the transverse excitation waves and the electromagnetic waves, the retardation of the forces, the molecular polarizability, and the non-analytic behavior of the energy bands to be included in the theory. A further modification of the theory allows for the finite lifetime of the excited state and produces changes in the energy bands, the extinction coefficient, and the reflectivity.

644. THE USE OF GENERAL MODELS FOR THE INTERPRETATION OF THE ELECTRONIC SPECTRA OF COMPLEX ORGANIC MOLECULES

Mason, S. F.
***Tetrahedron*, v. 19, Supplement 2, pp. 265–276, 1963**

General models are devised for the collective treatment of the electronic spectra given by a group of structurally related molecules. The use of symmetry relations is illustrated by an analysis of the long-wavelength absorption of di- and triarylmethyl ions—diphenyl, triphenyl, bis(*p*-biphenylyl), bis(*p*-biphenylyl)methyl, tris(*p*-biphenylyl), and tris(*m*-biphenylyl).

Hückel orbitals of homonuclear π-electron models are employed to interpret the spectra of analogous heteronuclear conjugated molecules, and the general scope of spectroscopic applications of the Hückel theory is discussed.

645. THE ELECTRONIC SPECTRA OF SUBSTITUTED AROMATIC HYDROCARBONS

Murrell, J. N.
***Tetrahedron*, v. 19, Supplement 2, pp. 277–287, 1963**

A critical comparison is presented of the quantum mechanical models which may be used for interpreting the spectra of substituted aromatic hydrocarbons. The model based on electronic states of the isoelectronic, equivalent hydrocarbon is supported by the experimental fact that replacing a C atom by O or N in a conjugated system usually has only a small effect on the positions of the π–π absorption bands. In the case of the other model in which states are built up from orbitals localized either on the hydrocarbon or on the substituent, the states are divided into two classes: those involving an excitation between different orbitals of the hydrocarbon, or between different orbitals of the substituent, and those involving the transfer of an electron between the hydrocarbon and the substituent.

646. THE ANALYSIS OF ELECTRON SPECTRA OF MOLECULAR CRYSTALS

Gnoprienko, M. I.
***Ukrains'kii Fizichnii Zhurnal*, v. 7, no. 2, pp. 179–191, 1962**

The principles of the theory developed for free molecules are applied to the study of the energetic states of molecular crystals to which "localized" excitons correspond. A study of the spectra of molecular crystals is of interest in connection with the possibility of determining the polarization of electron transitions. As the polarization of transitions is closely related to the symmetry of the molecule, the possibility arises of determining the structure of the molecule on the basis of a study of the polarization of electron-oscillatory transitions. In addition, an analysis of the spectra permits interpreting the oscillation of molecules. As an illustration an analysis is given of the spectra of high temperature modifications of metaxylol crystals at 20°K in polarized light. The existence of electron transitions polarized along the x, y, and z axes of molecules is established. In addition, the existence is established of other electron transitions, the polarization of which does not coincide with the axes of the molecule. It is shown that the appearance of these transitions is due to slight deviations of the symmetry of the molecule from C_{2v}. A complex study of the polarization of electron-oscillatory transitions and the symmetry and form of the corresponding oscillations may be utilized for determining the real structure of the molecule. As an example the author considers the value of the oscillation of the bond R_{ap}–C for determining the deviations of this bond from the plane parallel to the carbon ring of the molecule. An interpretation of the basic molecular oscillation is given. (*PA*, 1962, #18,822)

647. THE EXCITED STATES OF HELICAL POLYMERS

Khoffmann, R.
***Vestnik Moskovskogo Universita, Seriya III, Fiziki, Astronomii*, v. 17, no. 1, pp. 69–77, 1962**

Various methods of theoretical treatment of the excited states are considered. Polymers containing chromomorphs (a group of atoms in the monomer molecule producing characteristic 1800-Å absorption) are considered. Examples are nucleic acids, with purines and pyrimidines as chromomorphs, and isotactic polystyrenes with the aromatic ring acting as chromomorph. Results of Tinoco's work are compared with these.

648. THE PRIMARY PHOTOCHEMICAL STEP IN PHOTOSYNTHESIS: A COMPARISON OF TWO THEORIES

Franck, J., Rosenberg, J. L., Weiss, C., Jr.
In "Luminescence of Organic and Inorganic Materials," International Conference Proceedings, New York University, N.Y., 1961, pp. 11–29
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N.Y., 1962

Observations of fluorescence, afterglow, and absorption spectra of chlorophyll *in vivo* and *vitro*, together with chemical kinetic data on photosynthesis rates under a variety of external conditions, have led the authors to a theory of the primary photochemical steps of photosynthesis.

Another theory, based on evidence of photoionization of chlorophyll in the chloroplasts, has been proposed several times and recently has been presented in more detailed form by Calvin, et al.

This paper contains a survey of the status of both theories, and a comparison of their conclusions with the available experimental evidence.

649. A SUMMARY OF QUENCHING STUDIES OF ENERGY TRANSFER IN ORGANIC SYSTEMS

Brown, F. H., Furst, M., Kallmann, H. P.
In "Luminescence of Organic and Inorganic Materials," International Conference Proceedings, New York University, N.Y., 1961, pp. 100–109
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N.Y., 1962

Quenching studies afford a convenient method for discriminating between the possible processes of nonradiative energy transfer. The similarities of the concentration dependence of energy transfer from solvent to solute to that of solvent quenching within the solvent system, and of the concentration dependence of energy transfer in liquids to that in rigid systems, show the importance of energy transport by migration in both liquid and rigid systems.

Further support for migration is found in the reduction of quenching rate obtained upon dilution with a nontransferring liquid. The connection of energy transfer and quenching by the energy transport process is demonstrated by the use of *o*-terphenyl as a quencher in liquid systems. It is found that this compound acts both as a quencher and as an energy transferring agent.

650. DECAY AND POLARIZATION OF FLUORESCENCE OF SOLUTIONS
Jablonski, A.
In "Luminescence of Organic and Inorganic Materials," International Conference Proceedings, New York University, N.Y., 1961, pp. 110–11
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N.Y., 1962

It is shown that measurements of the polarization of fluorescence of an isotropic luminophor, together with measurements of the mean durations $\tau^{\parallel}$ and $\tau^{\perp}$ of the components $I^{\parallel}$ and $I^{\perp}$ of the fluorescence parallel and perpendicular to the electric vector of plane polarized exciting light permit one, in the simplest cases, to obtain some new information on the processes causing depolarization of fluorescence. If the total fluorescence intensity I (emitted in all directions) decays according to $I(t) = I_0 \exp(-t/\tau)$ and its emission anisotropy $r = (I^{\parallel} - I^{\perp})/(I^{\parallel} + 2I^{\perp})$ according to $r(t) = r_0 \exp(-\phi t)$, such measurements permit the evaluation of both r_0 and ϕ (t is the decay time and τ the mean duration of total fluorescence; ϕ is a constant). It follows from the theory given by F. Perrin that in the case of fluorescent solutions, in which depolarization is caused by thermal rotations of luminescent molecules, $\phi = kT/v\eta$ (v is the volume of the luminescent molecule together with its solvation shell, η the viscosity coefficient of the solvent, and k and T have the usual meanings), provided that the rotations of the molecules are governed by the laws of Brownian rotation of spherical particles. Thus, in addition to r_0, v can also be evaluated. Appropriate experiments were performed by R. Bauer.

651. THEORY OF WEAK-FIELD EPR TRANSITIONS AMONG THE SUBLEVELS OF THE LOWEST TRIPLET STATE OF ETHYLENE
Csavinszky, P.
In "Luminescence of Organic and Inorganic Materials," International Conference Proceedings, New York University, N.Y., 1961, pp. 263–270
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N.Y., 1962

The present work investigates how the lowest triplet state of linear hydrocarbon molecules with one double bond is expected to behave in EPR experiments when circularly polarized RF fields are applied and the spin–constant magnetic field interaction is smaller than the spin–spin interaction. The approach is based on perturbation theory and the ethylene molecule is discussed in the π-electron approximation. The coordinate system is chosen in such a way that the C–C direction in the ethylene molecule coincides with the z-direction. The present treatment of EPR transitions is restricted to the case of a weak constant magnetic field.

652. THE FRANCK-CONDON PRINCIPLE APPLIED TO SOLUTIONS OF AROMATIC COMPOUNDS
Lippert, E.
In "Luminescence of Organic and Inorganic Materials," International Conference Proceedings, New York University, N.Y., 1961, pp. 271–273
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N.Y., 1962

The electronic structure of *p*-cyano-dimethylaniline is composed mainly of two resonance structures, a nonpolar one and a highly polar one with a positive charge on the amino nitrogen and a negative charge on the cyano nitrogen. The molecule emits a fluorescence band which is polarized in the direction of the long axis. This compound emits not only one fluorescence band—the long wavelength band—but it possesses also a second fluorescence band. The mechanism underlying the fluorescence is explained.

653. π^*–n TRANSITIONS
Lippert, E.
In "Luminescence of Organic and Inorganic Materials," International Conference Proceedings, New York University, N.Y., 1961, pp. 274–275
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N.Y., 1962

The spectrum of 9,10-diaza-phenanthrene is considered. This compound, unlike quinoline and pyridazine, emits fluorescent light. A $\pi^* \leftarrow n$ absorption band is exhibited and a $\pi^* \rightarrow n$ fluorescence is also noted. Comments are made regarding the separation of the phosphorescence and fluorescence bands.

654. INTERACTION OF THE VIBRATIONAL AND ELECTRONIC MOTIONS IN SOME SIMPLE CONJUGATED HYDROCARBONS. I. EXACT CALCULATION OF THE INTENSITY OF THE ${}^1A_{1g} \rightarrow {}^1B_{1u}$, ${}^1B_{2u}$ VIBRONIC TRANSITIONS OF BENZENE
Liehr, A. D.
***Zeitschrift für Naturforschung*, v. 13a, no. 4, pp. 311–335, April 1958 (in English)**

The finite intensities of the forbidden bands of 50,000 and 39,500 cm^{-1} are attributed to the interaction of rotational, vibrational, and electronic motions. The effect of the latter two is calculated; a form of perturbation theory suitable for computation is developed. Calculated oscillator strengths are 0.26 and 0.003, as opposed to experimental values of 0.1 and 0.002. Error due to incipient breakdown of the perturbation formulae is discussed, as are the large errors in the relative intensities of the vibrational components of the bands.

655. INTERACTION OF THE VIBRATIONAL AND ELECTRONIC MOTIONS IN SOME SIMPLE CONJUGATED HYDROCARBONS. II. ALGEBRAIC EVALUATION OF THE INTEGRALS
Liehr, A. D.
***Zeitschrift für Naturforschung*, v. 13a, no. 6, pp. 429–438, June 1958 (in English)**

An account is given of the evaluation of a number of integrals, not previously published, which were involved in a calculation of intensities of vibronically allowed transitions in the spectrum of benzene. (*PA*, 1959, #731)

656. INTERACTION OF THE VIBRATIONAL AND ELECTRONIC MOTIONS IN SOME SIMPLE CONJUGATED HYDROCARBONS. III. A SEMIEMPIRICAL FORMULATION

Liehr, A. D.
***Zeitschrift für Naturforschung*, v. 16a, no. 7, pp. 641–668, July 1961 (in English)**

A semiempirical theory of vibrational and electronic reciprocation, in both degenerate and nondegenerate electronic states, is developed under the assumptions that (1) a molecule may be accurately described by the adiabatic approximation; (2) solutions of the electronic and vibrational Schrödinger equations for some fixed molecular conformation are available; (3) the electronic wave functions may be analytically continued to vicinal geometries; (4) the power series expansion of the electronic wave functions and Hamiltonian operator, in terms of nuclear displacements, may be truncated at degree two; and (5) first-order perturbation theory is applicable. The formulae derived for non-degenerate electronic distributions are employed to compute the intensities of the Herzberg–Teller (1933) "vibronic" type absorptions of normal benzene, the cyclopentadienide ion, and the tropylium ion. For convenience in numerically evaluating the requisite phenomenological vibronic constants, the Lennard Jones (1937) approximation is introduced. The resultant accord of experiment and theory is good. To test the deduced mathematical expressions for either essentially or fortuitously degenerate electronic dispositions, extremal energy calculations are performed for the cyclobutadiene and benzene molecules, the cyclotadienyl radical, and the benzene plus one ion. It is found, in agreement with the Jahn–Teller theorem (1937), that all these systems are configurationally unstable with respect to some asymmetric nuclear displacement. The utilization of the Lennard-Jones approximation again permits a numerical specification of the required vibronic parameters. Application is then made to the ultraviolet spectrum of benzene: the second singlet absorption and the Rydberg spectrum are theoretically interpreted in the light of the reckoned predictions.

An attempt is made to answer the four cogent queries of Wilkinson concerning the nature of Jahn–Teller interactions in the Rydberg spectrum of benzene. A mathematical and pictorial description of the nuclear dynamics of Jahn–Teller and Herzberg–Teller molecules is also given, and the portraitures of the underlying potential surfaces are verbally and diagrammatically painted. In addition, a critical discussion of the reality of both the computational techniques and of the emergent algebraic forms is presented, and paths for future progress are indicated. A critical discussion on the misuse of the phrase "Jahn–Teller effect" is appended; it is recommended that its use be restricted to the dynamical manifestations of the theorem of Jahn and Teller (e.g., forbidden asymmetric vibrational progressions and abnormal paramagnetic behavior). Statical demonstrations of the theorem are better ascribed to intrinsic Jahn–Teller instability. (*PA*, 1961, #17,309)

657. BEOBACHTUNG VON ELEMENTARPROZESSEN AN ANGEREGTEN MOLEKÜLEN. CYCLOHEXAN (ELEMENTARY PROCESSES IN EXCITED MOLECULES. CYCLOHEXANE)

Schüler, H., Arnold, G.
***Zeitschrift für Naturforschung*, v. 17a, no. 8, pp. 670–675, August 1962**

658. DER EINFLUSS DES LÖSUNGSMITTELS AUF DIE ELEKTRONENSPEKTREN LUMINESZIERENDER MOLEKÜLE (EFFECT OF THE SOLVENT ON THE ELECTRON SPECTRA OF LUMINESCING MOLECULES)

Bilot, L., Kawski, A.
***Zeitschrift für Naturforschung*, v. 18a, no. 1, pp. 10–15, January 1963**

Bachschiew's fluorescence spectroscopic investigation on dissolving of phthalimide compounds is compared with the theory concerning the influence of the solvent on the electron spectra of the molecule. The equations obtained permit determination of the dipole moments of the excited states and also the angle between the dipole moments in ground and excited states.

659. BEOBACHTUNG VON ELEMENTARPROZESSEN AN ANGEREGTEN MOLEKÜLEN. II. *n*-BUTAN (ELEMENTARY PROCESSES IN EXCITED MOLECULES. II. *n*-BUTANE)

Schüler, H., Arnold, G.
***Zeitschrift für Naturforschung*, v. 18a, no. 1, pp. 15–19, January 1963**

(For Part I, see Entry #657.) Products formed by dissociation of excited *n*-butane by electron impact in the glow discharge are explained by innermolecular processes. A reaction scheme is discussed for the formation of the observed C$_2$- and C$_3$-hydrocarbons, which follow from cleavage of one or two C–C bonds. The experimental results establish this reaction scheme quantitatively within an error of 5%.

660. BEOBACHTUNG VON ELEMENTARPROZESSEN AN ANGEREGTEN MOLEKÜLEN. III. CYCLOHEXAN 2. TEIL (ELEMENTARY PROCESSES IN EXCITED MOLECULES. III. CYCLOHEXANE PART 2)

Schüler, H., Arnold, G.
***Zeitschrift für Naturforschung*, v. 18a, no. 5, pp. 604–607, May 1963**

In a previous paper it has been shown that C$_3$:C$_3$, C$_4$:C$_2$, and C$_2$:C$_2$:C$_2$ cleavages of the ring occur by primary dissociation processes of excited cyclohexane molecules. The percentage portions of the reaction products formed are constant within the different groups of cleavage. They have been explained by simple reaction schemes. Now it will be shown that a regularity exists also between these three different dissociation processes. It is remarkable that the C_4:C_2 and the C_2:C_2:C_2 dissociation processes are coupled and that the three dissociation processes discussed occur with integral intensities.

661. DIE BEEINFLUSSUNG DER FLUORESZENZ VON MOLEKÜLEN DURCH EIN ÄUSSERES ELEKTRISCHES FELD I. THEORIE (INFLUENCE OF AN EXTERNAL ELECTRIC FIELD ON THE FLUORESCENCE OF MOLECULES. I. THEORY)

Liptay, W.
***Zeitschrift für Naturforschung*, v. 18a, no. 6, pp. 705–718, June 1963**

The change of orientation of excited molecules which are capable of fluorescence is treated as a kinetic phenomenon. The application of the equations allows determination of the dipole moment of the excited state in suitable molecules. In an example, the dipole moment of *p*-dimethylamino-*p*′-cyanostilbene is calculated and the value found to be in good agreement with experimental data. The theory is applicable to molecules with or without permanent dipole moment and with isotropic or anisotropic polarizability. (For Part II, see Entry #813.)

662. ÜBER DIE TEMPERATURABHÄNGIGKEIT DER LICHTABSORPTION DURCH EXCITONEN (THE TEMPERATURE DEPENDENCE OF THE LIGHT ABSORPTION BY EXCITONS)

Biem, W.
***Zeitschrift für Physik*, v. 164, no. 2, pp. 199–221, August 3, 1961**

The temperature dependence of the absorption of light by excitons is considered. The eigenfunctions of the excitons are those of the vibrating crystal, introduced by Tjablikow, Lee, Low, and Pines. The model can only be used if the coupling between excitons and crystal vibrations is weak. The results are expressions for the production of excitons and simultaneous absorption or emission of phonons.

663. DIE INTENSITÄT VON ELEKTRONENÜBERFÜHRUNGSBANDEN IN ELEKTRONEN-DONATOR-AKZEPTOR-KOMPLEXEN (INTENSITY OF ELECTRON TRANSITION BANDS IN ELECTRON DONATOR-ACCEPTOR COMPLEXES)

Briegleb, G., Czekalla, J.
***Zeitschrift für Physikalische Chemie, Neue Folge*, Frankfurt, v. 24, no. 1, pp. 37–54, April 1960**

A relation is set up between $\varepsilon_{\max}$ (extinction coefficient), $h\nu_{\max}$, and R_N (resonance energy of complexes): $\varepsilon_{\max} = (7.7 \times 10^4)/(h\nu[R_N] - 3.5)$ If R_N is unknown, the equation can be used to estimate the range in which $\varepsilon_{\max}$ is to be expected. A great part of the experimental data lies within this range. Deviations are discussed.

664. ÜBER EINE LINEARE BEZIEHUNG ZWISCHEN DEN ANODISCHEN HALBSTUFENPOTENTIALEN UND DEN LANGSTWELLIGEN ABSORPTIONSBANDEN BEI ORGANISCHEN VERBINDUNGEN (A LINEAR RELATION BETWEEN THE ANODIC HALF-STEP POTENTIALS AND THE LONGEST-WAVE ABSORPTION BANDS IN ORGANIC COMPOUNDS)

Stanienda, A.
***Zeitschrift für Physikalische Chemie, Neue Folge*, Frankfurt, v. 33, no. 1–4, pp. 170–180, July 1962**

Linear relations are found in organic compounds with conjugated double bonds between the maximum of the longest-wave absorption bands and the anodic half-step potentials which are explained by the relative position of the terms. The relation has the general form: $E_{1/2} = a + b\nu$, where ν = wave number in cm^{-1}, and a and b are constants within a group of compounds. 26 references.

665. THE NATURE OF EXTINCTION OF CHLOROPHYLL FLUORESCENCE BY OXIDIZING AND REDUCING AGENTS

Dilung, J. J., Chernyuk, [illegible]
***Zhurnal Fizicheskoi Khimii*, v. 37, no. 5, pp. 1100–1105, May 1963**

Both oxidizing and reducing agents may play the part of extinguishers of fluorescence in the case of chlorophyll-type pigments. With oxidizing agents the extinction is greater the stronger the electron acceptor activity of the agent and the electron donor activity of the pigment. The reverse is true for reducing agents. This indicates that underlying the fluorescence extinction process is the reversible transfer of an electron between the fluorescent molecule and the extinguishing agent. This is further confirmed by the photochemical electron transfer reactions which take place in all cases of prolonged irradiation.

666. THE MOLECULAR ORBITAL SELF-CONSISTENT-FIELD DETERMINATION OF THE GROUND STATE OF FERROCENE

Shustorovish, E. M., Dyatkina, M. E.
***Zhurnal Strukturnoi Khimii*, v. 1, no. 1, pp. 109–121, May–June 1960**
(Translated from the Russian in *Journal of Structural Chemistry*, v. 1, no. 1, pp. 98–110, May–June 1960; published 1961)

The ground state of ferrocene, Fe $(C_5H_5)_2$, was determined using the MO self-consistent field treatment (Roothaan's modification). The molecular orbitals of the complex consisted of ten MOs representing the ring π-electrons, which were constructed from the $2p_z$ AOs of carbon, and of nine $3d^5\ 4s4p^3$ AOs of iron. The AOs were represented in the form of Slater wave functions. The formulas used for calculating the necessary matrix elements are discussed and their numerical values tabulated. The form and the energies of the MOs in the complex are given. The calculated ionizational potential (6.39 ev) is in a satisfactory agreement with the experimental value (7.05 ev). A detailed discussion of the results will be postponed until the calculations for similar molecules $(C_6H_6)_2Cr$, $(C_5H_5)_2Co^+$, and $(C_5H_5)_2Cr$ are completed.

EXPERIMENT

667. TRANSFER OF TRIPLET-STATE ENERGY IN FLUID SOLUTIONS. I. SENSITIZED PHOSPHORESCENCE AND ITS APPLICATION TO THE DETERMINATION OF TRIPLET-STATE LIFETIMES.

Backstrom, H. L. J., Sandros, K.
***Acta Chemica Scandinavica*, v. 14, no. 1, pp. 48–62, 1960 (in English)**

The photoluminescence spectra of biacetyl, benzil, and anisil, in O-free benzene solutions at room temperature, were determined by using the Hg line at 366 mμ as exciting light. All three substances show mainly phosphorescence, with a mean lifetime exceeding 5 × 10^{-5} sec, but also measurable fluorescence. Addition of an efficient phosphorescence quencher makes it possible to study the fluorescence spectra separately. Measurements on solutions containing both benzophenone and one of the three substances mentioned have shown that the latter may be excited to luminescence also by light primarily absorbed by benzophenone. The spectrum of this sensitized luminescence shows it to be pure phosphorescence. This proves that the sensitization occurs by a transfer of triplet state energy from sensitizer to acceptor. The triplet energy level of benzophenone lies 4000 cm^{-1} above that of biacetyl. From this difference, it is assumed that the transfer of triplet-state energy is a diffusion-controlled process, and the mean life of benzophenone in its triplet state can be calculated from measurements of the intensity of sensitized biacetyl phosphorescence as a function of the concentration of biacetyl. Experimental data are presented and interpreted.

668. FLUORESCENCE OF ADENINE AND INOSINE NUCLEOTIDES

Walaas, E.
***Acta Chemica Scandinavica*, v. 17, no. 2, pp. 461–463, 1963 (in English)**

Adenine and inosine nucleotides were shown to exert native fluorescence, although with low quantum yield. The inosine derivatives showed a low and constant fluorescence emission at any pH value between pH 1–10.0; the adenosine derivatives showed an increase in fluorescence at pH values below 5 which was related to the protonization of the amino group in the 6 position. The attachment of the ribosyl group to adenine increased the fluorescence intensity, but this increase was quenched by phosphate groups.

669. RELATIVE YIELDS OF FLUORESCENCE AND PHOSPHORESCENCE OF BIACETYL IN FLUID SOLUTIONS

Sandros, K., Almgren, M.
***Acta Chemica Scandinavica*, v. 17, no. 2, pp. 552–553, 1963 (in English)**

The phosphorescence mean life and the ratio of fluorescence to phosphorescence quantum yields of 10–15 m*M* biacetyl in benzene and in benzene–isopropyl alcohol solutions were determined, using Hg line 405- to 408-mμ excitation. The effect of gradual change of solvent was studied.

670. LUMINESCENCE PROPERTIES OF SOME PURINES AND PYRIMIDINES. A STUDY BY FLUORESCENCE SPECTROPHOTOMETRY OF THE SITES OF PROTONATION AND OF THE TYPES OF LOWEST EXCITED SINGLET STATES

Borresen, H. C.
***Acta Chemica Scandinavica*, v. 17, no. 4, pp. 921–929, 1963 (in English)**

The fluorescence of the following compounds in aqueous solution at room temperature was determined: adenine, adenosine, adenosine-5′-phosphate, -diphosphate, and -triphosphate, 2-amino-4-methylpyrimidine, benziminazole, 2,6-diaminopurine, guanine, guanine deoxyriboside, guanosine mixture of guanosine-3′- and guanosine-2′-phosphate, guanosine-5′-phosphate, -diphosphate, and -triphosphate, purine, and pyrimidine. The emission and fluorescence excitation spectra of the last compound were determined in Et_2O. It is assumed that transformation of the molecules from a nonfluorescent to a fluorescent form represented the replacement of a *n*, π state by a π, π state as the lowest excited singlet, and that the sites of protonation in acid solution were the N atoms of the heterocyclic rings.

671. LUMINESCENCE OF ADSORBED FLUORESCEIN

Lendvay, E.
***Acta Physica Hungarica*, v. 13, no. 2, pp. 249–252, 1961 (in English)**

The luminescence spectra of fluorescein adsorbed on Al_2O_3 films, prepared by anodic oxidation and treated with basic solutions, were examined. The results indicate that the different emitting centers present are due to different surface OH groups. (*PA*, 1961, #20,022)

672. LUMINESCENCE OF FLUORESCEIN ACTIVATED LAYER PHOSPHORS

Lendvay, E.
***Acta Physica Hungarica*, v. 13, no. 3, pp. 289–302, 1961**
(in English)

The sodium fluorescein adsorption of oxide layers formed on aluminum surfaces produces layer phosphors emitting green light under the excitation of high-pressure mercury vapor lamps. The intensity and energy distribution of the light depends on the physical and chemical structure of the layer. It is established that the activation of the oxide hydrate layers happens by chemisorption and that there is a relation between the hydration of the oxide surface and the energy distribution of the emission. (*PA*, 1962, #4184)

673. THE ROLE OF SURFACE HYDROXILS OF $Al_2O_3 \cdot xH_2O$ IN THE LUMINESCENCE OF ADSORBED FLUORESCEIN MOLECULES

Lendvay, E.
***Acta Physica Hungarica*, v. 13, no. 3, pp. 333–340, 1961**
(in English)

By producing various surface hydroxyl concentrations on Al_2O_3 films by surface reactions, it was found that there is a distinct relation between the emission and the adsorbed fluorescein and the number of —OH groups. The fact that the intensity of emission grows with the surface hydroxyl concentration indicates that the emitting centers are bound to the surface by hydrogen bonds. (*PA*, 1962, #4183)

674. THE LUMINESCENCE OF MANGANOUS PHTHALATE

Lendvay, E., Schanda, J.
***Acta Physica Hungarica*, v. 13, no. 4, pp. 469–471, 1961**
(in English)

The luminescence of manganous salts is discussed briefly. Manganous phthalate was found to be a phosphor and its properties were examined. The spectral distribution of the emission was examined at various temperatures, and it was found that the maximum intensity decreased with temperature rise, and at the same time the wavelength for maximum intensity shifted to shorter wavelengths. (*PA*, 1962, #8583)

675. INVESTIGATIONS OF THE EXTINCTION OF THE FLUORESCENCE OF 3,4-BENZOPYRENE

Morlin, Z., Sátinger, M.
***Acta Physica Hungarica*, v. 14, no. 2–3, pp. 211–216, 1962**
(in English)
(Paper presented at the International Symposium on Luminescence—Entry #495)

As a result of the effect of ozone, or ultraviolet irradiation generating ozone, the fluorescence of 3,4-benzopyrene decreases with increasing time of treatment, i.e., with increased amount of ozone introduced into the samples. At the same time the ultraviolet absorption peaks decrease too. If the treatment continues long enough the fluorescence is extinguished altogether. According to the measurements, the fluorescence intensity vs. time of the ozone treatment obeys a hyperbolic law. (*PA* 1963, #1696)

676. ON THE FUNDAMENTAL POLARIZATION OF THE FLUORESCENCE OF VISCOUS SOLUTIONS

Szalay, L., Gáti, L., Sárkány, B.
***Acta Physica Hungarica*, v. 14, no. 2–3, pp. 217–224, 1962**
(in English)
(Paper presented at the International Symposium on Luminescence—Entry #495)

The fundamental polarization of fluorescein in glycerine-water solutions was photoelectrically studied at a temperature of 30°C, taking into account the spectral characteristics of polarization, the rotation depolarization, the concentration depolarization and the influence of the secondary luminescence. The secondary luminescence was shown to play an important role, and after allowing for it, an experimental value of the fundamental polarization very near to the theoretical one, viz., 0.5, was found, contrary to earlier results. Some conclusions were drawn relating to the torsional vibration, solvation effects, etc. (*PA*, 1963, #1697)

677. CONCERNING THE ABSORPTION AND LUMINESCENT SPECTRA OF SOME DYES IN MONO- AND POLYMETHYL METHACRYLATE

Kawski, A., Polacka, B., Polacki, Z.
***Acta Physica Polonica*, v. 20, no. 11, pp. 903–914, 1961**
(in German)

The absorption and emission spectra of fluorescein, eosin, rhodamine B and rhodamine 6G were measured as solutions in methyl methacrylate (monomer and polymer), ethyl alcohol, and glycerin. When methyl methacrylate containing eosin is polymerized with ultraviolet light, a strong new absorption band appears at about 460 mμ. This band fades after ten days. Shifts in the positions of the absorption and emission maxima for all the solutions are dependent upon an interaction between the solvent and the solute. (*PA*, 1962, #9281)

678. EFFECT OF pH ON THE FLUORESCENCE OF FLUORESCEIN SOLUTIONS

Rozwadowski, M.
***Acta Physica Polonica*, v. 20, no. 12, pp. 1005–1017, 1961**
(in English)

The absorption and emission spectra, mean decay time, relative yield, and anisotropy of fluorescence emission of a fluorescein solution of a constant concentration of 10^{-5} g/cm^3 were investigated with respect to their dependence on the pH of the medium. The absorption and emission spectra were found to vary according to the pH value. This pH effect can be explained by the giving off of a proton by the molecule in the excited state. (*PA*, 1962, #2724)

679. ABSORPTION AND FLUORESCENCE SPECTRA OF FLUORESCEIN IN PMAM

Kawski, A., Polacka, B.
***Acta Physica Polonica*, v. 21, no. 2, pp. 193–195, 1962**
(in German)

680. DEPOLARIZATION OF FLUORESCENCE OF DYE SOLUTIONS BY THERMAL MOTION OF THE MOLECULES

Bauer, R., Szczurek, T.
***Acta Physica Polonica*, v. 22, no. 1, pp. 29–36, July 1962**
(in English)

By means of a high precision polarimeter, the fluorescence emission anisotropy of uranine in its dependence on the viscosity of the solution for different binary solvents (glycerol + ethanol, glycerol + methanol, glycerol + water) was investigated. In cases of even small water content in the solvent, the well-known deviations from the relations resulting from Perrin's theory (1962) of depolarization of fluorescence of solutions by thermal rotation of the luminescent molecules were found to occur. Such deviations are explained by the effect of water on the solvation envelope of the luminescent molecule. The volume and constitution of the solvation layer vary with the water percentage of the solvent. Hence, the moment of torsion acting on the luminescent molecule changes, affecting the depolarization by torsional vibrations of the molecules, not considered in Perrin's theory. The change in volume on the solvation layer effects depolarization by thermal rotation. Such changes in volume were found by one author (Bauer) in the course of experiments not yet published. (*PA*, 1963, #139)

681. INFLUENCE OF NEUTRAL SALTS ON THE PHOTOLUMINESCENCE OF VARIOUS IONIC FORMS OF FLUORESCEIN

Głowacki, J., Kamińska, U.
***Acta Physica Polonica*, v. 23, no. 1, pp. 43–51, 1963**
(in English)

Several properties of the univalent anion of fluorescein, identified in 1958 by Zanker and Peter, were studied. Neutral aqueous solutions in which three ionic forms of fluorescein (univalent and bivalent anions and neutral molecules) exist simultaneously were investigated. It was found that under the influence of quenchers of the neutral salt type (KCl, KBr, KCNS, KI) which are strong electrolytes, the univalent anion of fluorescein dissociates. It follows from an analysis of the absorption spectra that the bivalent anion and a proton are products of this dissociation. This protolytic process is accompanied by an increase in the luminescence intensity. The quenching of the luminescence is again observed for large concentrations of salts of particularly strong quenchers. (*PA*, 1963, #7212)

682. FOREIGN ADDITIVE QUENCHING IN LUMINESCING DYESTUFF SOLUTIONS

Szöllősy, L.
***Acta Universitatis Szegediensis, Pars Physica et Chemica Scientiarum Naturalium, Acta Physica et Chemica*,**
v. 8, no. 1-2, pp. 8–15, 1962 (in German)

The quantum yield for fluorescence of Na fluorescein in aqueous solutions of pH 12.5 was measured over the range of concentration of 10^{-3} to 5×10^{-6} mole/l of dye with 5×10^{-1} to 10^{-3} mole/l of KI as quencher. Corrections were made for reabsorption of fluorescence and secondary luminescence. The yield was largely independent of dye concentration; its variation with KI concentration was compared with earlier work, and with previous theoretical formulae of which Jablonski's gives the best fit. (*PA*, 1963, #3807)

683. LUMINESCENCE AND SCINTILLATION PROPERTIES OF SOME ORGANIC MIXED CRYSTALS

Naboikin, Yu. V., Soifer, L. M., Dobrokhotova, V. K., Uglanova, V. V.
In "Stsintillyatory i Stsintillyatsionnye Materialy, Vsesoyuznyi Nauchno-Issledovatelskii Institut Khimicheskikh Reaktivov, Materialy 2-go [i.e., Vtorogo] Koordinatsionnogo Soveshchaniya po Stsintillyatoram (Scintillators and Scintillation Materials, All-Union Scientific Research Institute of Chemical Reagents, Materials of the 2nd Coordination Conference on Scintillators), Moscow, USSR, 1957," pp. 124–129
Akademii Nauk SSSR, Moscow, 1960

The solubility of additives in naphthalene and the maximum scintillation of the mixed single crystals are given. The additives considered are anthracene, phenanthrene, fluorene, fluoranthene, chrysene, pyrene, triphenylene, *p*-terphenyl, and carbazole. The scintillation of naphthalene without additives is also given. In the system naphthalene–phenanthrene, a transfer of the excitation energy does not occur.

684. SCINTILLATION AND LUMINESCENCE PROPERTIES OF POLYSTYRENE SOLUTIONS OF SOME AROMATIC HYDROCARBONS

Kilimov, A. P., Nagornaya, L. L.
In "Stsintillyatory i Stsintillyatsionnye Materialy, Vsesoyuznyi Nauchno-Issledovatelskii Institut Khimicheskikh Reaktivov, Materialy 2-go [i.e., Vtorogo] Koordinatsionnogo Soveshchaniya po Stsintillyatoram (Scintillators and Scintillation Materials, All-Union Scientific Research Institut of Chemical Reagents, Materials of the 2nd Coordination Conference on Scintillators), Moscow, USSR, 1957," pp. 201–211
Akademii Nauk SSSR, Moscow, 1960

Polystyrene solutions of the following hydrocarbons were studied: biphenyl, diphenylmethane, diphenylethylene, diphenylacetylene, diphenylbutadiene, tetraphenylbutadiene, *p*-terphenyl, fluorene, phenanthrene, 2,5-diphenyloxazole, and 2-(α-naphthyl)-5-phenyloxazole. Absorption spectra were taken in heptane. Luminescence spectra were measured in a monochromator with a photoelectric device. Scintillation properties were measured under irradiation with Ag^{110} emitting γ-rays, 0.1 mc. Within the investigated concentration range, a close relation between luminescence and scintillation properties was established. This points to quantitative conformity between energy transfer and self extinction.

685. LUMINESCENCE OUTPUT OF PLASTIC SCINTILLATORS

Andreeshchev, E. A., Kilin, S. F., Rozman, I. M.
In "Stsintillyatory i Stsintillyatsionnye Materialy, Vsesoyuznyi Nauchno-Issledovatelskii Institut Khimicheskikh Reaktivov, Materialy 2-go [i.e., Vtorogo] Koordinatsionnogo Soveshchaniya po Stsintillyatoram (Scintillators and Scintillation Materials, All-Union Scientific Research Institut of Chemical Reagents, Materials of the 2nd Coordination Conference on Scintillators), Moscow, USSR, 1957," pp. 234–241
Akademii Nauk SSSR, Moscow, 1960

A method for measuring luminescence output is based on polystyrene with additions of 1.5 × 10^{-2}% of 1,1-4,4-tetraphenyl-1,3-butadiene irradiated with Co^{60} γ-rays. The scintillators used were in the form of spherical beads (5–9 mm D) in a plexiglass container placed in a photometric sphere. The luminescence intensity of the scintillators was determined from the difference in the current of the photomultiplier with and without the presence of the specimens in the container.

686. FINE STRUCTURE OF EMISSION SPECTRA OF CARBOXYAMIDO COMPOUNDS

Kobyshev, G. I., Terenin, A. N.
In "Fizika Problema Spectroskopiya, Akademiya Nauk SSSR, Materialy 13-go [Trinadtsatogo] Soveshchanie, Leningrad, 1960," Volume 1, pp. 206–208
Akademii Nauk SSSR, Moscow, 1962

687. TEMPERATURE EFFECTS OF THE DISLOCATION OF ELECTRONIC SPECTRA OF COMPLEX MOLECULES IN SOLUTIONS

Pikulik, L. G.
In "Fizika Problema Spectroskopiya, Akademiya Nauk SSSR, Materialy 13-go [Trinadtsatogo] Soveshchanie, Leningrad, 1960," Volume 1, pp. 297–300
Akademii Nauk SSSR, Moscow, 1962

The electronic spectra (+20 to −196°C) were investigated for 4-aminophthalimide, 4-amino-*N*-methylphthalimide, 4-dimethylamino-*N*-methylphthalimide, 3-aminophthalimide, 3-amino-*N*-methylphthalimide, 3-monomethylaminophthalimide, 3-monomethylamino-*N*-methylphthalimide, 3,6-diacetamido-*N*-methylphthalimide, (chloroamino) maleic imide, and acridine yellow in MeOH, EtOH, PrOH, iso-BuOH, benzyl alcohol, cyclohexanol, glycerol, acetoacetic ester, and dimethylphthalic acid. The regularity in the dislocation of fluorescence spectra is a function of the orientation polarization and relaxation effects of the solvent. Interaction with the environment, which is dependent on the dipole moments, differs in the excited and in the ground states. The distance between the transition levels differs with emission and with absorption. This effect occurs only if the lifetime of the excited state is much greater than the relaxation time of the solvent, which is at room temperature. The dislocation of the emission spectrum begins when the excited state of the phthalimides and the relaxation time of the environment agree. The mirror symmetries of the phthalimide spectra in solutions, both at room and low temperatures, determine the frequency of the electronic transition in the absorption and emission bands.

688. THE POLARIZATION OF THE FLUORESCENCE OF CRYSTALS OF PHTHALIMIDE DERIVATIVES

Sarzhevskii, A. M.
***Akademiya Nauk Belorusskoi SSR, Doklady*, v. 6, pp. 556–559, 1962**

Measurements were made on crystals of 22 derivatives of phthalimide.

689. FLUORESCENT PROPERTIES OF FLUORESCEIN ISOCYANATE

Bozhevolnov, E. A.
In "Metody Lyuminestsentnogi Analiza Materialy VIII Soveshchaniya po Lyuminestsentsii," pp. 65–70
Akademiya Nauk Belorusskoi SSR, Institut Fiziki, 1960
(Paper presented at the Eighth Conference on Luminescence —Entry #497)

The fluorescence of fluorescein isocyanate (I), aluminofluorescein (II), and fluorescein was studied in aqueous, alkaline, and acid media. The fluorescence of I solutions cannot be ascribed to either of the other two compounds which are formed from I. The dependence of intensity of the fluorescence of I and II on the concentration and pH of the medium was measured. The capacity of I to hydrolyze to II was studied and a rapid method given for determining the relative concentrations of the two in mixtures.

690. PHOTOELECTRIC EMISSION FROM SOLID LAYERS OF ORGANIC DYES

Vilesov, F. I., Terenin, A. N.
***Akademiya Nauk SSSR, Doklady*, v. 133, no. 5, pp. 1060–1063, August 11, 1960**
(Translated from the Russian in *Soviet Physics—Doklady*, v. 5, pp. 840–842, 1960)

In the present study layers of rhodamine 6G, erythrosin, β-carotene, metal-free phthalocyanin, and zinc phthalocyanin were investigated. The spectral distribution of the photoemission yield in relative units for some of the layers of dyes investigated is shown on a semilog scale. The distribution of photoelectrons with respect to their kinetic energies for the rhodamine 6C and β-carotene layers is also graphed for various photon energies. The values of the photoelectric work function, which were determined according to Einstein's equation from the energy distribution of photons, and the position of the Fermi level, determined by its position in the backing metal, are tabulated. The measurement error was of the order ± 0.1 ev.

The fundamental conclusions developing out of the present study are the following: (1) the photoelectric work function of layers of dyes has a value of 5.5–6 ev; (2) for different dyes a close similarity is found to exist between the spectral curves for the photoeffect in a quantum energy interval

6–10 ev; (3) a slow-electron group is observed for all of the layers investigated in the present study, which leads to the assumption that the slow electrons are for all of the dyes investigated of the same origin.

In organic dyes the electrons with the least strong bonds are the collectivized π-electrons. In this connection, the great similarity of the spectral photoemission curves and the curves of photoionization of complex organic molecules in the gaseous phase, accompanied by the detachment of one of the π-electrons, is noted. Moreover, the photoionization thresholds of the different classes of dye molecules lie very close to one another, within the limits of 7.0–7.3 ev. The similarity between data on the photoeffect and photoionization cannot be regarded as due to chance, since the dye molecules in a crystal interact relatively weakly with each other and to a certain extent can be considered as retaining their electronic structure.

Proceeding from these data, it is possible to explain the origin of the slow-electron group as follows: The absorbed light quantum energy is expended not only in breaking loose a π-electron and imparting kinetic energy to it, but in exciting the positive ion thus formed. A part of the energy of the absorbed quantum is dispersed as a result by intramolecular oscillations and electron transitions in the positive ion, which leads to failure to fulfill the fundamental law of the photoelectric effect (increase in kinetic energy of electrons with increase in quantum energy). This point of view is also found to be in complete consistency with the results of molecule photoionization.

The fraction of the photon energy dispersed in excitation of the positive ion depends on the structure of the molecule, particularly on the size of interatomic distances of the molecules and corresponding positive ion, and on the type of ejected electrons. If a light quantum is absorbed by an electron participating in the chemical bond, then considerable dispersion of energy in intramolecular oscillations must be expected. On the other hand, if there occurs excitation and breaking away of an electron that does not contribute to the bond, then such dispersion of energy should be only slight, and in the energy distribution of photoelectrons the fast-electron group can be observed. For the different types of electrons contributing to the chemical bonds, the dispersion of energy should also be different.

In the case of the conjugate system of bonds in β-carotene, there are no valence electrons that do not participate in the chemical bond, so that the appearance of the fast-electron group at quantum energies above 10 ev and abrupt increase in photoemission yield in this region can be explained by the ejection of σ-electrons.

691. PHOTOELECTRON EMISSION FROM SOLID LAYERS OF PINACYANOL AND PINAKRYPTOL

Vilesov, F. I., Terenin, A. N.
***Akademiya Nauk SSSR, Doklady*, v. 134, no. 1, pp. 71–73, September 1, 1960**
(Translated from the Russian in *Soviet Physics—Doklady*, v. 5, no. 5, pp. 999–1001, March–April 1961)

The energies and relative yields of photoelectrons from thick, polycrystalline layers of pinakryptol (I) and pinacyanol (II) prepared by deposition from alcoholic solution onto a nickel dish were measured. For photon energies of 7–11 ev, the yields of photoelectrons from the two dyes are similar to each other and to those reported for other dyes, and the logs of yields are proportional to the energies of the incident quanta. Below 7 ev the yield of electrons from I decreases sharply and is approximately 1/10 that from II when 6-ev photons are used. The reason for such low yields is hypothesized. The irradiation of I produces a large yield of electrons with energies of 0.3–0.4 ev, the distribution remaining constant with incident photons of 7 to 10 ev. The number of electrons with energies of 1–3 ev is less than that observed with other dyes. For photon energies <7.5 ev most of the electrons from II have energies of 0.2–2 ev. As the energy of the photons increases, the yield of 0.4-ev electrons increases, and this peak in the curve of yield vs. electron energy broadens as the photon energy increases from 8 to 11 ev. At 10.2 ev the base of the new peak extends from 0.2 to 2 ev. The changes are reminiscent of those observed with Cs_3Sb and Cs_2Te.

692. INVESTIGATION OF ENERGY TRANSFER ALONG A ~CH_2~ CHAIN BY LUMINESCENCE QUENCHING

Gusynin, V. I., Talroze, V. L.
***Akademiya Nauk SSSR, Doklady*, v. 135, no. 5, pp. 1160–1163, December 11, 1960**
(Translated from the Russian in *Proceedings of the Academy of Sciences of the USSR, Physical Chemistry Section*, v. 135, no. 5, pp. 1147–1150, December 1960)

The extinction of luminescence in dioxane solutions of terphenyl by adding MeOH, EtOH, PrOH, $C_6H_{13}OH$, $C_9H_{19}OH$, and H_2O is investigated. The extinction is also studied in a xylene solution of terphenyl with CCl_4. The experimental method is described, and data are graphed and tabulated. Mathematical treatment of the kinetics is presented.

693. THE MANIFESTATION OF AUTONOMY OF ELECTRON GROUPINGS IN THE LUMINESCENCE SPECTRA OF COMPLEX MOLECULES

Shigorin, D. N., Shcheglova, M. A., Dokunikhin, N. S.
***Akademiya Nauk SSSR, Doklady*, v. 137, no. 6, pp. 1416–1419, April 21, 1961**

Luminescence spectra at 77°K are presented for anthrone in n-C_4H_{14}, and for 3-bromomesobenzanthrone, phenanthrenequinone, and 1,5-dihydroxy- and 1,4,5,8-tetrahydroxyanthraquinone (I) in n-C_5H_{12}. The independence of chromophoric electronic groupings as the source of electronic excitation is demonstrated. The nonequivalence of the $C{:}O$ groups in α-chloroanthraquinone or in 1,8-dihydroxyanthraquinone is reflected in the production of separate spectra due to each group, on appropriate excitation. The spectrum of I, which can form four quasi-aromatic rings by hydrogen bonding, is similar to that of coronene.

694. THE DURATION OF ULTRAVIOLET FLUORESCENCE OF CERTAIN AROMATIC COMPOUNDS

Ivanova, T. V., Kudriashov, P. I., Sveshnikov, B. Ya.
***Akademiya Nauk SSSR, Doklady*, v. 138, no. 3, pp. 572–574, May 21, 1961**
(Translated from the Russian in *Soviet Physics—Doklady*, v. 6, no. 5, pp. 407–409, November 1961)

A modification of the phase fluorometer devised by A. M. Bonch-Bruevich, I. V. Kazarin, V. A. Molchanov, and V. I. Shirokov is described. Fluorescence lifetimes in both nonoutgassed and outgassed solutions of a number of organic substances were determined, for the most part, at 2700 - Å illumination. Results and effects of different solvents are discussed.

695. ANOMALOUS ABSORPTION OF LIGHT NEAR THE EXCITON BANDS OF MOLECULAR CRYSTALS DUE TO IMPURITIES

Broude, V. L., Rashba, E. I., Sheka, E. F.
***Akademiya Nauk SSSR, Doklady*, v. 139, no. 5, pp. 1085–1088, August 11, 1961**
(Translated from the Russian in *Soviet Physics—Doklady*, v. 6, no. 8, pp. 718–721, February 1962)

The exciton bands observed at 20°K in single crystals of naphthalene at about 31,500 cm^{-1} were found to be modified in the presence of a few percent of deuteronaphthalene, α-tetradeuteronaphthalene or β-tetradeuteronaphthalene. Results are presented for radiation polarized parallel to the *a*- and *b*-axes. (*PA*, 1962, #2234)

696. THE DETERMINATION OF THE FREQUENCY OF TRANSITION BETWEEN DIFFERENT STATES OF ACTIVATOR MOLECULES IN ORGANIC PHOSPHORS

Aristov, A. V., Sveshnikov, B. Ya.
***Akademiya Nauk SSSR, Doklady*, v. 141, no. 3, pp. 586–589, November 21, 1961**
(Translated from the Russian in *Soviet Physics—Doklady*, v. 6, no. 11, pp. 998–1000, May 1962)

The determination from experimental data of the frequency of transition between the fluorescent, phosphorescent, and the normal states is discussed, and it is shown that all the transition frequencies can be determined upon the sole assumption that the spontaneous radiative transitions from the fluorescent and phosphorescent states do not depend upon the presence of quenchers or upon temperature. Apparatus for the investigation of the spectra of the radiations is briefly described. (*PA*, 1962, #6625)

697. THE NATURE OF THE RELATIONSHIP BETWEEN CHEMILUMINESCENCE AND OXIDATION BY MOLECULAR OXYGEN

Vasilev, R. F., Vichutinskii, A. A.
***Akademiya Nauk SSSR, Doklady*, v. 142, no. 3, pp. 615–618, January 21, 1962**
(Translated from the Russian in *Proceedings of the Academy of Sciences of the USSR, Physical Chemistry Section*, v. 142, no. 3, pp. 83–86, January 1963)

In the present work it is shown that in radical reactions the increased chemiluminescence on adding oxygen is of a chemical nature. It is connected with the appearance of peroxy radicals in the reaction and with high luminescence yields during the recombination of these peroxy radicals.

The kinetics of chemiluminescence in the thermal decomposition of α,α'-azobisisobutyronitrile (AIBN) in hydrocarbon solutions has been studied first. The solution filled a thermostatted glass vessel placed in front of a photomultiplier. The principal experiments were carried out at 60°C.

The steps of radical formation and chemiluminescence during recombination of radicals when AIBN is in the presence of a hydrocarbon are mentioned. With the introduction of oxygen, a chain reaction for hydrocarbon oxidation and recombinations involving ROO radicals must occur. It is shown that then the luminescence intensities in the absence and presence of oxygen must be different.

If this conclusion, and hence the initial premise concerning the way in which O$_2$ influences chemiluminescence, are correct, then with a progressive decrease in the concentration of dissolved oxygen a change should be noted in luminescence intensity connected with the replacement of ROO radicals by R. This effect has been observed for several hydrocarbons. In these experiments the solution was saturated with air or oxygen, and then the reaction vessel was closed with a ground glass stopper such that no gas bubbles remained and consumption of dissolved oxygen began within the vessel. After a long (ten minute) period of constant intensity, when the reaction rate and concentration of ROO radicals are independent of oxygen concentration and are constant, there occurred a steep drop in intensity. Data are presented and explained.

698. SPECTRA OF THE UNIVERSAL FLUORESCENCE OF POLYMERS

Gachkovskii, V. F.
***Akademiya Nauk SSSR, Doklady*, v. 143, no. 1, pp. 150–152, March 1, 1962**

The spectra of polymers previously examined were studied quantitatively. It was found that the universal luminescence of these polymers depends not only on their chemical structure and the degree of polymerization, but also on the joining of linear chains into spatial two- or three-dimensional lattices, on the state of aggregation of the polymer (solid or as solute), on temperature, deformation and other factors. If the chains of the continuous system contain conjugated bonds, then, as a rule, one finds in all cases a sudden shift of the luminescence intensity toward the longer wavelengths. (*PA*, 1962, #12,632)

699. QUENCHING OF FLUORESCENCE IN SOLUTIONS BY ALIEN SUBSTANCES IN THE PRESENCE OF HIGH CONCENTRATIONS OF FLUORESCENT MATERIAL

Kianskaia, L. A., Kudriashóv, P. I., Sveshnikov, B. Ya.
***Akademiya Nauk SSSR, Doklady*, v. 143, no. 3, pp. 563–566, March 21, 1962**
(Translated from the Russian in *Soviet Physics—Doklady*, v. 7, no. 3, pp. 214–216, September 1962)

In order to explain contradictory observations, the quenching by foreign substances of fluorescence of solutions containing high concentrations of the fluorescing substances was again investigated. Two dyes (fluorescein and trypaflavine), two quenching agents (potassium iodide and aniline), and three solvents (water, ethyl alcohol, and glycerine) were taken.

In the first place, the effect was studied of concentration of the fluorescing substance and additions of quenching agent on the absorption and fluorescence spectra of the solutions.

The following explanation is offered for the observed phenomena. In the time during which the excitation energy is present in the molecule excited directly from a light source or in that molecule to which it had transmitted excitation energy during energy migration, in low-viscosity solutions the position of the quenching agent molecules with respect to the excited molecule changes continually and rapidly, and at a certain fairly close distance between them quenching of the fluorescence commences. In this case both quenching processes—concentration quenching and quenching by foreign substances—can be considered as being independent. The situation is different in viscous media. The diffusion of quenching agent molecules to a dye molecule during its existence in the excited state is very small; however, since the excitation energy migrates from one dye molecule to another, this energy can be transmitted to a dye molecule which is close to a quenching agent molecule.

In viscous media, energy migration therefore leads not only to concentration quenching of fluorescence but also to an increase in quenching by foreign substances.

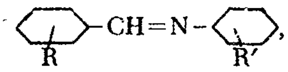
700. LUMINESCENCE SPECTRA OF METHYLENEIMINE COMPOUNDS

Nurmukhametov, R. N., Kozlov, Yu. I., Shigorin, D. N., Puchkov, V. A.
***Akademiya Nauk SSSR, Doklady*, v. 143, no. 5, pp. 1145–1148, April 11, 1962**
(Translated from the Russian in *Proceedings of the Academy of Sciences of the USSR, Physical Chemistry Section*, v. 143, no. 5, pp. 294–296, April 1962)

It was shown previously that hydroxyazo compounds can fluoresce during intra- or intermolecular H-bond formation, leading to consolidation of the molecular system, in which the $n \rightarrow \pi^*$ transition in the azo group ($-N=N-$), after electronic excitation, is responsible.

The aim of the present work was to investigate, by the appearance of fluorescence, the intramolecular reactions favored in methyleneimine compounds. Luminescence spectra were investigated in powders and in n-hexane solutions ($C \sim 10^{-4}$ mole/l) at 293 and 77°K. The method of recording the spectra was described previously.

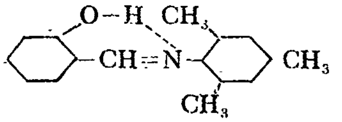
Data are given for methyleneimines with the general formula,

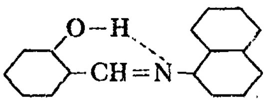


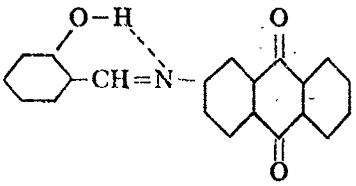
with the following substituents:

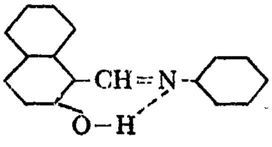
(1) $R = R' = H$
(2) $R = o\text{-OH}$, $R' = H$
(3) $R = p\text{-OH}$, $R' = H$
(4) $R = o\text{-OCH}_3$, $R' = H$
(5) $R = H$, $R' = o\text{-OH}$
(6) $R = H$, $R' = p\text{-OH}$
(7) $R = H$, $R' = p\text{-OCH}_3$
(8) $R = o\text{-Cl}$, $R' = o\text{-OH}$
(9) $R = R' = o\text{-OH}$
(10) $R = p\text{-N(CH}_3)_2$, $R' = H$
(11) $R = H$, $R' = p\text{-N(CH}_3)_2$
(12) $R = p\text{-NO}_2$, $R' = H$
(13) $R = p\text{-NO}_2$, $R' = p\text{-CH}_3$
(14) $R = p\text{-NO}_2$, $R' = p\text{-OH}$
(15) $R = p\text{-NO}_2$, $R' = p\text{-OCH}_3$

Data are also given for the compounds.

(16)


(17)


(18)


(19)


701. THE MECHANISM OF THE EFFECT OF AROMATIC AMINES ON THE FLUORESCENCE AND PHOTOCHEMICAL OXIDATION OF ANTHRACENE COMPOUNDS

Vember, T. M.
***Akademiya Nauk SSSR, Doklady*, v. 147, no. 1, pp. 123–126, November 1, 1962**
(Translated from the Russian in *Proceedings of the Academy of Sciences of the USSR, Physical Chemistry Section*, v. 147, no. 1, pp. 761–765, November 1962)

In order to make a further study of the mechanism of the effect exerted by fluorescence extinguishers on the quantum yields from fluorescence and photooxidation of anthracene compounds, the extinction constants of the fluorescence of several anthracene compounds were found for a whole series of aromatic and aliphatic amines, as well as the changes produced by these amines in the quantum photooxidation yields (ϕ_p) of 9,10-di-*n*-propylanthracene. All of the measurements were made with alcoholic solutions. The bimolecular extinction constants were calculated using a formula derived from the expression for the quantum fluorescence yield in the presence of an extinguisher

$$K_E = (B/B_E - 1):[E] \cdot \tau,$$

where B and B_E are the quantum fluorescence yield in air without and with the extinguisher present, $[E]$ is the extinguisher concentration, and τ is the lifetime of the excited state in air with no extinguisher. The values of B_E were found for several extinguisher concentrations, and the resulting data were averaged graphically. The values of B were taken for all the compounds except 9,10-di-*n*-propylanthracene, for which $B = 0.60$. The values of τ, averaged over several measurements on a phase fluorometer, are given.

702. FERROMAGNETISM OF ORGANIC STRUCTURES

Blyumenfeld, L. A.
***Akademiya Nauk SSSR, Doklady*, v. 148, no. 2, pp. 361–364, January 11, 1963**

Deoxyribonucleic acid (DNA) and several polymers with conjugated bonds were studied. Magnetic resonance spectra were obtained and magnetization curves plotted. Ferromagnetic effects observed in organic structures cannot be considered a result of ferromagnetic impurities. In several organic compounds (e.g., DNA) the amount of iron contained in samples was insufficient to explain the ferromagnetism observed. It is pointed out that in polymers with conjugated bonds containing only C and H atoms the ferromagnetic domains form an integral part of the basic organic structure, as shown by the narrowness of the resonance lines.

703. LUMINESCENCE OF THE URANYL–PHTHALOCYANIN COMPLEX

Lialin, G. N., Kobyshev, G. I.
***Akademiya Nauk SSSR, Doklady*, v. 148, no. 5, pp. 1053–1056, February 11, 1963**

704. LUMINESCENCE VARIATIONS OBSERVED DURING THE EXAMINATION OF DIFFERENTIAL SPECTRA OF PHOTOSYNTHESIZING ORGANISMS

Karapetian, N. V., Litvin, F. F., Krasnovskii, A. A.
***Akademiya Nauk SSSR, Doklady*, v. 149, no. 6, pp. 1428–1431, April 21, 1963**

705. QUENCHING OF FLUORESCENCE OF CAROTENOID ADSORBATES

Lialin, G. N., Kobyshev, G. I., Terenin, A. N.
***Akademiya Nauk SSSR, Doklady*, v. 150, no. 2, pp. 407–410, May 11, 1963**

706. LIGHT SCATTERING BY MOLECULES AND THE LIFETIME OF THE EXCITED STATE

Shorygin, P. P., Ivanova, T. M.
***Akademiya Nauk SSSR, Doklady*, v. 150, no. 3, pp. 533–536, May 21, 1963**

Study of the Raman spectra of diphenylpolyenes Ph-(CH:CH)$_n$-Ph in acetone solutions, with $n = 5$ and with $n = 6$, showed that the Raman scattering frequencies corresponding to normal vibrations of nuclei coincided with absorption and fluorescence spectra frequencies. The lifetime of the excited state was long shown by the pronounced vibrational structure of the absorption bands. Because of the long polyene chain, resonance spectra resulted in which the absorption region was separated from the fluorescence region by an extensive range of frequencies. Two very intense absorption lines, at frequencies of 1140 and 1550 cm^{-1}, were observed for both polyenes. Lines of the second and higher orders could be observed in resonance spectra of both.

707. SPONTANEOUS AND INDUCED BIOCHEMILUMINESCENCE OF PLANTS IN AEROBIC AND ANAEROBIC CONDITIONS

Gasanov, R. A., Mamedov, T. G., Tarusov, B. N.
***Akademiya Nauk SSSR, Doklady*, v. 150, no. 4, pp. 913–915, June 1, 1963**

708. CHEMILUMINESCENCE AND THE REACTION MECHANISM IN THE CATALYZED BREAKDOWN OF ETHYLBENZENE HYDROPEROXIDE

Zakharov, I. V., Shliapintokh, V. J.
***Akademiya Nauk SSSR, Doklady*, v. 150, no. 5, pp. 1069–1072, June 11, 1963**

709. THE EVALUATION OF THE DEGREE OF SPIRALIZATION OF TRANSPORT RIBONUCLEIC ACIDS FROM THE FLUORESCENCE PROPERTIES OF THEIR COMPLEXES WITH ACRIDINE DYES

Borisova, O. F., Kiselev, L. L., Tumerman, L. A.
***Akademiya Nauk SSSR, Doklady*, v. 152, no. 4, pp. 1001–1004, October 1, 1963**

710. POLARIZED LUMINESCENCE OF REDUCED FORMS OF PORPHYRINS

Gurinovich, G. P., Shulga, A. M., Sevchenko, A. N.
***Akademiya Nauk SSSR, Doklady*, v. 153, no. 3, pp. 703–705, November 21, 1963**

711. THE SPECTRA OF THE ELECTRON DONATOR-ACCEPTOR COMPLEXES OF 4-NITRODIPHENYL-ALKANES CONTAINING A DONOR GROUP IN THE OTHER NUCLEUS. THE ELECTRON-SPIN RESONANCE EFFECT

Glushenkov, V. A., Izmailskii, V. A., Moshkovskii, Iu. Sh.
***Akademiya Nauk SSSR, Doklady*, v. 153, no. 6,**
pp. 1363–1366, December 21, 1963

712. NATURE OF RADIOTHERMOLUMINESCENCE OF ORGANIC COMPOUNDS

Nikolskii, V. G., Alfimov, M. V., Buben, N. Ya.
***Akademiya Nauk SSSR, Izvestiya, Otdelenie Khimicheskikh Nauk*, no. 5, p. 955, 1963**

Hydrocarbons (hexane, nonane, benzene, etc.) bombarded with fast electrons at 77°K gave luminescence after excitation with visible light. The effects of prolonged illumination, subsequent thawing, and mechanical destruction are noted. The electron paramagnetic resonance spectra indicated that free-radical population did not change during the illumination. Causes of color and luminescence are considered.

713. INVESTIGATION OF THE TEMPERATURE DEPENDENCE OF THE INTERACTION BETWEEN MOLECULES IN THE VAPOR STATE

Klochkov, V. P.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 5, pp. 516–520, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 5, pp. 523–526, 1960)

Observations of decrease in absorption of β-naphthylamine vapor on addition of light gases to the vapor, and the limit to such decrease which is dependent on β-naphthylamine concentration, led to the idea that a study of decrease in absorption might be used as a sensitive method to ascertain molecular interaction, even at the relatively long range of hundreds of angstroms.

It was found that below a certain vapor concentration c_0, which depends on the nature of the compound and the temperature, the magnitude of the limiting absorption decrease does not change with further decrease of the concentration, i.e., at a certain sufficiently large separation between the molecules, their interaction virtually ceases. Hence, by determining the limit concentration c_0, the degree of molecular interaction can be gaged. As a measure of this interaction, therefore, either the limit concentration c_0 or the corresponding vapor pressure p_0 can be taken. This method was used to study the long range forces as a function of molecular structure. It was previously shown that with increase of conjugation in the phthalimide series, there is a shift of the spectra to the long wavelength side and enhancement of the molecular interaction. The present work is a continuation of these studies and is devoted to determining the temperature dependence of the interaction energy of aromatic molecules.

The following compounds were investigated: anthracene, 1,4-diphenylbutadiene-1,3, phthalimide and its 3- and 4-amino derivatives. The light gas used was helium since it has the strongest effect on the absorption of aromatic compounds. The results of measurements of p_0 and the corresponding concentration c_0, obtained here and in an earlier study, are tabulated and interpreted.

714. TEMPERATURE DEPENDENCE OF THE FLUORESCENCE EFFICIENCY OF COMPLEX MOLECULE VAPORS

Borisevich, N. A., Tolkachev, V. A.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 5, pp. 521–524, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 5, pp. 527–530, 1960)

An investigation is reported of the yields of Stokes and anti-Stokes fluorescence of 3,6-tetramethyldiaminophthalimide, 3-aminophthalimide and 1,4-dihydroxyanthraquinone (quinizarin) in the vapor state with variation of the temperature in a relatively wide range. Results are discussed.

715. ELECTRONIC SPECTRA OF ANTHRAQUINONE VAPORS

Borisevich, N. A., Gruzinskii, V. V.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 5, pp. 545–548, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 5, pp. 551–554, 1960)

The present work was devoted to a systematic investigation of the fluorescence and absorption spectra of eight anthraquinones.

The fluorescence spectra were measured by means of a high sensitivity photoelectric spectrometer, and the absorption spectra by means of a photoelectric setup assembled about an SF-4 spectrophotometer. The measurements were carried out under vacuum conditions (10^{-5} mm Hg). For the investigation the following anthraquinones, differing in position and character of the substituent groups, were chosen: anthraquinone, 2-chloroanthraquinone, 2-ethylanthraquinone, 1-chloroanthraquinone, 1,5-dichloroanthraquinone, 1-aminoanthraquinone, 1,2-dihydroxyanthraquinone (alizarin), and 1,4-dihydroxyanthraquinone (quinazarin). All the compounds were thoroughly purified by recrystallization and subsequent vacuum distillation. Experimental results are presented.

716. LUMINESCENCE OF ANTHRACENE SOLID SOLUTIONS

Broude, V. L., Medvedev, V. S.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 5, pp. 549–552, 1960**

(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 5, pp. 555–558, 1960)

The luminescence excitation spectra of various anthracene solutions were studied over the first absorption band (3950–3300 Å). Solutions in styrene, polystyrene (added to molten solvent), naphthalene and dihydroanthracene show no vibrational structure. Copolymers of anthracene and styrene show a vibrational structure in anti-correlation with the absorption spectrum. A similar structured excitation spectrum is produced in the other solutions by prolonged ultraviolet radiation. The effects are attributed to the formation of labile nonvalence linkages between anthracene and the solvent through π-electron interaction. (*PA*, 1962, #14,743)

717. LUMINESCENCE OF CRYSTALLINE NAPHTHALENE CONTAINING MINOR IMPURITIES

Shpak, M. T., Sheka, E. F.

***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 5, pp. 553–555, 1960**

(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 5, pp. 559–561, 1960)

From the experimental results, which are described, it is concluded that light energy absorbed by the crystal is transferred from the host lattice by exciton migration to impurity molecules (β-methyl-naphthalene), in which radiative transitions occur. With increasing crystal purity, luminescence is, however, primarily associated with exciton annihilation, which is favored at higher temperatures, as in the intrinsic luminescence of naphthalene crystals. The temperature range investigated extends from 20 to 300°K. (*PA*, 1962, #14,747)

718. CONCERNING THE LUMINESCENCE AND PHOTOCONDUCTIVITY OF ANTHRACENE CRYSTALS

Faidysh, A. N.

***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 5, pp. 556–560, 1960**

(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 5, pp. 562–566, 1960)

The luminescent spectrum of anthracene films of various thicknesses (~ 0.1 to 10 μ), with and without impurities (principally naphthalene), was investigated at various temperatures. The large increase in short-wavelength luminescent intensity in the thinner crystals is attributed to surface emission effects, and to impurity molecules. The influence on luminescence of oxygen and of the method of preparation of the anthracene crystals is also investigated, as well as photoconductivity, which is found to be strongly dependent on photooxidation and crystal orientation (*b*-axis conductivity is five times that along *a*-axis). (*PA*, 1962, #14,744)

719. EFFECT OF β-RADIATION ON THE PHOTOLUMINESCENCE OF MOLECULAR CRYSTALS

Khan-Magometova, Sh. D., Zhevandrov, N. D., Gribkov, V. I.

***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 5, pp. 561–566, 1960**

(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 5, pp. 567–572, 1960)

The effect of β-radiation from Sr^{90} and H^3 sources (up to maximum doses of 2×10^6 rad and 3.5×10^{10} rad, respectively) on the photoluminescence of pure anthracene and anthracene with different concentrations of naphthacene was investigated. The results show an overall depression of the luminescence spectrum with pure anthracene, and a smaller depression for the mixed crystals, the extent of which decreases with increasing naphthacene content. Various mechanisms are considered in an attempt to explain the observations.

720. EFFECT OF TEMPERATURE ON THE ELECTRONIC SPECTRA OF COMPLEX MOLECULES IN SOLUTIONS

Pikulik, L. G.

***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 5, pp. 572–576, 1960**

(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 5, pp. 578–582, 1960)

In order to elucidate the reasons for the shift of the spectra of solutions with decrease in temperature, the absorption and fluorescence spectra of a number of phthalimides, as well as of a number of typical dyes, were investigated at liquid nitrogen temperature.

Solvents that retained their transparency incident to freezing were employed, as well as a number of solvents that cracked and fissured when frozen. Among the solvents that freeze without fissuring, ethyl, propyl, and isobutyl alcohols were used. By way of media which become glass-like when frozen but do not fissure to any great extent, glycerol, glycol, benzyl alcohol, and cyclohexanol were tried. Displacement of the fluorescence spectra of phthalimides in these solvents with decrease of temperature had been observed earlier. In addition to the above, in the present study solid solutions based on gelatin, sugar, and starch were prepared, and transparent plastics (lucite) and nitrocellulose films colored with the investigated compounds were also used.

The results of measurements of the fluorescence and absorption spectra of seven phthalimides (4-aminophthalimide, 4-amino-*N*-methylphthalimide, 4-dimethylamino-*N*-methylphthalimide, 3-aminophthalimide, 3-amino-*N*-methylphthalimide, 3-monomethylaminophthalimide, and 3-monomethylamino-*N*-methylphthalimide) are presented.

721. INFLUENCE OF SOME FLUORESCENCE QUENCHERS ON THE QUANTUM EFFICIENCY OF PHOTOCHEMICAL CONVERSION OF 9-METHYLANTHRACENE AND 9-METHYL-10-METHOXYMETHYLANTHRACENE

Vember, T. M., Cherkasov, A. S.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 5, pp. 577–581, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 5, pp. 583–587, 1960)

Experiments seem to show that toluidine (1) quenches singlet excited molecules without transition of the molecule to the triplet state, (2) interacts with the intermediate photooxide yielding the initial substance, and (3) does not deactivate the triplet molecule. On the other hand, KI (1) quenches by causing transitions of the molecule from singlet excited state to the triplet state, and (2) decreases photooxidation efficiency by a mechanism not clearly understood. (*PA*, 1962, #14,745)

722. INFLUENCE OF THE SOLVENT ON THE FLUORESCENCE SPECTRA OF ACETYLANTHRACENES

Cherkasov, A. S.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 5, pp. 591–595, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 5, pp. 597–601, 1960)

Changes in the fluorescence spectra of two acetylanthracenes were investigated for numerous solvents. The nature of the solvent is an important factor in determining the spectrum, and frequency shifts of as much as 4950 cm^{-1} were observed. These shifts increase with the refractive index in nonpolar solvents, but no similar consistent correlation occurs in polar solvents. This dependence on ε is verified by examining the change in peak frequency and ε as a function of temperature for one nonpolar solvent. (*PA*, 1962, #15,600)

723. PRINCIPAL PROCESSES OF DEACTIVATION OF EXCITED STATES OF COMPLEX ORGANIC MOLECULES

Borgman, V. A., Zhmyreva, I. A., Zelinskii, V. V., Kolobkov, V. P.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 5, pp. 601–606, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 5, pp. 607–611, 1960)

The variation of the fluorescence yield q_f with the frequency $\nu_f^{\max}$ of the fluorescence peak is given for different series of related organic compounds at −180°C. It is evident from these results that q_f varies regularly with $\nu_f^{\max}$ at these temperatures. It is found that a decrease in q_f caused by some substituents is not compensated by the appearance of phosphorescence, so that the total luminescence yield is reduced. The nature of the results suggests that a long- and a short-wavelength deactivation process may occur. At high $\nu_f^{\max}$, a deactivation process is considered which involves a nonradiative transition from the excited state to the ground state with probability that increases with $\nu_f^{\max}$. It is proposed that a predissociation level may act as the intermediate level for transitions to a metastable state. (*PA*, 1962, #14,740)

724. INFLUENCE OF STRUCTURE ON THE LUMINESCENCE CHARACTERISTICS OF COMPLEX ORGANIC MOLECULES

Zelinskii, V. V., Reznikova, I. I.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 5, pp. 607–609, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 5, pp. 612–614, 1960)

The normal variation of fluorescence yield q_f with fluorescence peak frequency $\nu_f^{\max}$ is not obeyed when substituents such as the hydroxyl and nitro groups, phenyl and the halogens (I and Br) are used. The influence of such groups at −180°C is examined. The results indicate that the quenching mechanism with phenyl or the nitro group is different from that involved with the halogens. (*PA*, 1962, #14,741)

725. OPTICAL PROPERTIES OF CHLOROPHYLL AND PHEOPHYTIN AT LOW TEMPERATURES

Kravtsov, L. A.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 5, pp. 610–612, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 5, pp. 615–617, 1960)

The temperature variation and relative efficiencies of the luminescence spectra and the temperature variation of the red absorption band were investigated from −100 to +20°C for solutions of chlorophyll-*a* and pheophytin-*a*. Petroleum ether and isobutyl alcohol were used as solvents. With decrease in temperature the absorption band and the luminescence band become narrower and shift toward one another. It is thought that the results indicate that in petroleum ether at low temperatures, clustering of chlorophyll or pheophytin molecules occurs, and associated with this clustering is a new distinctive absorption spectrum but no luminescence. (*PA*, 1962, #15,601)

726. LUMINESCENCE EFFICIENCY OF CHLOROPHYLL IN DIFFERENT SOLVENTS

Ivanov, N. P.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 5, pp. 613–615, 1960**

(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 5, pp 618–620, 1960)

The quantum efficiency in various solvents was investigated by measuring the area under the luminescence bands and comparing it with that for a reference material whose efficiency is known and which is excited under identical conditions to the chlorophyll. In most solvents the efficiency is of the order of 30–33% and appears to be reasonably independent of the solvent for low chlorophyll concentrations. (*PA*, 1962, #15,602)

727. AGGREGATION OF CHLOROPHYLL AND CHLOROPHYLLIDE MOLECULES

Efremova, R. V.
***Akademiya Nauk SSSR, Izvestiya. Seriya Fizicheskaya*, v. 24, no. 5, pp. 616–619, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v 24, no. 5, pp. 621–623, 1960)

The absorption and luminescence spectra of chlorophyll and chlorophyllide were investigated for the purpose of determining the ability of these molecules to aggregate, i.e., to form dimers and higher polymers. The spectra of chlorophyll-*a* in ethyl alcohol and in ethyl alcohol/water solutions and those of chlorophyllide-*a* in water and in ethyl alcohol/water solutions are graphed.

728. ABSORPTION AND FLUORESCENCE SPECTRA OF PERYLENE AT LOW TEMPERATURES

Personov, R. I.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 5, pp. 620–622, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Phusical Series*, v. 24, no. 5, pp. 624–628, 1960)

The long-wavelength region of the absorption spectra of frozen solutions of perylene in ethyl alcohol and normal paraffins was studied at 77°K. In addition, the fluorescence spectra of these solutions and of crystalline perylene were investigated at the same temperature. The form of the results is discussed in detail. In particular the sharp absorption and fluorescence spectra in a hexane solution are used to attribute the shortest wavelength line in the fluorescence to 0 → 0 transition. (*PA*, 1962, #16,867)

729. SPECTROSCOPY OF SOME PYRENE DERIVATIVES IN FROZEN SOLUTIONS

Khesina, A. Ya.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 5, pp. 623–626, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 5, pp. 629–634, 1960)

Fluorescence, phosphorescence, and absorption spectra of crystalline 3,4-naphtho-6,7-benzopyrene, 3′-methyl-4′,5-ethylene-3,4,6,7-dibenzopyrene, and 3,4,5,6,7-tribenzopyrene, and their solutions in oil, alcohol, and *n*-alkanes, were obtained at room and liquid nitrogen temperatures. The frozen solutions in the *n*-alkanes showed line-like (grouped in multiplets) fluorescence and phosphorescence spectra. The results enabled the author to establish (1) characteristic wavelengths in the luminescence and absorption spectra that can be utilized for the identification of the substances, which are known to be carcinogenic, and (2) the vibrational structure of the ground and the first excited electronic states and the determination of the normal vibration frequencies of the molecules. (*PA*, 1962, #18,871)

730. ULTIMATE LINES OF 3,4-BENZOPYRENE DISSOLVED IN NORMAL HYDROCARBONS AT DIFFERENT TEMPERATURES

Bogomolov, S. G., Pemova, F. D., Kolosova, L. P.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 6, pp. 725–727, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR Physical Series*, v. 24, no. 6, pp. 728–730, 1960)

The luminescence spectra of solutions of 3,4-benzopyrene in hexane were recorded in the range of concentration from 10^{-4} to 10^{-8} g/ml. The spectra at room temperature consisted of a few diffused bands, whose intensity increased with the lowering of the temperature. At the liquid nitrogen point line spectra were obtained. With the reduction of the solute concentration the number of lines decreased (from 21 at 10^{-4} g/ml to 4 at 10^{-8} g/ml). The intense surviving lines, named "ultimate lines" in analogy with the atomic resonance lines, were used for chemical analysis.

731. LUMINESCENCE OF SOLUTIONS OF THIOINDIGO AND ITS DI-DERIVATIVES AT 77°K

Nurmukhametov, R. N., Shigorin, D. N., Dokunikhin, N. S.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 6, pp. 728–729, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 6, pp. 731–732, 1960)

Luminescence spectra of frozen solutions of thioindigo, 5,5′-dimethylthioindigo, and 6,6′-diethoxythioindigo at 77°K showed vibrational structure, which gradually smeared out in going from hexane to nonane as the solvent. The absorption spectrum of thioindigo in hexane also showed structure. The luminescence and absorption spectra are interpreted in terms of three vibrational modes: 220, 480, and 1540 cm^{-1}, and

200, 480, and 1500 cm^{-1}, respectively. It is concluded that, although the thioindigo molecule contains four heteroatoms, the long wavelength absorption and emission bands are associated with the $\pi \rightarrow \pi^*$ transition and not with the usual $n \rightarrow \pi^*$ transition. The influence of media with possible intermolecular hydrogen bonding was also investigated. (*PA*, 1962, #17,473)

732. TEMPERATURE DEPENDENCE OF THE FLUORESCENCE EFFICIENCY OF SOME PHTHALIMIDES IN DIFFERENT SOLVENTS

Pikulik, L. G., Sevchenko, A. N.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 6, pp. 729–733, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 6, pp. 732–736, 1960)

The quantum efficiency of fluorescence of 4-dimethylamino-N-methylphthalimide increased with temperature in benzyl alcohol and cyclohexanol whereas it decreased with temperature in dimethylphthalate. In the latter case the band shifted to shorter wavelengths compared to the alcohols. Similar observations were made with a number of other phthalimide-solvent pairs. The results are explained in terms of the curve characterizing the variation of quantum efficiency with the frequency of the luminescence peak. Temperature quenching of fluorescence was observed in dimethylphthalate, vaseline oil, ethyl acetoacetate and ethyl benzoate as solvents. The lifetimes of the excited states at different temperatures were also measured. Change in relative efficiency was found to be accompanied by change in relative lifetime of the excited state. (*PA*, 1962, #17,474)

733. CONCERNING THE RELATION BETWEEN THE ABSORPTION AND LUMINESCENCE SPECTRA OF COMPLEX MOLECULES

Alentsev, M. N., Pakhomycheva, L. A.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 6, pp. 734–737, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 6, pp. 737–739, 1960)

Divergences between experimental results on low concentration aqueous solutions of erythrosine and the theory of Stepanov giving the relation between the absorption and luminescence spectra of complex molecules in solutions are examined and discussed.

734. INFLUENCE OF SECONDARY IMPURITIES ON THE ABSORPTION AND LUMINESCENCE SPECTRA OF THE PRIMARY IMPURITY IN MOLECULAR CRYSTALS

Solovev, A. V.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 6, pp. 737–739, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 6, pp. 740–742, 1960)

The luminescence spectra of naphthalene impurity in dibenzyl crystals at 20°K as a result of the introduction of a second impurity—diphenyl acetylene—were examined. The naphthalene concentration was kept constant and the diphenyl acetylene concentration was increased in steps for each specimen. The results imply that clear sharp bands observed in the spectrum of naphthalene impurity in dibenzyl crystals are connected with the crystal structure of the host, and that the alterations observed in the spectrum in the range of low concentrations of the additional impurity are connected with distortion of the host crystal lattice. Similar changes in the spectrum were obtained using paraditolyl instead of diphenyl acetylene, a fact which tended to confirm the theory since a similar change in the character of the spectrum would be expected regardless of the nature of the second impurity. (*PA*, 1962, #16,865)

735. POLARIZATION OF THE LUMINESCENCE OF MOLECULAR CRYSTALS IN DIFFERENT REGIONS OF THE SPECTRUM

Gribkov, V. I., Zhevandrov, N. D., Khan-Magometova, Sh. D.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 6, pp. 740–744, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 6, pp. 743–747, 1960)

A description is given of a continuation of a previous investigation by polarization methods of the role of free and trapped electrons in the luminescence of molecular crystals. In the earlier experiments, measurements were made of the wavelength dependence of the polarization of luminescence with excitation by 365-mμ light for stilbene crystals cut along different crystallographic planes. The present work shows that the luminescence of stilbene comprises emission due to free excitons. The authors have also investigated the wavelength dependence of the polarization of anthracene crystals doped with naphthacene. In another investigation the polarization of luminescence of benzil crystals has been studied. Similar results to those obtained for benzil were found also for solutions of optically active substances, viz., tryptophan and riboflavin. (*PA*, 1962, #16,868)

736. VITRIFICATION OF POLYMERS AND PHOSPHORESCENCE

Anufrieva, E. V., Zaitseva, A. D.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 6, pp. 755–758, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 6, pp. 758–760, 1960)

Vitrification of polymers involves immobilization of the macromolecules. Below the vitrifying temperature the equilibrium structure obtaining at higher temperatures is "frozen." Reference is made to various methods of studying the mobility of macromolecules in polymers. An investigation is reported of the influence of vitrification of polymers on the phosphorescence of the luminophor introduced into the polymer or on the specific interaction of the luminophor with the medium, i.e., the interaction responsible for the appearance of phosphorescence. The temperature dependences of the phosphorescence intensity of rhoduline orange, rhodamine B, and other organic compounds were investigated. Significant information was obtained on the relaxation time of macromolecules in polymer at temperatures close to the vitrification point. (PA, 1962, #15,079)

737. PHOSPHORESCENCE OF CERTAIN SOLVENTS AND THEIR EFFECT ON THE ABSORPTION SPECTRA OF ORGANIC PHOSPHORS

Kislyak, G. M.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,* v. 24, no. 6, pp. 766–768, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 24, no. 6, pp. 769–771, 1960)

It is shown that formic and acetic acids at low temperature have a significant intrinsic phosphorescence. Moreover, formic acid, and to some extent acetic acid, deform the absorption spectra of acridine dyes and also significantly alter the decay of their phosphorescence. It is considered that these factors are important in investigating the phosphorescence of acridine dyes. (*PA*, 1962, #15,605)

738. CORRELATION BETWEEN THE ABSORPTION AND LUMINESCENCE SPECTRA OF SOME ORGANIC COMPOUNDS

Ryazanova, E. F., Fadeeva, M. S., Pavlina, T. S.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,* v. 24, no. 6, pp. 769–771, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 24, no. 6, pp. 771–773, 1960)

Brief reference is made to experimental tests of certain inferences arrived at in the theoretical investigations of Stepanov, Alentsev and Pakhomysheva, and Neporent (1957–1958). These are concerned with the relation between the luminescence and absorption spectra of complex molecules (*m*-phenylenediamine, brassidic acid, and adipic acid in the crystalline state at room temperature). Certain divergences from the theoretical deductions are noted which are not explained by the influence of the solvent molecules on the excited molecules of the luminescent substance. (*PA*, 1962, #14,749)

739. INVESTIGATION OF THE LUMINESCENCE OF IONIC FORMS OF URANIN AND FLUORESCEIN

Grigoryan, E. V., Kantardzhyan, L. T., Chirkinyan, S. S.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,* v. 24, no. 6, pp. 771–775, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 24, no. 6, pp. 774–777, 1960)

Usually the luminescence of fluorescein is attributed either to the doubly charged anion in basic solutions or to the cation in acid solutions. One of the authors has shown, however, that in a wide pH range the luminescence of fluorescein and uranin is due to the simultaneous presence of both anions and cations. An experimental investigation is now described of the spectra of these substances in various mixtures of dioxane plus water, sulphuric acid or ammonia, and also in solutions of caustic soda and nitric acid. In some of these cases the spectra are shown. In agreement with Zanker and Peter, it is now shown that there exist three forms of ions in uranin solutions, including a singly charged anion. (*PA*, 1962, #15,606)

740. LUMINESCENCE SPECTRA OF HALOGEN DERIVATIVES OF ANTHRAQUINONE IN FROZEN SOLUTIONS

Shigorin, D. N., Shcheglova, N. A., Dokunikhin, N. S.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,* v. 24, no. 6, pp. 778–781, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 24, no. 6, pp. 781–784, 1960)

Specifically, in the present work the luminescence spectra were studied of α and β halogen derivatives of anthraquinone in normal paraffin solutions at 77°K ($c = 10^{-4} - 10^{-5}$ mole/l; excitation by the 313-mμ line of Hg). In view of the peculiarities of the structure of α and β halogen derivatives of anthraquinone, substantial differences between their spectra can be reasonably expected. Replacement of the hydrogen atom in the α position by a halogen atom results in nonequivalence of the two carbonyl groups in the anthraquinone ring, since one of the $C=O$ groups may exert a mutual influence on the $C-Hal$ group through π-electron interaction, inasmuch as the two groups simultaneously interact with the same carbon atom. This does not occur in β derivatives because in them the carbonyl groups are virtually equivalent. The nature of the halogen atom on the spectra of the α and β derivatives of anthraquinone must also be taken into account. It is known that the electronegativity decreases in going from fluorine to iodine, and the electronegativity of iodine is almost the same as that of carbon. In view of this, the probability of participation of the unshared electron pairs of the halogens in the π-electron interaction will increase in going from fluorine to iodine, which is in accord with the amount of energy expended on their excitation.

Thus the F atom is characterized by a strong inductive effect that can lead to a certain deformation of the π-electron density at the neighboring carbon atoms, which is equivalent to some shortening of the conjugated chain. Hence, introduction of fluorine should lead to shift of the bands to the short wavelength side. Characteristic of Cl, Br and, particularly, I atoms is participation of the unshared electron pairs in the π-electron interaction of the molecules, which can lead to lengthening of the conjugated chain and, consequently, to shift of the bands to the side of longer wavelengths. These differences in the behavior of halogen atoms should be evinced particularly strongly in the excited state of the molecules.

The substantial difference between the size of the halogen atoms can also result in differences in their effect on the luminescence spectra of α halogen derivatives of anthraquinone. Whereas in view of its small size ($R_B = 1.35$ A) the F atom cannot have a steric deforming influence on the C=O group, Cl and, particularly, Br and I ($R_B = 2.15$ A) should have a steric deforming effect. Repulsive forces arise between the halogen atoms with large radii (Cl, Br, and, particularly, I) and the oxygen atom of the C=O group; such repulsive forces lead to distortion of valence angles of the >C=O and >C−Hal bonds and to some alteration of the electronic state of the groups. One can also expect the nature and position of the halogen atoms in the anthraquinone ring to exert and influence on the intensity and character of changes in the electronic-vibrational spectra of the molecules.

The experimental investigation reported here of the luminescence spectra of the halogen derivatives of anthraquinone largely substantiated the above inferences. Spectra with fine vibrational structure were obtained for all the α and β monohalogen derivatives. Data are presented and interpreted.

741. CORRELATION BETWEEN THE THERMAL ACTIVATION ENERGY FOR CONDUCTIVITY AND THE ABSORPTION AND PHOSPHORESCENCE SPECTRA OF SOME ORGANIC SUBSTANCES

Vartanyan, A. T., Rozenshtein, L. D.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 25, no. 3, pp. 428–430, March 1961**
(Paper published at the Ninth Conference on Luminescence —Entry #498; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 25, no. 3, pp. 416–419, March 1961)

A report is given for the thermal activation energy of conductivity for a number of organic compounds in solid layers. The compounds studied are: malachite green, brilliant green, fuchsin, crystal violet, aqueous blue, uranin, eosin, erythrosine, phloxin, bengal rose, rhodamine B, colorless products of rhodamine B, rhodamine 6G, fluorescein, phenosafranine, trypoflavine, phosphine, capri blue, nile blue, thionine, indigo, pinacyanol, orthochrome T, phthalocyanin, Cu phthalocyanin, Zn phthalocyanin, benzophenone, anthranilic acid, phenylanthranilic acid, and several phthalimide derivatives. Temperature dependence of conductivity is given for 11 of the compounds listed. The data show that the free carriers in the dark conductivity of the phosphorescing compounds are produced incident to singlet-singlet electron transitions. (*PA*, 1963, #958)

742. DEACTIVATION OF THE TRIPLET STATE OF AROMATIC MOLECULES

Terenin, A. N., Ermolaev, V. L.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 26, no. 1, pp. 21–32, January 1962**
(Paper presented at the Tenth Conference on Luminescence —Entry #500; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 26, no. 1, pp. 21–32, January 1962; published 1963)

Sensitized phosphorescence in solutions containing both donor molecules (such as aromatic aldehydes and ketones) and acceptor molecules (such as naphthalene and its halogenated derivatives) was shown experimentally to be due to nonradiative transfer of energy between triplet states by means of resonance exchange interaction, and is a significant mode of deactivation of triplet states. (*PA*, 1963, #11,799)

743. SPECTRAL-LUMINESCENT INVESTIGATION OF PORPHYRINS

Sevchenko, A. N.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya* v. 26, no. 1, pp. 53–60, January 1962**
(Paper presented at the Tenth Conference on Luminescence —Entry #500; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 26, no. 1, pp. 54–61, January 1962, published 1963)

This paper reviews the data on the absorption and fluorescence spectra, efficiencies, decay times, and polarization of the porphyrins. The problems of identifying the electronic and vibrational states associated with the transitions are discussed in detail. (*PA*, 1963, #9467)

744. INVESTIGATION OF EXCITATION ENERGY MIGRATION IN MOLECULAR CRYSTALS BY OBSERVATION OF THE POLARIZATION OF THEIR LUMINESCENCE

Zhevandrov, N. D.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 26, no. 1, pp. 67–73, January 1962**
(Paper presented at the Tenth Conference on Luminescence —Entry #500; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 26, no. 1, pp. 67–73, January 1962; published 1963)

This is a survey of previous work, mostly by the author. A molecular crystal is considered as a kind of gas in which the molecules are orientated but do not interact. Measurements of the polarization of fluorescence as a function of the angle between exciting beam and direction of observation are in qualitative agreement with calculation for stilbene crystals in the six possible crystallographic orientations, though quantitatively the polarization is less than that calculated from the gas model. Tolane in which stilbene impurity causes the luminescence has similar properties. In single crystals the polarization is independent of the orientation of the electric vector of the incident light, contrary to expectation if there were no energy migration between molecules. The polarization is independent of the wavelength of the excitation, but owing to the presence of free excitons, the luminescence spectrum shows a sharp change in polarization at the short wavelength end in stilbene, though not in crystals activated by impurities. (*PA*, 1963, #11,000)

745. LUMINESCENCE OF GADOLINIUM SALTS

Zaidel, A. N., Lazeeva, G. S., Ostrovskaya, G. V., Yakimova, P. P.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya, v. 26, no. 1, pp. 74–80, January 1962
(Paper presented at the Tenth Conference on Luminescence —Entry #500; translated from the Russian in _Bulletin of the Academy of Sciences of the USSR, Physical Series,_ v. 26, no. 1, pp. 74–81, January 1962; published 1963)

Excitation by the Fe spark of solid Gd chloride and sulphate, and of solutions of these salts and Gd ethyl sulphate, produces line and band emission spectra between 3000 and 3600 Å. These are detailed with attributions of the transitions involved. The main groups of lines at 3060 and 3110 Å have equal decay times within the accuracy of measurement. The chloride solution decreases in fluorescent intensity during excitation, probably on account of radiation below 2500 Å. (*PA*, 1963, #10,988)

746. RELAXATION OF THE SOLVENT DURING THE EXCITED LIFETIME OF THE SOLUTE MOLECULES AND FLUORESCENCE SPECTRA

Cherkasov, A. S.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya, v. 26, no. 1, pp. 81–83, January 1962
(Paper presented at the Tenth Conference on Luminescence —Entry #500; translated from the Russian in _Bulletin of the Academy of Sciences of the USSR, Physical Series,_ v. 26, no. 1, pp. 81–84, January 1962; published 1963)

An account is given of earlier experiments, mostly by the author. When the solvent interacts differently with normal and excited solute molecules, e.g., in hydroxyl-containing solvents, the solvent molecular orientation changes after excitation and the spectral location of the emission is found to depend on the temperature. Closer solvent–solute association causes longer wavelength of emission, and the fluorescence decay is slower at the longer wavelength end of the emission band. Quenchers act preferentially on molecules of the longest life and therefore cause displacement of spectra to higher frequencies. (*PA*, 1963, #9468)

747. ABSORPTION AND LUMINESCENCE SPECTRA OF STILBENE AND TOLAN IN FROZEN CRYSTALLINE SOLUTIONS AT 77°K

Gobov, G. V.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya, v. 27, no. 1, pp. 11–14, January 1963
(Paper presented at the Fourteenth Conference on Spectroscopy, Gorkii, July 5–12, 1961; translated from the Russian in _Bulletin of the Academy of Sciences of the USSR, Physical Series,_ v. 27, no. 1, pp. 13–17, 1963)

The fine structure of spectra was studied in *n*-paraffin solutions (from hexane to undecane).

748. SPECTRAL METHOD OF INVESTIGATION OF HIGH-MOLECULAR-WEIGHT COMPOUNDS AND ITS POSSIBILITIES

Savostyanova, M. V., Chernyshev, V. A.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya, v. 27, no. 1, pp. 62–64, January 1963
(Paper presented at the Fourteenth Conference on Spectroscopy, Gorkii, July 5–12, 1961; translated from the Russian in _Bulletin of the Academy of Sciences of the USSR, Physical Series,_ v. 27, no. 1, pp. 66–68, 1963)

When a high-molecular-weight substance is added to an aqueous solution of an ionic dye, absorption and luminescence spectra are constantly changing, especially if both substances are in stoichiometric proportions and of opposite charge. Examples of the systems rhodamine 6G + Na dodecyl sulfate and pinachrome blue + deoxyribonucleic acid are detailed.

749. IMPURITY EXCITON SPECTRA OF MIXED CRYSTALS OF ISOTOPIC NAPHTHALENE FORMS

Sheka, E. F.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya, v. 27, no. 4, pp. 503–509, April 1963
(Paper presented at the Eleventh Conference on Luminescence, Minsk, September 10–15, 1962; translated from the Russian in _Bulletin of the Academy of Sciences of the USSR, Physical Series,_ v. 27, no. 4, pp. 501–507, 1963)

Curves and experimental points are presented for shifts of *A*1 and *B*1 bands in the absorption spectra of mixtures of naphthalene and deuterionaphthalenes, α-mono- , α-tetra- , β-tetra- , and octadeuterionaphthalene. Calculated frequencies for position and intensity of *A*1 and *B*1 bands in binary and ternary mixtures are tabulated and interpretations are compared with measured spectra.

750. LUMINESCENCE OF CRYSTALLINE BENZENE

Shpak, M. T., Solovev, A. V., Sheremet, N. I.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya, v. 27, no. 4, pp. 510–511, April 1963
(Paper presented at the Eleventh Conference on Luminescence, Minsk, September 10–15, 1962; translated from the Russian in _Bulletin of the Academy of Sciences of the USSR, Physical Series,_ v. 27, no. 4, pp. 508–510, 1963)

Luminescence spectra of C_6H_6 were obtained at 20.4 and 77°K. The bands at the two temperatures are presented. The C_6H_6 luminescence at low temperature is thought to be due to transitions from exciton zones of the first excited state of the crystal to the system of levels of the normal state.

751. INFLUENCE OF THE STRUCTURE OF THE CRYSTAL LATTICE ON ABSORPTION AND LUMINESCENCE SPECTRA OF THE IMPURITY IN MOLECULAR CRYSTALS

Vatulov, V. M.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 4, pp. 512–514, April 1963**
(Paper presented at the Eleventh Conference on Luminescence, Minsk, September 10–15, 1962; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 27, no. 4, pp. 510–512, 1963)

Impurity spectra are sensitive indicators of polymorphic phase transitions or of the location at different lattice defects. Octahydroanthracene and dihydroanthracene are used as examples.

752. THE DEPENDENCE OF THE POLARIZATION OF STILBENE SINGLE CRYSTAL LUMINESCENCE ON THE RADIATED WAVELENGTH AT LIQUID-AIR TEMPERATURE

Gribkov, V. I., Zhevandrov, N. D., Chebotareva, E. I.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 4, pp. 515–518, April 1963**
(Paper presented at the Eleventh Conference on Luminescence, Minsk, September 10–15, 1962; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 27, no. 4, pp. 513–516, 1963)

Stilbene crystals were slowly cooled to 77°K by passage through liquid N at 3 mm/hr to prevent cracking. At 77°K, as compared to room temperature, the 380-mμ band is weakened and a new strong band appears at shorter wavelengths. The new shorter wavelength band can be attributed to a change in potential curves of the ground and excited states. The ratio of trapped to free excitons seems to be varied.

753. INVESTIGATION OF SPECTRA AND OF TRANSFER CONDITIONS FOR ELECTRON EXCITATION ENERGY IN PURE AND DOPED ANTHRACENE CRYSTALS

Zima, V. L., Korsunskii, V. M., Faidish, O. M.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 4, pp. 519–523, April 1963**
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A study was made of anthracene crystals containing naphthalene, phenazine, acridine, or anthraquinone at 293 and 90°K. The quantum outputs of anthracene luminescence, B_a, were measured for varying concentrations and the energy transfer coefficients were derived and tabulated. Absorption and emission spectral measurements were also performed; only the naphthalene spectrum could be measured in anthracene. The other impurity spectra were measured in C_6H_6 solution, and a shift correction of 400 cm^{-1} was applied.

754. LUMINESCENCE OF MOLECULAR CRYSTALS CONTAINING IMPURITIES WITH DIFFERENT SOLUBILITY IN THE SOLID PHASE

Kovalev, V. P., Dobrokhatova, V. K., Naboikin, Yu. V., Kukushkin, L. S.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 4, pp. 524–526, April 1963**
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Luminescence kinetics of phenylbiphenylethylene and of β,β'-dinaphthylethylene in naphthalene and biphenyl single crystals were investigated. Impurities create in molecular crystals local excited states by distortion of electronic states of the host molecules.

755. TRIPLET STATES IN MOLECULAR CRYSTALS

Naboikin, Yu. V., Sidorov, S. V., Avdeenko, A. A.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 4, pp. 527–529, April 1963**
(Paper presented at the Eleventh Conference on Luminescence, Minsk, September 10–15, 1962; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 27, no. 4, pp. 524–526, 1963)

Single crystals of naphthalene grown with a benzophenone content of 0.05–0.5% by weight showed at 77°K yellow-green luminescence with a decay time of 2.3 sec. Quasi-line spectra of such crystals are identical with quasi-line spectra of benzophenone crystals containing 0.05% naphthalene as impurity. Some triplet luminescence is also induced by benzophenone impurities in phenanthrene crystals. The method of measuring the triplet spectra is explained, and the absence of triplet luminescence in crystals is attributed to an absence of nonradiative transitions to the metastable level.

756. ABSORPTION AND LUMINESCENCE OF SOLUTIONS AND ORIENTED FILMS OF Ψ-ISOCYANINE

Broude, V. L., Moisya, E. G.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 4, pp. 530–532, April 1963**
(Paper presented at the Eleventh Conference on Luminescence, Minsk, September 10–15, 1962; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 27, no. 4, pp. 527–530, 1963)

Absorption spectra of oriented 20-μ films of ψ-isocyanine were studied with polarized light at 293, 77, and 20°K. The half-width of the polymer absorption band is temperature dependent. The band decreases in intensity on drying of the gelled solution film and is absent in a dry sample. $M1$ is displaced in a dry sample and $M2$ is unchanged. The orientation of molecules in the polymer chain is discussed on the basis of $M1$ and $M2$ band polarization. The luminescence spectrum has a line structure at 20°K.

757. TRANSFER OF ELECTRON EXCITATION ENERGY IN RIGID SOLUTIONS OF ORGANIC MATERIALS

Andreeshchev, E. A., Kilin, S. F., Rozman, I. M., Shirokov, V. I.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya, v. 27, no. 4, pp. 533–539, April 1963
(Paper presented at the Eleventh Conference on Luminescence, Minsk, September 10–15, 1962; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 27, no. 4, pp. 530–536, 1963)

A study is reported of four luminophors prepared by polymerization of styrene solutions. The donor-acceptor pairs were: (1) *p*-terphenyl and 1,3,5-triphenyl-Δ^2-pyrazoline (*3FP*); (2) 1,1′,5,5′-tetraphenyl-3,3′-bipyrazolyl and *3FP*; (3) 2,5-diphenyl-1,3,4-oxadiazole and 1,1′,4,4′-tetraphenyl-1,3 butadiene (*4FB*); and (4) (*4FB*)-dibiphenyleneethylene. The work was intended to determine the quantum yield of energy transfer from donor to acceptor, and the conductivity as represented by the ratio of quantum yield of donor fluorescence with acceptor to the same quantum yield without an acceptor, and also to compare the transfer parameter with a theoretical value. Rather good correlation was obtained, but there seemed reason to doubt the completeness of the Förster–Galanin theory.

758. MECHANISM OF CONCENTRATION QUENCHING IN GLYCEROL SOLUTIONS OF FLUORESCEIN, RHODAMINE B AND TRYPAFLAVINE

Sveshnikov, B. Ya., Shirokov, V. I., Limareva, L. A.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya, v. 27, no. 4, pp. 551–553, April 1963
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Experimental data are plotted and an attempt is made to express results by modification of previously calculated forms.

759. TEMPERATURE EFFECT ON THE QUANTUM YIELD OF THE LUMINESCENCE OF VAPORS OF ORGANIC COMPOUNDS

Klochkov, V. P.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya, v. 27, no. 4, pp. 570–575, April 1963
(Paper presented at the Eleventh Conference on Luminescence, Minsk, September 10–15, 1962; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 27, no. 4, pp. 566–571, 1963)

The quantum yield (γ) of vapor fluorescence of 9-methyl- (I), 9,10-dimethyl- (II), and 9-diacetamidoanthracene (III) was investigated in the range 100–300°C, with γ of I and II increasing above 150–250°C, γ of III decreasing at high temperatures. Addition of another gas (isopentane) served to take up the surplus of vibrational energy by collision and changed the fluorescence spectra, with γ of I and II increasing and III decreasing. Such phenomena are in disagreement with the idea of a simple exchange of vibrational energy upon collision.

760. ELECTRON SPECTRA OF N-METHYLPHTHALIMIDE VAPORS

Korotkevich, V. T., Zelinskii, V. V., Borisevich, N. A.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya, v. 27, no. 4, pp. 576–579, April 1963
(Paper presented at the Eleventh Conference on Luminescence, Minsk, September 10–15, 1962; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 27, no. 4, pp. 572–575, 1963)

Fluorescence and absorption spectra were obtained from vapors of 3-dimethylamino-, 3-diphenylamino-, 3,6-diamino-, 3-monomethylamino-6-amino-, 3,6-tetramethyldiamino-, and 3,6-di(monomethylamino)-*N*-methylphthalimides, and of 3-diethylamino-*N*-ethylphthalimide. The first and last do not fluoresce. For the other five, the introduction of groups shifts the absorption and luminescence spectra toward the red, and the fluorescence spectra broaden with increasing *T*. Vibrational heat capacities are calculated.

761. EXCITON LUMINESCENCE OF MOLECULAR CRYSTALS

Broude, V. L., Sheka, E. F., Shpak, M. T.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya, v. 27, no. 5, pp. 596–605, May 1963
(Paper presented at the Eleventh Conference on Luminescence, Minsk, September 10–15, 1962; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 27, no. 5, pp. 597–607, 1963)

Exciton luminescence corresponding to electrovibrational levels can be differentiated from exciton-induced impurity luminescence by studying the temperature dependence of the half-widths of corresponding bands. Naphthalene is taken as an example and investigated at 4, 20, and 77°K. A complete interpretation and compilation of bands in naphthalene are tabulated.

762. FLUORESCENCE SPECTRA AND PHOSPHORESCENCE OF ALPHA- AND BETA-METHYL NAPHTHALENES IN NORMAL AND ISOPARAFFIN SOLVENTS AT 77°K

Levshin, V. L., Mamedov, K. I.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya, v. 27, no. 5, pp. 606–608, May 1963
(Paper presented at the Eleventh Conference on Luminescence, Minsk, September 10–15, 1962; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 27, no. 5, pp. 607–610, 1963)

763. INNER DEACTIVATION PATHS OF EXCITED AROMATIC MOLECULES IN VITREOUS SOLUTIONS

Ermolaev, V. L.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya, v. 27, no. 5, pp. 617–622, May 1963
(Paper presented at the Eleventh Conference on Luminescence, Minsk, September 10–15, 1962; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 27, no. 5, pp. 619–624, 1963)

All quenching in donor and acceptor molecules stems from nonradiative energy loss in the triplet state. Experiments were made on the quantum yields of fluorescence and phosphorescence and on the decay time of phosphorescence of $C_{10}D_8$, $C_{12}D_{10}$, $C_{10}H_8$, and $C_{12}H_{10}$ in an ethyl alcohol–ether mixture 2:1 at 77°K.

764. DEPENDENCE OF ABSORPTION AND FLUORESCENCE SPECTRA OF COMPLEX MOLECULES IN SOLUTION ON TEMPERATURE

Piterskaya, I. V., Bakhshiev, N. G.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 5, pp. 623–627, May 1963**
(Paper presented at the Eleventh Conference on Luminescence, Minsk, September 10–15, 1962; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 27, no. 5, pp. 625–629, 1963)

Absorption and fluorescence spectra of 4-amino-, 3-amino-, and 3,6-diaminophthalimide in benzene, ethyl acetate, and isoamyl alcohol are displaced as a function of temperature. The solutions were sealed in evacuated glass ampuls and displacements measured from 20 to 350°C. Experimental values are compared with theoretical ones.

765. ABSORPTION AND FLUORESCENCE OF VINYLANTHRACENES AND CHANGE OF MOLECULE CONFIGURATION IN THE EXCITED STATE

Cherkasov, A. S., Voldaikina, K. G.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 5, pp. 628–633, May 1963**
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9-Vinyl-, 1-vinyl-, and 2-vinylanthracene were synthesized. Different configurations of vinylanthracenes must lead to differences in absorption spectra which can be best derived by comparison with the corresponding Me anthracenes. Introduction of the vinyl group causes considerably more displacement to longer wavelengths than does the introduction of the CH_3 group. Oscillator strength is increased. A considerable displacement appears in luminescence spectra, indicating interaction of π-electrons with the anthracene nucleus. The presence of two possible configurations (*s-cis* and *s-trans*) can easily be observed on 2-vinylanthracene.

766. TEMPERATURE DEPENDENCE OF THE QUANTUM YIELD OF THE PHOSPHORESCENCE OF ORGANOPHOSPHORS

Pilipovich, V. A., Tursunov, N. I.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 5, pp. 641–643, May 1963**
(Paper presented at the Eleventh Conference on Luminescence, Minsk, September 10–15, 1962, translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 27, no. 5, pp. 642–644, 1963)

A method of measuring accurately the quantum yield of phosphorescence is proposed. This method was used to measure the relative quantum yield of trypaflavine fluorescence in solid-sugar solution and of fluorescein in B_2O_3 at +18 to −196°C. The course of both curves is the same and confirms previously published theoretical results. The measurement apparatus comprises a Hg light source, one set of disks on a rotating phosphoroscope, a second set of disks between the specimen and the monochromator, the monochromator, a photomultiplier, a wide-band amplifier, and an oscilloscope. Total light and phosphorescence may be read directly by suitable positioning of the slits in the disks.

767. KINDLING OF PHOSPHORESCENCE OF ORGANIC LUMINOPHORS

Khalupovskii, M. D.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 5, pp. 644–646, May 1963**
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768. CARBAZOLE AND PHENANTHRENE PHOSPHORESCENCE AT LIQUID-OXYGEN TEMPERATURE

Pyatnitskii, B. A., Vlasenko, A. I.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 5, pp. 647–650, May 1963**
(Paper presented at the Eleventh Conference on Luminescence, Minsk, September 10–15, 1962; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 27, no. 5, pp. 648–650, 1963)

The decay of phenanthrene phosphorescence was investigated at −183°C on crystals and solutions in normal paraffin and in EtOH; carbazole phosphorescence was investigated from 20 to −183°C on a crystal and at −183°C on a solution in ether. An exponential law is followed. Experimental results are presented.

769. EMISSION SPECTRA OF SOME POLYPHENYLS AND DIPHENYL POLYENES

Bolotnikova, T. N., Gobov, G. V.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 5, pp. 683–685, May 1963**
(Paper presented at the Eleventh Conference on Luminescence, Minsk, September 10–15, 1962; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 27, no. 5, pp. 681–684, 1963)

Luminescence spectra for frozen normal paraffin solutions of biphenyl, terphenyl, quaterphenyl, stilbene, and diphenylbutadiene were determined. The basic frequencies are tabulated and attributed to structural variations. The frequency of the purely electronic transition decreases on addition of each Ph ring by 2600 cm^{-1}.

770. LUMINESCENCE SPECTRA OF SOLUTIONS OF INDIGO AND SOME OF ITS DERIVATIVES AT 77°K

Nurmukhametov, R. N., Shigorin, D. N., Kozlov, Yu. I.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,* v. 27, no. 5, pp. 686–689, May 1963**
(Paper presented at the Eleventh Conference on Luminescence, Minsk, September 10–15, 1962; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 27, no. 5, pp. 685–688, 1963)

Fluorescence and long-wavelength absorption spectra are discussed for indigo, dimethylindigo, 5,5′-dichloroindigo, and tetrachloro- and tetrabromoindigo in hexane + dioxane solution (15:1) and of indigo in alcohol + dioxane (2:1), and xylene + aniline solutions, frozen at 77°K and excited with 365 mμ radiation.

771. SPECTRA OF FROZEN SOLUTIONS OF TWO IMPURITIES AT 77°K

Dobrokhotova, V. K., Kulchitskii, V. A., Naboikin, Yu. V.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,* v. 27, no. 5, pp. 690–692, May 1963**
(Paper presented at the Eleventh Conference on Luminescence, Minsk, September 10–15, 1962; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 27, no. 5, pp. 689–691, 1963)

The method of frozen hexane solutions at 77°K was used to study a system with resonant energy transfer, naphthalene + 1,2-di-9-anthrylethylene. Forty lines are tabulated, together with their analysis. All lines are interpreted as combinations of normal molecular vibrations, 239, 407, 1180, 1280, 1417, 1569, and 1666 cm^{-1}, with the purely electronic transition.

772. LUMINESCENCE SPECTRA OF PERYLENE AND DIISOBUTYL-3,9-PERYLENE-DICARBOXYLATE AT 20.4°K

Valdman, M. M., Sheremetev, G. D.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,* v. 27, no. 5, pp. 693–695, May 1963**
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Perylene spectra obtained from solutions in dibenzylaminoethanol, frozen to 20.4°K, show three groups of narrow lines forming doublets with distances between components of 60 cm^{-1}. Experimental results are presented.

773. SPECTRA AND QUANTUM YIELDS OF THE FLUORESCENCE OF SOME COUMARIN DERIVATIVES

Petrovich, P. I., Borisevich, N. A.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,* v. 27, no. 5, pp. 703–707, May 1963**
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Quantum yields of fluorescence and absorption data are tabulated for coumarin; 4,7-dimethylcoumarin; 3-(*p*-methoxyphenyl)-4,7-dimethylcoumarin; 7-hydroxycoumarin, 4-methyl-7-hydroxycoumarin; 4-methyl-7-aminocoumarin; 4-methyl-7-sulfomethylaminocoumarin (Na salt); 4-methyl-7-diethylaminocoumarin; 3,4-dimethyl-7-diethylaminocoumarin; 3-phenyl-4-methyl-7-diethylaminocoumarin; 3-acetyl-5, 6-benzocoumarin; 4-methyl-7,8-benzocoumarin; and Et 5,6-benzocoumarin-3-carboxylate. The group in the 7 position of the coumarin ring seems to determine spectral characteristics. There is little overlap between fluorescence and absorption spectra.

774. LUMINESCENCE OF SOLUTIONS AND CRYSTALS OF ORGANIC RARE EARTH COMPLEXES

Sevchenko, A. N., Kuznetsova, V. V., Khomenko, V. S.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,* v. 27, no. 6, pp. 710–716, June 1963**

Complex compounds were synthesized of 14 rare-earth elements with organic molecules, e.g., dibenzoylmethane, benzoylacetone, acetylacetone, derivatives of salicylic aldehyde, salicylic acid, *o*-oxyquinoline, and α-substituted pyridine compounds. The metal is combined with three molecules of the organic compound, so the coordination number of the rare-earth metal is 6. Addition of the rare-earth ion decreases k by $\sim$20% and shifts the spectrum by 5–7 mμ. Luminescence of crystals and solutions can be excited by ultraviolet light in compounds containing Eu, Sm, Tb, Yb, and Dy (no other rare-earth metals). The luminescence is thought to be brought about by the interaction of the π-electron system of the complex and the $4f$ electrons of the metal. The $4f$ electrons do not participate in the bonding. Energy transfer inside the complex leads to rare-earth ion luminescence if its resonance level is the lowest of all excited levels; if the triplet level is lower, only phosphorescence from the organic molecule is observed. The second resonance level is always higher than the triplet level and no transitions from it are observed. The effects of temperature and phase changes are considered, and specific reagents are suggested for the different rare earths.

775. EFFECT OF TEMPERATURE ON THE PHOSPHORESCENCE OF ORGANIC MATERIALS

Kislyak, G. M., Lisenko, G. M.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,* v. 27, no. 6, pp. 717–719, June 1963**

The phosphorescence of fluorescein, uranin, and sulfanilic and anthranilic acids was investigated, at temperatures of 160 to −183°C, when incorporated in alums in B_2O_2. The uranin phosphor afterglow changes color with temperature. Two metastable levels are indicated in uranin and in sulfanilic and anthranilic acids.

776. EFFECT OF THE MEDIUM ON THE ELECTRONIC SPECTRA OF METHYLNAPHTHALENE

Kharitonova, O. P.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,* v. 27, no. 6, pp. 745–747, June 1963**

777. LUMINESCENCE OF NAPHTHYL AND ANTHRYL DERIVATIVES OF ETHYLENE

Nagornaya, L. L., Nurmukhametov, R. N., Malkes, L. Ya., Shubina, L. V.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 6, pp. 748–753, June 1963**

The effect of the α-naphthyl and 9-anthryl radicals on the luminescence was examined at 20°C and 77°K on powders and solutions of 1,2-di-α-naphthylethylene, 1-phenyl-2-(9-anthryl)ethylene, 1-(naphthyl)-2-(9-anthryl)ethylene, and of two stereoisomers of dianthrylethylene. The stability under ultraviolet illumination was also investigated.

778. EFFECT OF SUBSTITUENTS ON THE LUMINESCENCE PROPERTIES OF AZOMETHINES

Terskoi, Ya. ., Bolotin, B. M., Brudz, V. G., Drapkina, D. A.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 6, pp. 754–757, June 1963**

Forty-four azomethine compounds, derivatives of salicylic acid and β-hydroxynaphthaldehyde, and an additional five derivatives of *p*-dimethylaminobenzaldehyde were synthesized and studied. Data of both groups are tabulated. Although there is no hydrogen bonding in azomethines, the luminescence is strong in crystals and in frozen solutions; this luminescence seems to be related to the field created by substituents in para and meta positions, in agreement with the steric conditions of the N-containing nucleus.

779. LUMINESCENCE SPECTRUM OF PENTAPHENYL

Matveeva, E. N., Medvedev, M. N., Rubina, O. G., Shafranov, M. D.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 6, pp. 763–764, June 1963**

Spectra are shown of biphenyl, terphenyl, quaterphenyl, and pentaphenyl. The polyphenyls having an even number of rings have bands at 4950, 4625, 4340, 4020, and 3870 Å, but polyphenyls with an odd number of rings have broad maxima. The pentaphenyl spectrum is displaced to the long wavelength end and does not have a pronounced band structure.

780. LUMINESCENCE OF *p*-VINYLBIPHENYL

Matveeva, E. N., Medvedev, M. N., Pisareva, M. G., Shafranov, M. D.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 6, pp. 765–766, June 1963**

p-Vinylbiphenyl was synthesized by dehydration of *p*-biphenylylmethylcarbinol over $KHSO_4$, purified in a chromatographic column over activated Al_2O_3 in petroleum ether, and recrystallized from alcohol. It was easily polymerized by heating in evacuated glass ampuls with a catalyst. Luminescence spectra are shown of a polycrystalline sample, of a melt, of the polymer, and of the polymer with 0.1% 1,4-bis(5-phenyl-2-oxazolyl)benzene. The luminescence is in the 4000- to 6000-Å range. A pink luminescence due to the monomer disappears under illumination with ultraviolet because of polymerization.

781. SPECTRAL AND LUMINESCENCE PROPERTIES OF BENZOPORPHYRINS

Solovev, K. N., Shkirman, S. F., Kachura, T. F.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 6, pp. 767–771, June 1963**

782. SPECTRAL LUMINESCENT INVESTIGATION OF PHOTOCHEMICAL PORPHYRIN TRANSFORMATIONS

Gurinovich, G. P., Pateeva, M. V., Shulga, A. M.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 6, pp. 777–781, June 1963**

Photochemical transformations of porphyrins were studied in solvents of pyridine, alcohol, mixtures of the two, and mixtures with H_2O, and also in acetone and H_2O, using ascorbic acid as reducer (approx. 50 mg per 10 cc). The spectral characteristics are reported.

783. ABSORPTION AND FLUORESCENCE SPECTRA OF THE WATER SOLUBLE ANALOGS OF CHLOROPHYLL

Savkina, I. G., Evstigneev, V. B.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 6, pp. 782–786, June 1963**

784. LUMINESCENCE OF CHLOROPHYLL SOLUTIONS

Sidko, F. Ya., Eroshin, N. S.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 6, pp. 787–790, June 1963**

A study was made of the absorption and luminescence spectra of H_2O–alcohol solutions of chlorophyll *a* as a function of aggregation. The chlorophyll was obtained by suspending single-cell water plants (*Chlorella*) in H_2O or extracting its pigments with EtOH. The luminescence was studied after absorption in the long-wavelength region. The chlorophyll is monomeric in alcohol and polymeric in H_2O. As H_2O is added to alcohol solutions, polymerization increases, the quenching of luminescence increases, and the peak of the red absorption band becomes displaced to longer wavelengths.

785. LUMINESCENCE OF GLYCININE

Karyakin, A. V., Chmutina, L. A.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 27, no. 6, pp. 791–795, June 1963**

A spectral investigation was made of glycinine fluorescence with and without the addition of Na fluorescein at different pH. Absorption spectra were measured in the region 220–600 mμ, and luminescence spectra in the region 410–560 mμ. The intensity increases with the pH of the protein solution, showing, however, a sharp minimum at pH 5.0. The intensity of albumin fluorescence also increases with the pH and the maximum is shifted from 435 mμ (pH 2.2) to 490 mμ (pH = 12.0). The fluorescence intensity of Na fluorescein solutions is decreased by protein, but the maximum of the luminescence band does not change its position, pointing to an interaction of protein and dye molecules.

786. THE PROBLEM OF THE CORRELATION OF THE PROCESSES OF INDUCTIVE MUTUAL ACTION OF EXCITED AND NONEXCITED MOLECULES

Rubinov, V. M., Kizel, V. A.
Akademiya Nauk Uzbekskoi SSR, Izvestiya, Seriya Fiziko-Matematicheskikh Nauk, no. 4, pp. 63–66, 1961

When varying the concentration of the studied dye, either the force of the absorption oscillator or the luminescence yield changes. The variation of the force (f) of the absorption oscillators is shown to depend on the mean distance for molecules of rhodamine 6G, fuchsine, crystal violet, and methylene blue. It is observed that, beginning from a certain critical intermolecular distance R_1 (14–31 Å), f falls rapidly. To confirm the view that this fall was related to the inductive mutual action of the absorption oscillators of the dye molecule, the dependence of the luminescence quenching on the concentration of all the above cited dyes has been studied. The Förster theory of the inductive mutual action yields a R_2/R_1 ratio, where R_2 is the intermolecular distance where the luminescence fall begins, which agrees, in magnitude, with that found experimentally. Thus, for wide lines, the mechanism of inductive mutual action is the same, whether for oscillators of absorption or for those of radiation, in agreement with the phenomenological theory of the inductive mutual action.

787. PROTOLYTIC DISSOCIATION OF ELECTRONICALLY EXCITED ORGANIC ACIDS

Bartok, W., Lucchesi, P. J., Snider, N. S.
American Chemical Society, Washington, D.C.
Paper 140, Division of Physical Chemistry, presented at the 140th Meeting, ACS, Chicago, Ill., September 3–8, 1961

Förster and Weller have shown that excitation by the absorption of ultraviolet light enhances the rate of dissociation of certain aromatic acids in aqueous solutions. Thus, the values of the acid dissociation constant for the excited singlets of 1-naphthol or 2-naphthol, for example, are smaller by as much as 6–7 pK_a units than the corresponding values for the ground state.

In the present work, the effects of excitation by absorption of ultraviolet light on the protolytic dissociation of p-substituted phenols were studied. The absorption and fluorescence spectra of phenol, p-cresol, and p-chlorophenol and of the corresponding anions were obtained, respectively, in neutral water and in 0.1M aqueous sodium hydroxide solution. From the absorption and fluorescence spectra of the acids and the anions, the values of pK_a^* for the excited state could be calculated. The values were found to be 5.71 ± 0.69, −0.63 ± 0.47, 3.05 ± 0.79 for phenol, p-cresol, and p-chlorophenol, respectively. The ground state values of pK_a^* for the above three compounds are 10.02, 10.27, and 9.38, in accord with the Hammett equation. Attempts to determine pK_a^* for p-nitrotoluene by this spectroscopic method failed as the fluorescence was completely quenched in aqueous solutions. Apart from the large increases in acidity with excitation, no correlation could be found for the dissociation constants of the excited phenols. In the light of the relatively small inductive effects of p-substituents compared with the influence of electronic excitation, the large fluctuation of pK_a^* values is unexpected. The work will be extended to other substituents as well as other series of compounds.

788. THE FLUORESCENCE AND PHOSPHORESCENCE OF SOME ALIPHATIC ALDEHYDES IN THE VAPOR PHASE

Borkowski, R. P., Ausloos, P. J.
American Chemical Society, Washington, D.C.
Paper 15, Division of Physical Chemistry, presented at the 141st Meeting, ACS, Chicago, Ill., March 20–29, 1962

The fluorescence and phosphorescence of propionaldehyde, n-butyraldehyde, isobutyraldehyde, trifluoroacetaldehyde, and pentafluoropropionaldehyde have been investigated at incident wavelengths of 2652, 2804, 3025, 3130, and 3341 Å. Both triplet- and singlet-state emissions were observed for the two perfluoroaldehydes, while the other aldehydes exhibited only singlet-state emissions, except at 2652 Å where no fluorescence was observed. Propionaldehyde, however, does sensitize emission from biacetyl at 3130 Å, which indicates that a triplet state may exist for these aldehydes, but does not emit. The fluorescence yields for each of these aldehydes are dependent upon the concentration, temperature, and incident energy. The trends observed by studying the effects of these parameters on the fluorescence yields of the nonfluorinated aldehydes indicate that these results may be explained on the basis of the same reaction mechanism. Another reaction mechanism was used to explain the results for the perfluoroaldehydes. Both schemes, however, involve a competition of the fluorescence process with collisional deactivation and decomposition. A brief study was also made on the fluorescence yields of acetone and acetaldehyde. These yields were compared with those of the other aldehydes.

789. TRIPLET EXCITATION MIGRATION AND DELAYED FLUORESCENCE IN BENZENE AND NAPHTHALENE CRYSTALS

Nieman, G. C., Robinson, G. W.
American Chemical Society, Washington, D.C.
Paper 11, Division of Physical Chemistry, presented at the 142nd Meeting, ACS, Atlantic City, N.J., September 9–14, 1962

Experiments on isotopic mixed crystals of benzene and naphthalene suggest that nearest neighbor triplet resonance interactions in these crystals are greater than 1.2 cm^{-1}. Even though this is a conservative lower limit, it is orders of magnitude greater than that estimated on the basis of first-order exchange coupling. Because of the large magnitude of these interactions, migration of triplet excitation over considerable distances may take place during the long triplet state lifetime. In a dilute crystal at low temperature, the triplet excitation is trapped by the dilute component, providing its excitation energy is lower. Excitation then proceeds to move from trap to trap in a time which may be fast compared with the triplet state lifetime. Triplet–triplet annihilation can produce higher singlet and triplet states, the rate increasing with increasing concentration of the traps. In an isotopically pure crystal this process is a major source of fast triplet quenching. In a dilute crystal some of the singlets thus produced radiate back to the ground state as delayed fluorescence. At low concentrations the delayed fluorescence may have an apparent activation energy which, because of tunneling, is always smaller than the actual trap depth.

The unexplained delayed fluorescence experiments of Sponer, Kanda, and Blackwell, and of Blake and McClure, can be understood on the above basis if β-methylnaphthalene is taken as the trap. This explanation removes the necessity of invoking ionization and electron trapping as a means of slow energy transfer in these crystals. The production of a high energy state from the interaction between migrating low energy states is reminiscent of the primary process in photosynthesis. The ability of triplet excitation to migrate more rapidly than previously supposed might be pertinent to the photosynthetic problem and to many other problems of chemical and biological interest.

790. ULTRAVIOLET ABSORPTION SPECTRA OF *o*-, *m*-, AND *p*-PHENYLENEDIAMINES AND THEIR MONO AND DIHYDROCHLORIDES IN AQUEOUS SOLUTION

Gallagher, P. K.
American Chemical Society, Washington, D.C.
Paper 12, Division of Physical Chemistry, presented at the 142nd Meeting, ACS, Atlantic City, N.J., September 9–14, 1962

Equilibrium quotients were determined at room temperature in aqueous solution for the proton dissociation reactions of *o*-, *m*-, and *p*-phenylenediamine dihydrochlorides. These values were calculated from pH titrations at an ionic strength of $1.0M$. Acid strengths are of the order $p > m > o$. The ultraviolet absorption spectra were measured for each of the nine species at 25°C and ionic strength $1.0M$. The spectra agreed well with the data available in the literature. The ionic species, with the exception of the divalent ortho ion, demonstrate that the addition of a proton to the free electron pair on the nitrogen cancels the original effect of the amine group upon the benzene spectrum.

791. ORGANIC COMPLEXES OF RARE EARTH IONS IN POLYMERIC HOSTS AS POTENTIAL OPTICAL MASER MATERIALS

Filipescu, N., Serafin, F. A., Kagan, M. R., McAvoy, N.
American Chemical Society, Washington, D.C.
Paper 153, Division of Physical Chemistry, presented at the 144th Meeting, ACS, Los Angeles, Calif., March 31–April 5, 1963

Single crystals and inorganic glasses have been successfully used as hosts for solid state optical maser materials. Line fluorescence characteristic of f^n orbital transitions for rare-earth chelates uniformly dissolved as molecular units in vinylic monomers and polymerized to solid solutions has been previously reported. The spectroscopic properties of europium tris(4,4,4-trifluoro-1,2-thienyl-1,3-butanedione) chelate dissolved in polymethylmethacrylate have been investigated at different temperatures and concentrations. The mechanism responsible for the line fluorescence is attributed to an intramolecular energy transfer from the lowest triplet state of the organic complex to the $^5D_0$ resonance energy level of the central europium ion. This mechanism involves absorption from the singlet ground state to excited singlet and triplet states followed by radiationless transitions to the lowest triplet state and subsequently to the $^5D_0$ resonance level, from which fluorescence transitions to all low lying ^7F levels of the europium ion occur. The concentration and temperature dependent fluorescence spectra of the europium chelate have been investigated. Absorption and phosphorescence spectra of the identical gadolinium chelate were related to the overall transfer mechanism and the lowest triplet state. The surrounding electric field splitting effects are observed as a function of temperature for the $^5D_0 \rightarrow {}^7F_{0,1,\ldots}$ transitions. The fluorescence lifetime and line width as function of temperature are also reported.

792. MOLECULAR COMPLEXES AND THEIR SPECTRA. XII. ULTRAVIOLET ABSORPTION SPECTRA CAUSED BY THE INTERACTION OF OXYGEN WITH ORGANIC MOLECULES

Tsubomura, H., Mulliken, R. S.
***American Chemical Society, Journal of the*, v. 82, no. 23, pp. 5966–5974, December 5, 1960**

D. F. Evans and others have found that extra absorption spectra appear when oxygen is dissolved in some organic solvents. In the present research, extra absorption spectra caused by oxygen have been measured by bubbling oxygen into ethyl alcohol, dioxane, *n*-butylamine, benzene, mesitylene, pyrrole, triethylamine, aniline, *N*,*N*-dimethylaniline, etc. It has been found that the smaller the ionization potential of the organic solvent molecule, the longer the wavelength at which the oxygen-induced band lies. This and other experimental results seem to indicate that the extra absorption bands are caused by charge-transfer interaction between oxygen as an electron acceptor and the organic solvents as electron donors, although no stable complexes are formed between them. Wave functions for various excited states of the O_2-donor pair including the charge-transfer states have been set up and the matrix elements of the Hamiltonian between these states estimated. It is concluded that the charge-transfer interaction between oxygen and an organic donor molecule can indeed give rise to charge-transfer absorption, with an intensity which is enhanced by interaction between the charge-transfer state and a singlet excited state or states of the donor. It is found that the charge-transfer state can also interact with triplet excited states of the donor and thereby cause the observed enhancements by oxygen of the singlet–triplet absorption bands.

793. DECAY KINETICS OF THE 1-NAPHTHALDEHYDE AND BENZOPHENONE TRIPLET STATES IN BENZENE

Bell, J. A., Linschitz, H.
***American Chemical Society, Journal of the*, v. 85, no. 5, pp. 528–532, March 5, 1963**

Flash excitation studies have been made on the metastable (triplet) states of 1-naphthaldehyde and benzophenone in benzene solution with added hydrogen donors and heavy metal chelates. This technique permits direct measurement of the rate constants for triplet decay, k_d, hydrogen abstraction, k_r, and triplet quenching, k_q. The ratios k_d/k_r and k_q/k_r calculated from the direct measurements agree well with previous values for the ratios obtained from photochemical data. The effect of impurities is discussed and found to play a major role in the decay of triplet states in solution. The short lifetime of benzophenone triplet in benzene solution seems to be anomalous.

794. ELECTRON DONOR PROPERTIES OF ZINC PHTHALOCYANINE

McCartin, P. J.
***American Chemical Society, Journal of the* v. 85, no. 13, pp. 2021–2022, July 5, 1963**

It has been previously shown that electron transfer from phthalocyanine, in the ground and excited states, to chloranil is an efficient mechanism of charge carrier production in semiconducting films. Such processes also have been shown to have considerable biological importance. Recent studies of the luminescence and associated properties of phthalocyanines appear to demonstrate analogous electron-donor tendencies in fluid solution.

It was found that the absorption band of zinc phthalocyanine at 668 mμ is depressed and broadened in the presence of strong acceptors 2,4,6-trinitrotoluene, *sym*-trinitrobenzene, and 2,4,7-trinitro-9-fluorenone, spectral effects being consistent with the formation of 1:1 complexes of the (predominantly) charge-transfer type.

A detailed study of the quenching of fluorescence of zinc phthalocyanine by a series of aryl nitro-compounds has established the following: (1) the emission spectra of the quenched and unquenched solutions are identical; (2) the extent of quenching is greater than can be accounted for by ground state complex formation alone; and (3) the ratio of fluorescence yields (γ^0/γ) in the absence and presence of the aryl nitro-compounds varies linearly with the quencher concentration $[A]$ for weaker quenchers, whereas, (4) for the strongest quenchers, the data are closely fitted by the expression

$$\gamma^0/\gamma = \{1 + k[A]\}\,\{1 + K_c[A]\}$$

where k is a constant and K_c is the ground state equilibrium constant determined independently from the absorption spectra. The sequence of values of the constant k appears to be that of the electron affinities of the quenchers.

795. DETERMINATION OF IRRADIATION PRODUCED TRIPLET EXCITATION BY FLASH SPECTROSCOPY

McCollum, J. D., Wilson, W. A.
August 1961
American Oil Company, Research and Development Dept., Whiting, Ind.
Report for February 1960–May 1961, ASD TR-61-170, AF 33(616)-7089

Triplet excited states accompanying pulsed electron irradiation of solutions of anthracene, phenanthrene, naphthalene, and 9-acetylanthracene have been detected by flash absorption spectroscopy. Energy transfer from the solvent and subexcitation electron impact appear to be important in triplet formation. Decay rates for the above triplets are of the order 10^3 sec^{-1} in paraffin oil and 10^4 sec^{-1} in cyclohexane and benzene. The first-order rate constants increase with dose and temperature. The triplet decay process is interpreted as diffusive free radical quenching by radicals produced simultaneously with triplets during irradiation. The temperature coefficient is due primarily to decrease in solvent viscosity with increasing temperature thereby increasing diffusion.

796. PARAMAGNETIC RESONANCE OF THE PHOSPHORESCENT STATES OF NAPHTHALENE-LIKE HETEROCYCLIC MOLECULES

Vincent, J. L.
American Physical Society, New York, N.Y.
Paper S14, presented at the American Physical Society Winter Meeting, California Institute of Technology, Pasadena, Calif., December 19–21, 1963

Paramagnetic-resonance absorption has been measured in the phosphorescent states of quinoline (I), quinoxaline (II), and cinnoline (III), (1-aza-, 1,4-diaza-, and 1,2-diazanaphthalene, respectively). Measurements were made at X-band on dilute solid solutions in single crystals of durene at 77°K during irradiation with an AH-6 mercury arc. Parameters for the spin Hamiltonians of I and II are reported, and are consistent with (π–π^*) triplet ($S=1$) states. The principal axes of the zero-field splitting tensor of I are found to be rotated by (±) 13°C from the symmetry axes of durene about the axis perpendicular to the molecular plane. The principal axes of the g tensor coincide with those of the zero-field-splitting tensor within experimental error. Hyperfine structure observed in I and II is assigned, and weak satellites split from the main lines of II by $\pm\gamma_H H_0/\gamma_e$ are assigned to simultaneous electron–proton spin flips. The paramagnetic resonance of III is due to a (n–π*) triplet state resulting from the excitation of a N-atom nonbonding electron to an antibonding π-orbital. It is estimated that the zero-field-splitting parameter D is in excess of 0.3 cm^{-1}, in contrast with I, II, and naphthalene, for which D=0.1 cm^{-1}.

797. THE LIMITING POLARIZATION OF THE FLUORESCENCE OF POLYATOMIC MOLECULES

Sevchenko, A. N.
***Analele Ştiinţifice ale Universităţii "A. I. Cuza," din Iasi (Serie Nouă), Secţionea I: Matematică, Fizică, Chimie,* v. 6, no. 4 (Supplement) pp. 809–818, 1960 (in Russian)**

If the emission and absorption spectra are symmetrical with respect to the frequency of the electronic transition, so are also the degrees of polarization of fluorescence. The fluorescent radiation P depends on the energy of molecular oscillation, and the limiting polarization P_0 is given by the ordinate of the point of intersection of two straight lines which portray the degrees of polarization. For phthalimide compounds P_0 was found to be 48% (theoretical value 50%). Symmetrical curves were obtained for porphyrin. Complex molecules of tetraphenylporphyrin with Mg and Zn have a D_{4h} symmetry structure (P_0 = 13%). In neutral solutions the equivalence of the pyrrol cycles is not preserved (P_0 = 40%). The presence of a Mg atom in the center of a chlorophyll molecule does not enhance its symmetry as significantly as in the case of porphyrin. (*PA*, 1963, #2635)

798. INTENSITY OF CHEMILUMINESCENCE IN MIXTURES OF LUMINOL AND A SOURCE OF HYDROXYL RADICALS AND ITS DEPENDENCE ON pH

Totter, J. R., Gordillo, A. E.
***Anales de la Facultad Medicina, Montevideo,* v. 46, pp. 37–40, 1961**

Investigation of the kinetics of light production during enzymic reactions in the presence of luminol (I) had suggested that oxidizing free radicals could play an important part in chemiluminescence. The relation between pH and the maximum light intensity emitted by solutions of I and $K_2S_2O_8$ was investigated. Half maximum intensity was observed at pH 11–12.

799. INFLUENCE OF THE CYANIDE ION ON THE CHEMILUMINESCENT REACTION OF LUMINOL WITH PEROXYDISULFATE IN ALKALINE MEDIUM

Bianchi, B., Demichelli, G., Prodanov, E.
***Anales de la Facultad Medicina, Montevideo,* v. 46, pp. 240–244, 1961**

A considerable increase in the maximum intensity was found, the effect being highest at pH close to 11. The variation in intensity of light with pH depended on the presence or absence of CN$^-$.

800. FLUORESCENCE OF SOME TETRACYANOETHYLENE COMPLEXES

Wyant, R. E., Poziomek, E. J., Poirier, R.H.
***Analytica Chimica Acta,* v. 28, no. 5, pp. 496–498, 1963**

801. FLUORESCENCE PROPERTIES OF TETRAHYDROFOLATE AND RELATED COMPOUNDS

Uyeda, K., Rabinowitz, J.C.
***Analytical Biochemistry,* v. 6, no. 1, pp. 100–108, 1963**

802. SPECTROFLUOROMETER CALIBRATION IN THE ULTRAVIOLET REGION

Parker, C.A.
***Analytical Chemistry,* v. 34, no. 4, pp. 502–505, April 1962**

A simple method is described for calibrating a fluorescence spectrometer so that corrected fluorescence emission spectra in the ultraviolet region can be determined. The method utilizes a fluorescent screen monitor originally designed to allow direct recording of corrected fluorescence excitation spectra. Corrected fluorescence emission spectra and relative fluorescence efficiencies of anthracene, naphthalene, phenol, and benzene are presented. (*PA*, 1962, #11,483)

803. FLUORESZENZEMISSION, ABSORPTION UND TEMPERATURSTRAHLUNG VON LÖSUNGEN (FLUORESCENCE EMISSION, ABSORPTION AND TEMPERATURE RADIATION OF SOLUTIONS)

Ketskemety, I., Dombi, J., Horvai, R.
***Annalen der Physik,* v. 8, no. 7–8, pp. 342–352, September 4, 1961**

Stepanov's relation between absorption and emission spectra of solutions is criticized. A modified equation is developed and shown to agree well with experimental determinations on fluorescein, eosin, rhodamine B, and trypaflavin in aqueous and ethyl alcoholic solutions. Three different optical arrangements were used. The emission spectrum for eosin and rhodamine varies with the exciting wavelength, and a calculated "effective molecular temperature" T^* is greater than the true temperature T of the solution. If a solution is excited by a wavelength such that T^* proves equal to T, then the quantum efficiency at a given wavelength of emission is proportional to the quotient of the emission by the temperature radiation of the solution at that wavelength. (*PA*, 1962, #1156)

804. APPLICATION OF ELECTRON SPIN RESONANCE TO THE STUDY OF FREE RADICALS PRODUCED BY IRRADIATION OF DEOXYRIBONUCLEIC ACID

Van de Vorst, A., van der Kaa, J. M., Depireux, J., Duchesne, J., Bertinchamps, A. J.

**_Archives des Sciences_, Geneva, v. 13, Special Number,
pp. 279–300, 1960 (in French)
(Paper presented at the Ninth Ampere Colloquium, Pisa,
September 12–16, 1960—Entry #501)**

805. FLUORESCENCE OF SOME QUINOLINE SALTS

**Sljivic, S., Nikolic, K.
Arhiv za Farmaciju, Belgrade, v. 12, no. 2, pp. 61–63, 1962
(in Croatian)**

Fluorescence of some quinoline salts and the effect of anions of various acids on fluorescence in solutions of the same acidity were investigated. Only quinoline picrate did not show fluorescent properties in the crystalline state; however, intense fluorescence occurred in solutions in which there was dissociation of the salt, because of the formation of a positive quinolinium ion.

806. LIGHT EMITTED UPON DISSOLUTION IN LUMINESCENT LIQUIDS OF IRRADIATED NaCl, LiF, KI, AND SOME ORGANIC SOLIDS

**Westermark, T., Grapengiesser, B.
Arkiv för Kemi, v. 17, pp. 139–149, 1961 (in English)**

A study was made to determine if irradiated solids dissolved in liquid scintillators could excite the solutes electronically and thus cause light emission. NaCl, LiF, KI, and some organic solids were irradiated by Co^{60} γ-rays and 2 Mev electrons in doses from a few Mrad up to 200 Mrad. Measuring apparatus is explained. The solutes were Tl^+, lanthanides, diphenyloxazole (PPO), dioxane, dioxane plus naphthalene, and a commercial naphthalene-sulfonic acid treated with HCHO, called Belloid TD. Irradiated glucose and sucrose also gave light pulses in water. Possibly electrons trapped in *F*-centers represent a potential energy which is released in some unknown way upon dissolution. The positive results for Tl^+, PPO, and Belloid TD show that these compounds were electronically excited. The output of irradiated organic solids and the lack of enhancement of light output of irradiated organic solids by Tl^+, PPO, and Belloid TD may be due to various surface phenomena. It appears that storage in humid atmosphere destroys the irradiation effect in hydrophilic organics.

807. FLUORESCENCE EXCITATION BY X-RAYS IN HIGHLY DILUTE AQUEOUS SOLUTIONS OF AROMATIC COMPOUNDS

**Sommermeyer, K., Prütz W., Birkwald, V.
Atomkernenergie, v. 6, no. 11, pp. 445–451, November 1961**

The reactions immediately following the absorption of ionizing radiation in water are of great importance in radiochemistry, but are by no means cleared up. To this end, the fluorescence of aromatic compounds in water produced by ionizing radiation was investigated. In this paper the experimental results are reported. (*PA*, 1962, #7222)

808. BIOLUMINESCENCE AS A PHYSIOLOGICAL INDEX

**Berliner, M. D., Laughlin, L. L., Jr.
1962
Avco Corporation, Research and Advanced Development Div., Wilmington, Mass.
Report**

Certain organisms, particularly wood-decaying fungi, emit a portion of the waste energy of oxidation as light rather than heat. Thus, the cell respiration is intimately connected to the production of light. Changes in the intensity of luminescence serve as an indicator of physiological changes both within the organism and the environment. Several species have proven to be ideal test organisms and are being intensively studied from all aspects of normal and variable environments. Luminescence is continuous for 30 days or longer, and accurate photometric techniques make monitoring routine. Preliminary work on the effects of temperature, light, X-ray, and ultraviolet irradiation is reported. Effects of other physiological parameters are under continuing study.

809. DIE ORIENTIERUNG DER OPTISCHEN ÜBERGANGSMOMENTE IN PHENANTHREN UND SEINEN AZADERIVATEN (THE ORIENTATION OF THE OPTICAL TRANSITION MOMENTS IN PHENANTHRENE AND ITS DERIVATIVES)

**Gropper, H., Doerr, F.
_Berichte der Bunsengesellschaft für Physikalische Chemie
(formerly Zeitschrift für Elektrochemie)_, v. 67, no. 1
pp. 46–54, 1963**

The absorption, fluorescence, and phosphorescence spectra of 7,8-benzoquinoline, 5,6-benzoquinoline, phenanthridine, phenanthridine cation, *o*-phenanthroline, *m*-phenanthroline, *p*-phenanthroline, and benzoquinoxaline are determined and compared with the spectrum of the basic compound phenanthrene. The transition moment of the triplet–singlet phosphorescence is shown to be perpendicular to the molecular plane in all the compounds examined.

810. SENSIBILISIERTE FLUORESZENZ NACH STRAHLUNGSLOSEM ENERGIEÜBERGANG DURCH DÜNNE SCHICHTEN (SENSITIZED FLUORESCENCE WITH RADIATIONLESS ENERGY TRANSITION THROUGH THIN FILMS)

**Drexhage, K. H., Zwick, M. M., Kuhn, H.
_Berichte der Bunsengesellschaft für Physikalische Chemie
(formerly Zeitschrift für Elektrochemie)_, v. 67, no. 1,
pp. 62–67, 1963**

A monomolecular layer of a dyestuff *S* is situated at a distance of, say, 50 Å from a monomolecular layer of a dyestuff *A*. If the molecules of *S* are excited by light, excitation energy is transferred from *S* to *A* without any radiation and sensitized fluorescence of *A* can be observed. If at a distance of, say, 50 A from the A layer there is a monomolecular layer of another dyestuff A', then after compound S has been optically excited an energy transfer, without radiation, to A occurs, and from there further to A', and the fluorescence of A' can be observed. The compounds S, A and A' are constituted in such a way that the absorption maximum of A is at about the same point as the fluorescence maximum of S, and similarly the absorption maximum of A' is at about the same point as the fluorescence maximum of A.

811. DIE POLARISATION DER TRIPLETT-SINGULETT-PHOSPHORESZENZ EINIGER AROMATEN UND HETEROCYCLEN II. MITTEILUNG: CHINOLIN, ISOCHINOLIN, FLUOREN, CHRYSEN, TRIPHENYLEN, DIBENZOCHINOXALIN, 1,2–3,4-DIBENZOPHENAZIN, CORONEN (THE POLARIZATION OF THE TRIPLET-SINGLET PHOSPHORESCENCE OF SOME AROMATICS AND HETEROCYCLICS. PART II. QUINOLINE, ISOQUINOLINE, FLUORENE, CHRYSENE, TRIPHENYLENE, DIBENZOQUINOXALINE, 1,2–3,4-DIBENZOPHENAZINE, AND CORONENE)

Doerr, F., Gropper, H.
Berichte der Bunsengesellschaft für Physikalische Chemie (formerly Zeitschrift für Elektrochemie), v. 67, no. 2, pp. 193–201, 1963

Phosphorescence and phosphorescence-polarization have been measured. Phosphorescence of these compounds had strong, negative polarization relative to all singlet–triplet transitions; it is deduced that the transition moment must be perpendicular to the plane of the molecule. Explanation of the result is based on the assumption that triplet–singlet emission arises as a result of intramolecular spin–orbit interaction. The value of the degree of polarization of phosphorescence changes along the spectrum.

812. DIE POLARISATION DER π–π-PHOSPHORESZENZ VON N-HETEROCYCLEN BEI ANREGUNG IN DER n–π-BANDE. CHINOXALIN, 2,3-DIMETHYLCHINOXALIN, CHINAZOLIN, BENZOCHINOXALIN (POLARIZATION OF THE π–π PHOSPHORESCENCE OF N-HETEROCYCLICS IN THE CASE OF EXCITATION IN THE n–π BAND. QUINOXALINE, 2,3-DIMETHYLQUINOXALINE, QUINAZOLINE, AND BENZOQUINOXALINE)

Doerr, F., Gropper, H., Mika, N.
Berichte der Bunsengesellschaft für Physikalische Chemie (formerly Zietschrift für Elektrochemie), v. 67, no. 2, pp. 202–205, 1963

Experiments in this report confirm ideas that the transition moment of triplet–singlet phosphorescence in unsubstituted aromatic and heterocyclic molecules is perpendicular to the plane of the molecule. It is therefore possible to establish submerged n–π bands by measurements of the polarization of the phosphorescence.

813. DIE BEEINFLUSSUNG DER FLUORESZENZ VON MOLEKÜLEN DURCH EIN ÄUSSERES ELEKTRISCHES FELD II. BESTIMMUNG VON DIPOLMOMENTEN ANGEREGTER MOLEKÜLE (EFFECT OF AN EXTERNAL ELECTRIC FIELD ON THE FLUORESCENCE OF MOLECULES. II. DETERMINATION OF DIPOLE MOMENTS OF EXCITED MOLECULES)

Czekalla, J., Liptay, W., Meyer, K. O.
Berichte der Bunsengesellschaft für Physikalische Chemie (formerly Zeitschrift für Elektrochemie), v. 67, no. 5, pp. 465–470, 1963

(For Part I, see Entry #661.) When molecules capable of fluorescence are irradiated in an external electrical field, the polarization degree, p_B, of the emitted light depends on the square of the electrical field strength. The ratio of Δp_B to the square of the field strength is determined by the dipole moments and polarizabilities of the molecules in the fundamental and in the excited state, and by the direction of the transition moment of the absorption and the emission. It is a function of the excitation and emission wave numbers. Only rigid molecules with one definite direction of the transition moment a_m for the absorption and e_m for the emission are considered. The polarization degree was determined as a function of the wave number of the fluorescence. The dipole moments in the fundamental state were determined and compared with values for the excited, fluorescence-capable singlet state. The following compounds were studied in benzene and/or dioxane: p-amino-p'-nitrobiphenyl; p-dimethylamino-p'-nitrobiphenyl; p-amino-p'-nitrostilbene; p-dimethylamino-p'-nitrostilbene; p-dimethylamino-ω-nitrostyrene; 2-amino-7-nitrofluorene; p-amino-p'-cyanobiphenyl; p-dimethylamino-p'-cyanostilbene; and p-dimethylaminobenzonitrile. Results are compared with dipole moments of the excited state obtained by other methods.

814. FERROMAGNETIC RESONANCE IN DNA SAMPLES

Shulman, R. G., Walsh, W.M., Jr., Williams, H. J., Wright, J. P.
Biochemical and Biophysical Research Communications, v. 5, no. 1, pp. 52–56, 1961

Electron spin resonance spectra measured *in vacuo* at 11.7 kMc in a 250-mg sample of low molecular weight DNA extracted from herring sperm are reported. At room temperature the broad resonance has a g-factor of 2.20 ± 0.05 and a line width between points of maximum slope of roughly 1200 gauss. As the temperature was lowered to 4.2°K, both the g-factor and the line width increased. The integrated intensity of the broad line, however, remained constant within ±20% as the temperature was lowered. The intensity was measured relative to that of DPPH free radical whose intensity exhibits the $1/T$ dependence characteristic of a paramagnet.

The g-factor is compatible with an iron group ferromagnetic compound or metal since values of g between 2.1 and

2.2 are characteristic of these materials. Further evidence for the ferromagnetic nature of the sample of herring sperm DNA is found in the measurements of the static susceptibility. In addition to the broad ferromagnetic resonance signal, another narrower resonance with a temperature independent g-factor of 2.070 ± 0.005 and a line width of 90 gauss was observed at 77, 20, and 4.2°K in the herring sperm sample. The intensity of this line was proportional to $1/T$ as expected for a paramagnetic material. It can be seen, however, that its integrated intensity is considerably less than the broad line.

Similar broad temperature independent electron resonances were observed in three other samples of DNA.

815. THE EXTENT OF ENERGY MIGRATION AND CHLOROPHYLL A ORIENTATION IN CHLORELLA

Teale, F. W. J.
***Biochimica et Biophysica Acta*, v. 42, no. 1, pp. 69–75,**
July 29, 1960 (in English)

A method is described by which $\bar{n}$, the average number of energy transfers between different chlorophyll-*a* molecules during the mean lifetime of the excited state, can be measured *in vivo*. The effect produced by added quencher molecules on the fluorescence excitation spectrum and yield enables $\bar{n}$ to be calculated without assumptions regarding the mutual orientation of the pigment molecules. The calculated mean value of $\bar{n}$ was 275. Although subject to error, this value is comparable with $\bar{n}_r$ measured in *Chlorella* and in concentrated chlorophyll solutions by fluorescence depolarization. Because $\bar{n}_r$ is calculated on a basis of random molecular orientation, the chlorophyll-*a* molecules *in vivo* cannot possess a high degree of preferred orientation. The time interval occupied by each transfer process is calculated, together with the trapping efficiencies to be expected *in vivo*.

816. ENERGY TRANSFER IN AQUEOUS SOLUTIONS

Posthuma, J., Berends, W.
***Biochimica et Biophysica Acta*, v. 51, no. 2, pp. 392–394,**
August 5, 1962 (in English)

For several reasons a triplet–triplet transfer of excitation energy in the aqueous solutions is considered most acceptable. One of the main arguments for this assumption is the parallelism between the effect of different types of compounds on the quenching of the riboflavin phosphorescence and the inhibition of the photodynamic conversion of pimaricin. Paramagnetic ions are particularly active as quenchers of phosphorescence; these ions shorten the lifetime of triplet states.

The effects of para- and diamagnetic ions on the systems riboflavin–pimaricin (under aerobic conditions) and lumichrome–pimaricin (anaerobic conditions) are investigated. The presence of paramagnetic ions apparently results in an inhibition of the transfer of the excitation energy between sensitizer and acceptor.

Diamagnetic ions do not show any effect at all. The direct destruction of pimaricin by ultraviolet light is not affected by paramagnetic ions. Because pimaricin has a complicated structure preventing theoretical explanation of decrease of extinction, *cis*- and *trans*-stilbene carboxylic acid-4, simpler compounds, were tested. Irradiation either of the *cis*- or the *trans*- form in the presence of lumichrome rapidly leads to a spectrum which in the region above 250 mμ agrees with a mixture of approximately 40% *cis* and 50% *trans* of the original concentration. This equilibrium mixture slowly decomposes on further irradiation. A similar equilibrium mixture is obtained by irradiation in the absence of a sensitizer with light of 253.7 mμ. Apparently a *cis–trans* and a *trans–cis* rearrangement is involved.

Similarities are noted between the stilbene compounds and the pimaricin.

817. THE EFFECT OF PHOTOSYNTHESIS INHIBITORS ON OXYGEN EVOLUTION AND FLUORESCENCE OF ILLUMINATED CHLORELLA

Zweig, G., Tamas, I., Greenberg, E.
***Biochimica et Biophysica Acta*, v. 66, no. 2, pp. 196–205,**
March 19, 1963 (in English)

Photosynthesis inhibitors, like symmetrical triazines, substituted ureas, and anilides, are able to stop oxygen evolution from illuminated *Chlorella* and cause a stimulation in fluorescence. These two phenomena seem to be interrelated as shown by partial inhibition studies. The exception to the rule was found to be cyanide which inhibited oxygen evolution but had no effect on fluorescence intensity.

818. THE ULTRAVIOLET FLUORESCENCE OF PROTEINS. I. THE INFLUENCE OF pH AND TEMPERATURE

Steiner, R. F., Edelhoch, H.
***Biochimica et Biophysica Acta*, v. 66, no. 3, pp. 341–355,**
May 21, 1963 (in English)

The intensity of the ultraviolet fluorescence of a group of extensively studied, highly purified proteins has been investigated as a function of pH and temperature. In those proteins whose structures are believed to be invariant to pH, the effects of pH were generally small at pH values acid to the ionization of their tyrosyl groups. In the latter pH zone, all proteins showed significant quenching of fluorescence which presumably resulted from the radiationless transfer of energy from tryptophanyl to ionized tyrosyl residues. In the pH zones where configurational transitions (reversible or irreversible) have been demonstrated by other procedures, these structural changes resulted in modifications in fluorescent intensity in all of the proteins studied. The influence of temperature on protein fluorescence in pH zones of thermal stability has been delineated in the case of several proteins. Deviations from a characteristic temperature dependence of fluorescence were observed in those pH zones in which the protein was known to undergo thermal denaturation. It would appear, therefore, that the observation of fluorescence intensity of protein solutions should provide a rapid and sensitive means of detecting and monitoring changes in protein structure.

819. THE FLUORESCENCE OF TYROSINE IN ALKALINE SOLUTION

Cornog, J. L., Jr. Adams, W. R.
***Biochimica et Biophysica Acta*, v. 66, no. 3, pp. 356–365, May 21, 1963 (in English)**

Contrary to previous reports in the literature, tyrosine in strongly alkaline solution (0.12*N* NaOH in these experiments) was found to have a measurable fluorescence, and determinations of the relative quantum yield of this species are presented.

It was found that tyrosine and two proteins exhibiting tyrosine fluorescence (insulin and RNAase) show a shift in the peak of their fluorescence spectra from 315 mμ in neutral H_2O to 345 mμ in 0.12 *N* NaOH.

Under neutral conditions the quantum yield of tyrosine incorporated in a protein is diminished when compared with that of free tyrosine in solution. This is not the case in 0.12 *N* NaOH, suggesting the presence under neutral conditions of a "structural quenching effect" not present under alkaline conditions.

820. ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF BIOLOGICAL MATERIALS. EFFECT OF DENATURATION OF THE ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF IRRADIATED PROTEINS

Blyumenfeld, L. A., Kalmanson, A. E.
***Biofizika*, v. 3, no. 1, pp. 87–91, 1958**
(Translated from the Russian in *Biophysics*, v. 3, no. 1, pp. 81–85, 1958)

A study is reported of the effect of prior thermal denaturation on EPR spectra of dry oxyhemoglobin, pepsin, ichthyocol, and casein. Doublet splitting is observed after irradiation of such materials. The radiation-induced free-radical concentrations are multiplied by several hundred with denaturation. An interpretation is offered.

821. SHORT-LIVED PHOSPHORESCENCE OF DL-TRYPTOPHANE IN SOLUTIONS

Barenboim, G. M.
***Biofizika*, v. 7, no. 2, pp. 227–232, 1962**

Short-lived phosphorescence, coinciding with fluorescence spectra, was observed. Lowering the temperature decreased intensity and increased duration. A triplet–singlet transition was indicated.

822. INTERACTION OF EXCITED BIOMOLECULES WITH OXYGEN. I. QUENCHING OF PHOTOLUMINESCENCE OF BIOMOLECULES BY O AND NO

Barenboim, G. M.
***Biofizika*, v. 8, no. 2, pp. 154–164, 1963**

The photoluminescence of amino acids, proteins, and nucleic acids was quenched uniformly in the whole luminescence spectrum by O and NO. The mechanism of quenching was explained by a transition of excited molecules to the triplet state owing to the paramagnetic molecules of quenching substance. The quenching by O is thought to be a primary oxidative reaction.

823. PROBABILITIES OF RADIATION AND NON-IRRADIATION TRANSITIONS IN MOLECULES OF ORGANIC DYES

Morozov, Yu. V.
***Biofizika*, v. 8, no. 2, pp. 165–171, 1963**

The lifetimes of phosphorescence and fluorescence, as well as the spectra of phosphorescence and total luminescence, were measured for trypaflavin in a solution of glucose and glycerol, for acridine orange in the same solution, and for acridine orange in an organic glass. The probabilities of transitions and of quenching on the triplet level are calculated.

824. NATURE OF SPONTANEOUS LUMINESCENCE OF ANIMAL TISSUES

Popov, G. A., Tarusov, B. N.
***Biofizika*, v. 8, no. 3, pp. 317–320, 1963**

The decomposition of H_2O_2 in saline extracts from rat livers is accompanied by slight chemoluminescence. The intensity of chemoluminescence depends on the degree of integrity of the tissue.

825. PECULIARITIES OF THE LUMINESCENCE OF ACRIDINE ORANGE AND OF RHODAMINE B DIMERS

Morozov, Yu. V.
***Biofizika*, v. 8, no. 3, pp. 331–334, 1963**

A bathochromic shift of fluorescence in values of about 110 and 70 mμ was noted in acridine orange and rhodamine B, respectively. Regarding phosphorescence, this shift was about 10 mμ for the former in glycerol with glucose, while it was not possible to determine phosphorescence of the monomer of the latter. Temperature effects on phosphorescence and fluorescence are compared.

826. NATURE OF ULTRAVIOLET CELL LUMINESCENCE

Konev, S. V., Lyskova, T. I., Bobrovich, V. P.
***Biofizika*, v. 8, no. 4, pp. 433–440, 1963**

The luminescence of suspensions of isolated rat-liver mitochondria and cell nuclei was studied by taking luminescence spectra, fluorescence excitation spectra, and fluorescence polarization spectra. The spectral-luminescent measurements were made in physiological saline or 0.25 *M* sucrose. Experimental results are discussed and interpreted.

827. ELECTRON SPIN RESONANCE IN ATP AND RNA

Maling, J. E., Taskovich, L. T., Blois, M. S., Jr.
***Biophysical Journal*, v. 3 no. 1, pp. 79–95, January 1963**

Cu^{++}, Mn^{++}, and Fe^{+++} account for the electron spin resonances observed in certain samples of ATP and RNA. The copper ion seems more loosely bound to these substances than ither iron or manganese. A striking similarity is observed etween the manganese spectra in manganese RNA, ATP, nd ADP, suggesting that the binding sites are similar in the hree compounds. The similarity of the ESR spectra of iron TP and of iron and manganese RNA, except for hyperfine pectrum in the latter, suggests that the two ions bind simi-rly in the two compounds. A detailed interpretation of the pectra is lacking, however, and these conclusions can only e tentative. When manganese TPP and ATP are heated or H changed, the ESR alters—indicating a change in the nvironment of the ion. The sharp 6-line manganese spectrum n both TPP and ATP at pH 1 suggests an almost "free" ion t this pH in the sense of an almost isotropic average environment.

828. ON THE ELECTRON SPIN RESONANCES IN DNA

Blois, M. S., Jr., Maling, J. E., Taskovich, L. T.
***Biophysical Journal*, v. 3, no. 4, pp. 275–297, July 1963**

Iron impurities are shown to account for characteristic electron spin resonances observed in samples of DNA. Com-arative ESR measurements on lyophilized samples were done n conjunction with static susceptibility measurements, trace nalyses, and molecular degradation experiments to establish his correlation. It has not been possible to extract this iron by treatment with a chelating agent. Such resonances were n part accounted for by ferromagnetic iron contamination during extraction and handling. By modifying the method of Kay, Simmons, and Dounce to eliminate or minimize metal ontamination—ionic and ferromagnetic—from sources both nternal and external to the tissues used, it was possible to prepare iron-free (<0.0004% Fe), ESR-free DNA.

829. THE EMISSION SPECTRA OF ORGANIC LIQUID SCINTILLATORS

Birks, J. B., Geake, J. E., Lumb, M.D.
***British Journal of Applied Physics*, v. 14, no. 3, pp. 141–143, March 1963**

The fluorescence emission spectra of toluene solutions of seven efficient scintillator solutes have been measured with a recording photoelectric spectrophotometer at a resolution of about 8 Å. The scintillator solutes investigated were: (1) p-terphenyl, (2) *p*-quaterphenyl, (3) 1,1′,4,4′-tetraphenylbutadiene, (4) 1,6-diphenyl-1,3,5-hexatriene, (5) 9,10-diphenyl anthracene, (6) 2,5-diphenyl oxazole, and (7) 2,2′-*p*-phenylene-*bis*-(5-phenyloxazole). The solutes were of "scintillation grade," and toluene was used as the solvent. The fluorescence was excited mainly by 2537-Å radiation from a low pressure mercury lamp with filters. Self-absorption effects were studied using different solution depths and concentrations.

830. DEPENDENCE OF LUMINESCENCE SPECTRA OF ORGANOPHOSPHORS ON CONCENTRATION

Baczynski, A., Czajkowski, M.
***Bulletin de l'Académie Polonaise des Sciences, Série des Sciences, Mathématiques, Astronomiques et Physiques*, v. 8, no. 11–12, pp. 651–654, 1960 (in German)**

Fluorescein in boric acid was examined. The maximum of emission was displaced toward lower wavelengths with increasing fluorescein concentration, but the intensity vs. wavelength curve remained practically the same shape.

831. THE CONCENTRATION QUENCHING OF THE FLUORESCENCE OF ANTHRACENE IN PLEXIGLAS

Kawski, A., Polacki, Z.
***Bulletin de l'Académie Polonaise des Sciences, Série des Sciences, Mathématiques, Astronomiques et Physiques*, v. 8, no. 11–12, pp. 817–819, 1960 (in German)**

Jabloński's theory of depolarization in solid solutions does not agree with earlier experimental results for concentrated solutions in plexiglas (Perspex), possibly because the theory neglects concentration quenching. New experiments show that this quenching begins at 10^{-2} mole/l, when the mean radius of the sphere of action of the molecule is 45 Å. (*PA*, 1961, #14,645)

832. AN ATTEMPT TO OBTAIN ELECTROLUMINESCENCE OF ORGANOPHOSPHORS

Łożykowski, H., Meczyńska, H.
***Bulletin de l'Académie Polonaise des Sciences, Série des Sciences, Mathématiques, Astronomiques et Physiques*, v. 9, no. 3, pp. 235–236, 1961 (in English)**

The same electroluminescence was observed from cellophane colored by various organic dyes, and from the uncolored material. (*PA*, 1961, #14,660)

833. ANOMALOUS PHOSPHORESCENCE OF NAPHTHALENE IN METHYL METHACRYLATE POLYMER

Czarnecki, S.
***Bulletin de l'Académie Polonaise des Sciences, Série des Sciences, Mathématiques, Astronomiques et Physiques*, v. 9, no. 3, pp. 561–563, 1961 (in English)**

Delayed fluorescence spectra of a 10^{-3} g cm^{-3} rigid solution were observed at temperatures of 293 and 77°K. The spectra are similar to the fluorescence spectra. The effect is attributed to double excitation of a molecule in the triplet state, by energy transfer from another triplet-excited molecule, leading to a singlet-excited molecule and an unexcited molecule. The effect was not observed with similar solutions of α-bromonaphthalene, α-iodonaphthalene, or phenanthrene. (*PA*, 1961, #20,023)

834. THE INFLUENCE OF ILLUMINATION ON VARIOUS IONIC FORMS OF FLUORESCEIN IN WATER SOLUTION

Głowacki, J.
Bulletin de l'Académie Polonaise des Sciences, Série des Sciences, Mathématiques, Astronomiques et Physiques, **v. 10, no. 2, pp. 115–119, 1962 (in English)**

Illumination produces photo reactions dependent on the type of fluorescein ion present. Blue-green light produces divalent from monovalent ions while red light reduces the optical absorption intensity for both kinds of ions. (*PA*, 1963, #3809)

835. ORGANIC ELECTROLUMINESCENCE

Bernanose, M. A.
Bulletin de la Société Française des Électriciens, **v. 3, Series 8, pp. 299–307, June 1962**

Specimens which exhibit electroluminescence under the influence of an alternating electric field are prepared by the impregnation of paper with organic fluorescent compounds. The specimens are subsequently treated to render them insensitive to water vapor. The construction, operation, and mechanism of the electroluminescent cells are discussed, and the influence of various factors on the electroluminescence is considered. (*PA*, 1963, #965)

836. CHARGE TRANSFER SPECTRA OF THE COMPLEXES OF IRON(II) WITH PYRIDINE-2-ALDOXIMATE

Israeli, Y.
Bulletin des Sociétés Chimiques Belges, **v. 72, no. 1–2, pp. 123–124, 1963 (in English)**

All the complexes of Fe(II) with pyridine-2-aldoximate have a narrow peak at 518 mμ, attributable to an electron charge transfer from the cation to the ligand. A theoretical expression is given for the charge transfer. This expression indicates that when the number of ligands bound to the cation increases, $\epsilon_{\max}$ should also increase. Agreement with the experimental data is noted.

837. FLUORESCENCE OF DRUGS AND RELATED COMPOUNDS. I. FLUORESCENCE OF BORON CHELATES OF o-HYDROXY CARBONYL COMPOUNDS

Shibazaki, T.
Bunseki Kagaku, **v. 12, pp. 385–389, 1963**

A fluorophotometer was built to determine the fluorescence intensity of samples. Twenty-three different samples were tested with a 3:7 Ac_2O–AcOH mixture containing 60 mg/10 ml H_3BO_3.

838. CHARGE-TRANSFER ASSOCIATION AND PARAMAGNETISM OF SOME ORGANIC SYSTEMS

Eastman, J. W.
August 1961
California, University of, Lawrence Radiation Lab., Berkeley
UCRL-9722, W-7405-eng-48

When p-xylene was combined with chloranil in n-heptane, charge-transfer optical absorption was observed. The magnitude of this absorption was used to calculate an equilibrium constant for the formation of a donor–acceptor complex. When p-xylene was combined with carbon tetrabromide and with carbon tetrachloride in n-heptane, no charge-transfer absorption was observed. Reactions of N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) with chloranil ($pQCl_4$) were observed in ethylene dichloride and acetonitrile. In both solvents adduct formation occurred initially, as observed by its charge-transfer absorption. In acetonitrile time-dependent ESR absorption was observed, and it was identified with the positive and negative radical ions of TMPD and $pQCl_4$, respectively. In this case a completely ionized electron transfer had occurred. Chloranil and other quinones were found to react with N,N-dimethylaniline, forming a crystal violet salt. The diamagnetic donor–acceptor complexes and also semiquinone radicals are intermediates which were observed. Some physical measurements of the kinetics of this reaction are described and correlated. When fluoranil was allowed to react with dimethylaniline, the hyperfine splitting by the fluorine atoms of the fluoranil radical was not resolved. Characteristics of the ESR absorption by this radical in dimethylaniline are discussed in terms of an electron transfer between the semiquinone and quinone, and between the semiquinone and hydroquinone ion. Paramagnetism was discovered in hydrocarbon-quinone solids. ESR absorption was assigned to imperfections in the solid which was normally diamagnetic. The preparation of these solids and some of their physical characteristics are described. (*NSA*, 1961, #29,098)

839. FLUORESCENCE EFFICIENCY OF CYCLOPENTANONE VAPOR AND ITS RELATION TO PHOTOLYSIS

La Paglia, S. R., Roquitte, B. C.
Canadian Journal of Chemistry, **v. 41, no. 2, pp. 287–292, February 1963**

Cyclopentanone vapor, when excited by light of wavelength 3130 Å, gives rise to four different photoproducts and fluorescence. The photochemistry of the molecule has been investigated by Srinivasan. In the present work, the fluorescence spectrum and fluorescence efficiency of cyclopentanone vapor are reported for the first time. The fluorescence spectrum is identical with that obtained from liquid solutions of cyclopentanone, with a maximum at 4100 Å. Time, temperature, oxygen, and inert gases do not affect the spectrum, which contains no component ascribable to phosphorescence, maximum 4450 Å. Beer's law is obeyed.

The fluorescence efficiency is also found to be independent of the variables temperature and pressure of inert gas, cyclopentanone, and oxygen. This is in marked contrast with the behavior of photochemical yields. The yields of cyclobutane and ethylene tend to increase at high vibrational energy content of the excited molecule (low pressure, high temperature, short exciting wavelengths), while the yield of pentenal increases under conditions of decreasing vibrational energy content (high pressures, etc.). The fact that fluorescence stabilization does not occur in cyclopentanone can be related to the results of photolysis.

840. FLUORESCENCE DECAY TIME MEASUREMENTS OF ORGANIC SCINTILLATORS
Falk, W. R., Katz, L.
***Canadian Journal of Physics*, v. 40, no. 8, pp. 978–991, August 1962**

The time dependence of the fluorescence emission from scintillators was measured for a number of commonly used organic scintillators under α-particle and γ-ray excitation. A sampling oscilloscope was used to record the pulses obtained from a fast scintillation counter. Using such a system, a gating arrangement can be employed which permits selection of only those scintillation events which deliver a predetermined total charge output from the photomultiplier. Noise within the sampling unit limits the measurements to the main fast components in the fluorescence emission. All of the plastic scintillators exhibit decay times between 2.1 and 4.4 nsec. Stilbene exhibits "particle type" discriminating characteristics with a strong second component in the decay (~35 nsec) appearing under α-particle excitation. In addition to the main component in the decay of anthracene, evidence of two shorter components was also found. For all the scintillators tested, the α-particle-induced scintillation had a slightly longer decay time than the corresponding γ-ray induced scintillation. (*PA*, 1962, #16,862)

841. MEASUREMENT OF EXTREMELY SHORT DECAY TIMES OF ORGANIC PHOSPHORS, EXCITED BY AN ELECTRON BEAM
Kloss, H. G.
***Ceskoslovensky Casopis pro Fysiku*, v. 12, pp. 628–633, 1962**

In a new type of fluorometer, having an accuracy to within 2×10^{-11} sec, a modulated electron ray is used to excite the phosphor, and the phase difference between excitation and light emission is measured electronically.

842. THE ELECTRONIC SPECTRA OF *N*-HETEROAROMATIC SYSTEMS. PART I. THE $n \rightarrow \pi$ TRANSITIONS OF MONOCYCLIC AZINES
Mason, S. F.
***Chemical Society, Journal of the*, London, v. 1959, pp. 1240–1246, March 1959**

843. THE ELECTRONIC SPECTRA OF *N*-HETEROAROMATIC SYSTEMS. PART II. SUBSTITUTED MONOCYCLIC AZONES
Mason, S. F.
***Chemical Society, Journal of the*, London, v. 1959, pp. 1247–1253, March 1959**

844. THE ELECTRONIC SPECTRA OF *N*-HETEROAROMATIC SYSTEMS. PART III. THE $n \rightarrow \pi$ TRANSITIONS OF MONOCYCLIC HYDROXY-AZINES
Mason, S. F.
***Chemical Society, Journal of the*, London, v. 1959, pp. 1253–1262, March 1959**

845. THE ELECTRONIC SPECTRA OF *N*-HETEROAROMATIC SYSTEMS. PART IV. THE VIBRATIONAL STRUCTURE OF THE $n \rightarrow \pi$ BAND OF *SYM*-TETRAZINE
Mason, S. F.
***Chemical Society, Journal of the*, London, v. 1959, pp. 1263–1268, March 1959**

846. THE ELECTRONIC SPECTRA OF *N*-HETEROAROMATIC SYSTEMS. PART V. THE ROTATIONAL STRUCTURE OF THE VIBRATIONLESS BAND IN THE $n \rightarrow \pi$ TRANSITION OF *SYM*-TETRAZINE
Mason, S. F.
***Chemical Society, Journal of the*, London, v. 1959, pp. 1269–1274, March 1959**

847. THE ELECTRONIC SPECTRA OF *N*-HETEROAROMATIC SYSTEMS. PART VI. THE $n \rightarrow \pi$ TRANSITIONS OF MONOCYCLIC AMINO- AND MERCAPTO-AZINES
Mason, S. F.
***Chemical Society, Journal of the*, London, v. 1960, pp. 219–224, January 1960**

848. THE ELECTRONIC SPECTRA OF *N*-HETEROAROMATIC SYSTEMS. PART VII. ANALOGUES OF THE CINNAMOYL ANION
Mason, S. F.
***Chemical Society, Journal of the*, London, v. 1960, pp. 1282–1286, March 1960**

849. THE ELECTRONIC SPECTRA OF *N*-HETEROAROMATIC SYSTEMS. PART VIII. THE CHARGE-TRANSFER SPECTRA OF QUATERNARY IODIDES
Mason, S. F.
***Chemical Society, Journal of the*, London, v. 1960, pp. 2437–2444, June 1960**

850. THE ELECTRONIC SPECTRA OF *N*-HETEROAROMATIC SYSTEMS. PART IX. $n \rightarrow \pi$ TRANSITIONS OF POLYCYCLIC AZINES
Mason, S. F.
***Chemical Society, Journal of the*, London, v. 1962, pp. 493–498, February 1962**

(For Part X, see Entry #549.)

851. THE LUMINESCENCE OF SOME SUBSTITUTED NAPHTHALENES

Corkill, J. M., Graham-Bryce, I. J.
***Chemical Society, Journal of the,* London, v. 1961,**
pp. 3893–3897, September 1961

The luminescence spectra of the fourteen isomeric nitronaphthylamines and ten isomeric dinitronaphthalenes have been measured at low temperatures. A new form of electronic phosphorometer was used. The emission from the nitronaphthylamines for all except three compounds was found to be fluorescence, and in all cases luminescence was weak. Comparison of fluorescent and phosphorescent maxima with absorption maxima suggests that the first excited singlet and triplet levels have similar energies. In the spectra of the dinitronaphthalenes, a wide separation was found between the first two bands, the usual interval being approximately 1400 cm^{-1}. Probable assignments are suggested for the bands found in these spectra.

852. STIMULATED LIGHT EMISSION IN ORGANIC MOLECULES

Morantz, D. J., White, B.G., Wright, A. J. C.
***Chemical Society, Proceedings of the,* London, v. 1962,**
pp. 26–27, January 1962

An intense flash of white light was used to populate the triplet state. The stimulated emission was generated by two parallel reflecting plates. The medium was a rigid organic glass at 77°K. The procedures and results were similar to those described for a ruby maser. Observations are summarized as follows. Sharp "bursts" of light were observed superimposed on the phosphorescent decay. After the burst the level of the phosphorescence was reduced below the value obtained without reflecting plates, and the amount of reduction is a function of the flash intensity. The greater the flash intensity, the less is the residual phosphorescence. At a critical light intensity a series of several consecutive major bursts were observed; when the flash intensity was increased above this critical value only one major burst was observed. Results obtained with acetophenone and benzaldehyde are graphed.

In addition to examining single species these phenomena have been observed in an energy-transfer system exemplified by benzophenone as donor and naphthalene as acceptor; the stimulated emission was observed in the acceptor.

853. THE PHOSPHORESCENCE AND DELAYED FLUORESCENCE LIFETIMES OF PYRENE IN LIQUID PARAFFIN

Stevens, B., Walker, M. S.
***Chemical Society, Proceeding of the,* London, v. 1963,**
p. 181, June 1963

A 0.01 *M* solution of pyrene in outgassed liquid paraffin emits both delayed fluorescence and phosphorescence over the temperature range from 0 to −30°C. In this investigation the decay constants k_D and k_T for each emission component (isolated by appropriate optical filters) were measured, using an apparatus previously constructed. In all cases the decay was exponential over the region of observation, and standard errors in the measured decay constants, obtained from least squares plots of log intensity against time, amounted to less than 5%.

854. ABSORPTION SPECTRA AND CATALYTIC BEHAVIOR OF THE COPPER (II) CHELATES OF SOME ALKYLATED ETHYLENEDIAMINES

Ojima, H., Sone, K.
***Chemical Society of Japan, Bulletin of the,* v. 35, no. 2,**
pp 298–303, February 1962

Visible absorption spectra have been investigated for the following chelates in their aqueous solutions:

$[\mathrm{Cu\ en_2}]^{2+}$
$[\mathrm{Cu(tetramethyl\text{-}en)_2}]^{2+}$
$[\mathrm{Cu\ pn_2}]^{2+}$
$[\mathrm{Cu}(N\text{-propyl-en})_2]^{2+}$
$[\mathrm{Cu}(N, N'\text{-dipropyl-en})_2]^{2+}$
$[\mathrm{Cu}(N, N\text{-diethyl-en})_2]^{2+}$
$[\mathrm{Cu}(N\text{-hydroxyethyl-en})_2]^{2+}$

Maximum frequencies and molar extinction coefficients were calculated. An approximate linear relation is shown between maximum frequencies and the log of stability constants. Spectral changes are noted with additions of NaOH to the solutions. The catalytic activities of the chelates on the chemiluminescent reaction of luminol with Na_2O_2 in alkaline solution are also considered.

855. ELECTRONIC SPECTRA AND ELECTRONIC STRUCTURES OF SOME BASIC HETEROCYCLIC *N*-OXIDES

Kubota, T.
***Chemical Society of Japan, Bulletin of the,* v. 35, no. 6,**
pp. 946–956, June 1962

The ultraviolet absorption spectra of pyrazine mono-*N*-oxide, 4-methylpyrimidine *N*-oxide and pyrazine di-*N*-oxide have been measured under various conditions, and band analyses of those spectra have been carried out. In order to interpret the spectra and other physicochemical properties of pyrazine di-*N*-oxide, semiempirical LCAO-MO calculations, including the treatments of configuration interactions, have been undertaken in a manner similar to previous calculations on pyridine *N*-oxide. On the other hand, the spectra of pyrazine mono-*N*-oxide and 4-methylpyrimidine *N*-oxide have been interpreted on the basis of the calculated results on pyridine *N*-oxide described in a previous paper. The high intensity bands (278, 274, and 323.6 mμ for 4-methylpyrimidine *N*-oxide, pyrazine mono- and di-*N*-oxide respectively) can reasonably be assigned to charge transfer bands such as the 282-mμ band of pyridine *N*-oxide.

These substances also exhibit weak bands in the longest wavelength region in nonpolar solvents. These weak bands may possibly be due to the n→π* transitions. SMO calculations on isoquinoline *N*-oxide and acridine *N*-oxide have also been carried out with the same parameters as those in the case of pyridine *N*-oxide in nonpolar solvents, and various physicochemical properties have been discussed on the basis of these calculations. As has been pointed out in a previous paper, the parameter for the oxygen atom used is too small. To estimate the most reasonable value, SMO calculations were carried out many times on pyridine *N*-oxide, which was used as a model compound. As a result, it was found that $k_0 \approx 0.8$ is the best value.

856. ON THE ELECTRONIC SPECTRUM OF 1,2-DI-9′-ANTHRYLETHANE

Akiyama, S., Nakagawa, M.
***Chemical Society of Japan, Bulletin of the*, v. 36, no. 3,**
p. 351, March 1963

The low absorption intensity reported in the literature is scarcely understandable in view of the presence of two anthracene nuclei in the molecule. In order to check on prior results, the synthesis of the hydrocarbon was carried out according to the method of Barnett with a modification starting from 10-methyleneanthrone, and the spectrum was measured. Expectedly, the spectrum exhibited much higher absorption intensity than that of the former investigation. The fact that the ε-value of the absorption maximum at the longest wavelength was found to be approximately double the corresponding ε-value of 9-methylanthracene is consistent with the additivity principle of absorption intensity of unconjugated chromophores.

857. THE ELECTRONIC STRUCTURE OF CARBAZOLE IN THE FLUORESCENT STATE

Mataga, N., Torihashi, Y.
***Chemical Society of Japan, Bulletin of the*, v. 36, no. 3,**
pp. 356–357, March 1963

A study has been made of various solvent effects on the absorption and fluorescence spectrum of carbazole, including the effect of hydrogen bonding in a nonpolar solvent and the effect of ionic dissociation in an aqueous alkaline solution. Some quantum mechanical studies of the electronic structure and spectra of this series of molecules have been made by the composite system method. A good agreement with the experimental observations has been obtained.

For the sake of simplicity, only the wave functions for the lowest and the second excited singlet state of carbazole are shown.

The increase of the dipole moment in the fluorescent state was calculated to be ~ 1.96 *D*. The value of $\Delta\vec{\mu}$ was determined experimentally by the method proposed by Lippert and by Mataga. The experimental value agrees well with calculated results.

858. SOLVENT EFFECTS ON THE FLUORESCENCE SPECTRUM OF THE ION-PAIR (NAPHTHOL-TRIETHYLAMINE SYSTEM)

Mataga, N., Kawasaki, Y., Torihashi, Y.
***Chemical Society of Japan, Bulletin of the*, v. 36, no. 3,**
pp. 358–359, March 1963

It has been previously demonstrated that the strong hydrogen bond between β-naphthol and triethylamine (TEA) in the equilibrium ground state and in the excited Franck–Condon state shifts to the ion-pair in the excited equilibrium state, from which fluorescent transition occurs, in benzene. This phenomenon has been interpreted as due to a strong charge transfer from the nitrogen nonbonding orbital of TEA to the OH antibonding orbital of naphthol in the Franck–Condon excited state, which is followed by an almost complete proton transfer from oxygen to nitrogen in the excited equilibrium state. This work has been extended here to systems including various solvents of different polarities, and results are obtained which seem to support the interpretation. The solvents used were monochlorobenzene, dichloroethane, and acetonitrile. Wave number shifts of band maxima due to complex formation are tabulated.

859. THE ESR SPECTRUM OF THE PHTHALONITRILE ANION RADICAL

Nakamura, K., Deguchi, Y.
***Chemical Society of Japan, Bulletin of the*, v. 36, no. 3,**
pp. 359–366, March 1963

When phthalonitrile was reduced in dimethoxyethane (DME) with potassium or sodium, the anion radical was formed. The following spectra are presented and discussed: ESR spectrum of phthalonitrile anion radical reduced with potassium in DME; calculated spectrum of phthalonitrile anion radical; and ESR spectrum of phthalonitrile anion radical reduced with sodium in DME.

860. SOLVENT EFFECTS ON THE ABSORPTION AND FLUORESCENCE SPECTRA OF NAPHTHYLAMINES AND ISOMERIC AMINOBENZOIC ACIDS

Mataga, N.
***Chemical Society of Japan, Bulletin of the*, v. 36, no. 6,**
pp. 654–662, June 1963

The absorption and fluorescence spectra of naphthylamines and isomeric aminobenzoic acids in various solvents have been measured.

From the observed results, the difference in the dipole moments in the fluorescent and ground states, respectively, i.e., $\Delta\vec{\mu}=\vec{\mu}_e-\vec{\mu}_g$, has been estimated for naphthylamines.

The effect of hydrogen bonding between solute and solvent molecules on the spectral shifts has been discussed. The hydrogen bonding between alcohol and amino nitrogen exerts an especially remarkable influence on the spectra, and the reorganization of this hydrogen bond during the lifetime of the excited solute molecule has been concluded from the observed results.

The intramolecular hydrogen bond of o-aminobenzoic acid considerably decreases the $\Delta\vec{\mu}$ value and the effect of the intermolecular hydrogen bonding on the spectra. This result has been explained as due to the charge transfer through the intramolecular hydrogen bond.

The $\Delta\vec{\mu}$ values for naphthylamines and naphthols have been calculated using the ASMO-CI method and compared with the observed results.

This comparison, together with the theoretical interpretation of the characteristics in the spectra of α- and β-isomers, respectively, has indicated that the lowest excited singlet state in the light absorption is ^1L_b, whereas the fluorescent state is ^1L_a in the case of α-naphthylamine and ^1L_b is the relevant excited state for both light absorption and fluorescence in the case of β-naphthylamine and naphthols.

The mechanism of this level reversal has been discussed as being due to the change in the structure of the amino group during the lifetime of the excited state.

861. ELECTRONIC SPECTRA OF AROMATIC MOLECULAR CRYSTALS. I. SUBSTITUTED BENZENE MOLECULES

Tanaka, J.
***Chemical Society of Japan, Bulletin of the,* v. 36, no. 7, pp. 833–847, July 1963**

The electronic absorption spectra of some substituted benzene molecules p-nitroaniline, benzoic acid, acetanilide, *trans*-cinnamic acid, and durene have been measured in ethanol or n-heptane solutions and as single crystals, using polarized light. The measurement of the crystalline spectra reveals in many respects the properties of the transitions of substituted benzene molecules. The 277 mμ of durene, which is reasonably regarded as a band analogous to the 260 mμ of benzene, is shown to be polarized perpendicular to the two-fold symmetrical axis of the molecule. Bands of the same type occur at 264 mμ in p-nitroaniline (crystal), at 284 mμ in benzoic acid, at 282 mμ in acetanilide, and at 299 mμ in *trans*-cinnamic acid. In addition, those molecules in which the benzene ring is substituted by the electron-accepting groups show a strong band, associated with intramolecular charge transfer, in the near ultraviolet region. The 370 mμ band of p-nitroaniline is shown to be polarized parallel to the long axis of the molecule, and the 230 mμ band of benzoic acid has a polarization parallel to the line connecting the centers of the benzene ring and the carbonyl group. The directions of the transition moments of the 240 mμ band of acetanilide and the 276 mμ band of *trans*-cinnamic acid are also shown to be on the line connecting the substituents and the benzene ring. Davydov splitting is observed in the crystal of p-nitroaniline; this splitting is in good agreement with the values calculated by the exciton theory.

862. THE ELECTRONIC SPECTRA OF AROMATIC MOLECULAR CRYSTALS. II. THE CRYSTAL STRUCTURE AND SPECTRA OF PERYLENE

Tanaka, J.
***Chemical Society of Japan, Bulletin of the,* v. 36, no. 10, pp. 1237–1249, October 1963**

A new crystalline form of perylene has been found, and its crystal structure has been determined by the two-dimensional X-ray diffraction method. The new form is monomeric, while the previously known form has a dimeric structure. The electronic absorption and fluorescence spectra of both forms have been measured; on the basis of these data, an assignment is proposed for the observed transitions. Although the fluorescence spectrum of the monomer form shows a small shift, that of the dimer form shows a larger shift than would be expected from the absorption spectrum. This is explained as a stabilization of the lowest excited singlet state by a charge-transfer resonance interaction between the molecules in a pair. Because this stabilization increases as the distance between two molecules decreases, it is suggested that the molecules in a pair approach each other after excitation. At the liquid helium temperature the motion of molecules in the crystal will be frozen out, the larger stabilization of the excited level cannot occur, and the green emission which is characteristic of the monomer form is observed from the dimer form. The rate process of the molecular motion at lower temperatures has been analyzed.

863. ELECTRONIC SPECTRA AND M.O.-L.C.A.O. STUDY OF AROMATIC ISOTHIOCYANATES

Zahradník, R., Vlachova, D., Koutecký, J.
***Collection of Czechoslovak Chemical Communications,* v. 27, pp. 2336–2348, 1962**

Electronic spectra for 45 aromatic isothiocyanates were investigated. First and second intense maxima are tabulated, absorption curves for three isocyanates are presented, and their reactivity discussed. Various energy quantities were calculated for 19 of the isocyanates, and the interdependence of the quantities was investigated.

864. SPECTRA AND APPARENT ASSOCIATION CONSTANTS OF FLUORESCING COMPLEXES OF SOME SALICYLALDEHYDE DERIVATIVES

Holzbecher, Z.
***Collection of Czechoslovak Chemical Communications,* v. 28, pp. 716–727, 1963 (in German)**

865. BEHAVIOR OF ORGANIC SCINTILLATOR UNDER HIGH VOLTAGE

Mitrani, L., Bonchev, T.
***Comptes Rendus de l'Académie Bulgare des Sciences,* v. 16, no. 5, pp. 477–479, 1963 (in English)**

866. ÉTUDE DES TRANSFERTS D'ACTIVATION ENTRE MOLÉCULES DE COLORANTS FLUORESCENTS EN SOLUTION SOLIDE DANS LE PLEXIGLASS (STUDY OF TRANSFER OF EXCITATION BETWEEN FLUORESCENT PIGMENTS IN SOLID SOLUTION IN PERSPEX)

Lafitte, E., Macé, N., Pujols, C.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 253, no. 23, pp. 2665–2667, December 4, 1961**

Fluorescent and nonfluorescent pigments are dispersed in Perspex and the effect of their spectral overlap characteristic on degree of polarization of fluorescence is measured. Transfer of excitation energy between fluorescent molecules does not seem to be affected by the second coloring material in some cases but in others transfer is strongly suppressed. Transfer is found to depend on overlap of absorption and emission spectra. (*PA*, 1962, #4164)

867. LA POLARISATION DE LA FLUORESCENCE ET LA FORME DE L'OSCILLATEUR DANS LE CAS DE COLORANTS DÉRIVÉS DU TRIPHENYLMÉTHANE (THE POLARIZATION OF THE FLUORESCENCE AND THE FORM OF THE OSCILLATOR IN THE CASE OF TRIPHENYLMETHANE DYE DERIVATIVES)

Laffitte, E., Macé, N., Pujols, C.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 253, no. 25, pp. 2911–2913, December 18, 1961**

Fluorescence polarization studies were made on crystal violet, methyl violet, and malachite green. The results are interpreted in terms of two excited singlet states with transitions, polarized at right angles to each other. These states are closely spaced in the first two compounds, but in malachite green they are well separated, and two fluorescence bands, one red and the other green, are observed. (*PA*, 1962, #6630)

868. SPECTRES ÉLECTRONIQUES A BASSE TEMPÉRATURE DU DURÈNE CRISTALLISÉ (LOW TEMPERATURE ELECTRONIC SPECTRA OF CRYSTALLIZED DURENE)

Bénarroche, M.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 254, no. 3, pp. 459–461, January 15, 1962**

The absorption and fluorescence spectra of durene (symmetrical tetramethyl benzene) were measured at 20 and 4°K. The absorption spectrum resembles that of benzene and does not vary much from 4 to 20°K. The fluorescence lines are single at 20°K and double at 4°K. (*PA*, 1962, #12,594)

869 TRANSFERTS D'ÉNERGIE ENTRE ÉTATS TRIPLETS EN MILIEU CRISTALLIN À 77°K (ENERGY TRANSFER BETWEEN TRIPLET STATES IN THE CRYSTALLINE PHASE AT 77°K)

Cadas, J. P., Courpron, C., Lochet, R., Rousset, A.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 254, no. 14, pp. 2490–2492, April 2, 1962**

Experiments on mixed crystals of benzophenone and naphthalene have shown that energy transfer does occur between benzophenone in the triplet state and naphthalene in the ground state, giving rise to the intense T-S spectrum of naphthalene. (*PA*, 1962, #12,592)

870. EXCITON DU NAPHTALENE ET DE L'OCTODEUTÉRONAPHTALÈNE À 4°K (EXCITON OF NAPHTHALENE AND OF DEUTERO-NAPHTHALENE At 4°K)

Ciais, A.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 254, no. 15, pp. 2741–2743, April 9, 1962**

The levels in the absorption spectrum of crystallized naphthalenes H_8 and D_8 are studied and tabulated. The frequencies ν' of the various levels agree with those calculated by the formula $\nu' = A - B/n^2$, where $A = 31930$, $B = 3816$ for naphthalene H_8, and $A = 32090$, $B = 3816$ for naphthalene D_8. The vibrations associated with the various levels are also given. A comparison is made between the results obtained for naphthalenes H_8 and D_8. The splitting of levels for naphthalene D_8, like naphthalene H_8, is verified. (*PA*, 1962, #16,817)

871. SPECTRES D'ABSORPTION ET DE FLUORESCENCE DU FLUORENE CRISTALLISÉ PUR AT 4°K (ABSORPTION AND FLUORESCENCE SPECTRA OF PURE CRYSTALLIZED FLUORENE AT 4°K)

Bénarroche, M.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 254, no. 20, pp. 3520–3522, May 14, 1962**

A quasi-hydrogen-like exciton absorption spectrum is observed, the distribution of rays being given by $\nu' = A - B_0/n^2$ cm^{-1} with $A = 33141$ and $B_0 = 3502$. The fluorescence spectrum consists of a weak part starting near the exciton band for $n = 3$ and a strong part displaced from the weak part by 1610 cm^{-1} toward low frequencies. The results are compared with those obtained by earlier workers for other organic crystals. (*PA*, 1962, #18,826)

872. FLUORESCENCE DU 2,6-DIMÉTHYLNAPHTALÈNE PUR DANS L'HÉLIUM LIQUIDE (FLUORESCENCE OF PURE 2,6-DIMETHYLNAPHTHALENE IN LIQUID HELIUM)

Bénarroche, M.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 254, no. 22, pp. 3836–3838, May 28, 1962**

The fine structure of the fluorescence spectrum is observed and analyzed. It is proposed that two exciton levels and six exciton sub-levels, none of which is observed in the spectrum, due to self-absorption, serve as the origins of the fluorescence spectrum. (*PA*, 1962, #18,870)

873. MESURE DE LA DURÉE DE VIE DANS L'ÉTAT TRIPLET (MEASUREMENT OF LIFETIME IN THE TRIPLET STATE)

Martinez, A.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 255, no. 3, pp. 491–493, July 16, 1962**

Using an oscilloscope screen, the lifetime Γ of delayed fluorescence was measured for organic materials diluted in rigid glasses; the fluorescence arose from emission from the metastable triplet state. The method was adapted to measure Γ in the range 10^{-6} to 10 sec; values are quoted for a number of materials.

874. LUMINESCENCE EN PHASE VAPEUR ET EN SOLUTIONS CRISTALLISÉES À 77°K, DE QUELQUES ALDÉHYDES ET CÉTONES AROMATIQUES (LUMINESCENCE OF SOME AROMATIC ALDEHYDES AND KETONES IN THE VAPOR PHASE AND IN CRYSTALLINE SOLUTIONS AT 77°K)

Longin, P.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 255, no. 5, pp. 865–867, July 30, 1962**

Benzaldehyde, acetophenone, benzophenone, and 2-chlorobenzophenone have similar emission spectra in crystalline solution at 77°K and in the vapor phase. Their luminescence is shown to be due to a single transition, localized in the carbonyl group, which has a lifetime of the order of 10^{-3} sec, corresponding to a triplet–singlet transition. 4-Chlorobenzophenone and anthraquinone have emission spectra similar to the other aromatic aldehydes and ketones at low temperatures, but their emission in the vapor phase is very different. (*PA*, 1963, #961)

875. SUR LA RELATION ENTRE LA DURÉE DE VIE ET L'INTENSITÉ DE LA FLUORESCENCE DANS LA RÉGION D'EXTINCTION THERMIQUE (THE RELATION BETWEEN THE LIFETIME AND INTENSITY OF FLUORESCENCE IN THE REGION OF THERMAL EXTINCTION)

Payen de la Garanderie, H.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 255, no. 20, pp. 2585–2587, November 12, 1962**

The complex salt used for study was $(C_5H_5NH)_2\ MnCl_4$. The decline of intensity of luminescence after excitation followed a simple exponential law. The ratio of the intensity of luminescence with constant excitation (a function of absolute temperature) to the lifetime of luminescence remained constant in the temperature range studied. Comparison with the Mott and Seitz law is presented.

876. EXCITATION D'UNE FLUORESCENCE RETARDÉE PAR DES PHOTONS D'ENERGIE INFÉRIEURE À CELLE DES PHOTONS ÉMIS (EXCITATION OF DELAYED FLUORESCENCE WITH THE EMITTED PHOTON ENERGY GREATER THAN THE INCIDENT PHOTON ENERGY)

Muel, B.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 255, no. 23, pp. 3149–3151, December 5, 1962**

A solution of 3,4-benzopyrene in ethanol, sensitized by auramine, fluorescein, or eosine, and frozen at −140°C, exhibits a delayed-emission band between 0.4 and 0.46 μ after excitation by radiation of wavelengths greater than 0.5 μ. A model is proposed in which the initial absorption occurs in energy levels of the sensitizer molecules, energy then being transferred to a triplet level of the 3,4-benzopyrene. A cooperative transition between two molecules excited in this manner is now assumed to occur, one molecule being raised to the first singlet state from which the emission is observed, the other returning to the ground state. Some experimental evidence is presented in support of this model. (*PA*, 1963, #8627)

877. UN EXEMPLE DE SÉPARATION RÉVERSIBLE DE CONFIGURATIONS DYNAMIQUES D'UNE MÊME MOLÉCULE ORGANIQUE EXCITÉE (EXAMPLE OF THE REVERSIBLE SEPARATION OF THE DYNAMIC CONFIGURATION OF THE SAME EXCITED ORGANIC MOLECULE)

Douzou, P.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 256, no. 8, pp. 1769–1771, February 18, 1963**

The molecule 1,3,3-trimethylindoline-6′-nitrobenzospiropyrane, excited by radiation at 3650 A, shows reversible color in blue at 293°K and in red at 77°K.

878. ABSORPTION ET LUMINESCENCE DU TRIPHÉNYLÈNE EN SOLUTION ÉTENDUE DANS L'HEXANE À 77°K: MISE EN ÉVIDENCE D'UNE FLUORESCENCE PAR ÉCHELON (TRANSITION T*→T) (ABSORPTION AND LUMINESCENCE OF TRIPHENYLENE IN A DILUTE SOLUTION OF HEXANE AT 77°K. EVIDENCE OF A FLUORESCENCE BY STEPS)

Dupuy, F., Nouchi, G., Rousset, A.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 256, no. 14, pp. 2976–2979, April 1, 1963**

In exciting a solution of triphenylene in *n*-hexane at 77°K, there has been obtained, besides the luminescences $T \rightarrow S$ and $S^* \rightarrow S$, a step fluorescence corresponding to a transition $T^* \rightarrow T$. These assignments are confirmed by a study of the absorptions $S^* \leftarrow S$ and $T^* \leftarrow T$.

879 TRANSFERT INTERMÉDIAIRE D'EXCITATION DANS LES SCINTILLATEURS À BASE DE XYLÈNE (INTERMEDIATE TRANSFER OF EXCITATION IN SCINTILLATORS BASED ON XYLENE)

Furst, M., Koechlin, Y., Raviart, A.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences,* v. 256, no. 17, pp. 3639–3642, April 22, 1963**

An intermediate process of transfer of nonradiative excitation has been made evident in scintillators based on xylene. This transfer is due to the presence of an impurity adsorbable by a 4-Å molecular sieve. It divides by a factor greater than ten the lifetime of the excited state of the xylene molecules, reducing it from 20 to 1.6 nsec. The transport time to the solute is evaluated at less than 2 nsec.

880. DÉTECTION DES ACTIVITÉS β SUR UN CHROMATOGRAMME EN COUCHE MINCE AVEC UN SCINTILLATEUR GÉLIFIABLE (DETECTION OF BETA ACTIVITY ON A THIN LAYER CHROMATOGRAM WITH A GELATINOUS SCINTILLATOR)

Roucayrol, J. C., Taillandier, P.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences,* v. 256, no. 22, pp. 4653–4654, May 27, 1963**

Aluminum 2-ethylhexanoate was added to a toluene-based scintillator to form a gel.

881. COMPARAISON DE L'ÉLECTROLUMINESCENCE DE L'ORANGE D'ACRIDINE ET DE LA PHOTOLUMINESCENCE PRODUITE PAR DÉCHARGE GAZEUSE (COMPARISON OF THE ELECTROLUMINESCENCE OF ACRIDINE ORANGE AND THE PHOTOLUMINESCENCE PRODUCED BY GASEOUS DISCHARGE)

Hoarau, J., Abetino, F.
***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences,* v. 257, no. 3, pp. 646–649, July 17, 1963**

A study is made of the influence of voltage and frequency on the emission luminescence of acridine orange absorbed in cellophane. Comparison of these results with those already known for electroluminescence shows that no fundamental difference exists between electroluminescent cells of acridine orange and the cells of gaseous discharge.

882. RESPONSE OF ANTHRACENE TO β-RAYS

Řezanka, I., Frána, J.
***Czechoslovak Journal of Physics,* v. 10, no. 9, pp. 686–687, 1960**

The scintillation response of an anthracene crystal in vacuum to electrons of energies from 30 to 400 kev was measured. The response vs. energy curve is linear with an intercept at 8.5 kev. The square of the reduced distribution width is found to be proportional to the electron energy, and yields a value of 2.4 ± 0.2 kev/photoelectron. (*PA*, 1961, #20,021)

883. LIFETIME STUDIES OF PHOSPHORESCENCE IN AROMATIC COMPOUNDS UNDER VARIOUS CONDITIONS AT LOW TEMPERATURES

Olness, D. U.
1961
Duke University, Durham, N.C.
Thesis
(Microfilm available as Mic 61-2925, University Microfilms, Ann Arbor, Mich.)

Decay curves of the triplet–singlet emission from naphthalene, hexamethylbenzene, and durene in the crystalline phase have been studied under various conditions of crystal formation and in the presence of different gases, at temperatures of 4.2°K and higher. Rigid glass solutions of these compounds at 77°K and a mixed crystal of naphthalene in durene at 4.2 and 77°K have also been studied. The decay from the crystalline samples did not obey an exponential law at any temperature studied. Crystalline durene was found to have two lifetimes, one on the order of seconds and the other on the order of tens of milliseconds. The longer-lived decay is interpreted as the true durene decay and the short-lived as that of an oxidation product of durene, which was produced photochemically and excited by sensitization. In general, the later portions of the decay curves from all of the substances were nearly exponential. When the mean half-life, measured in these later portions was plotted as a function of temperature, the lifetime was found to decrease with increasing temperature as $\log 1/T$ throughout the temperature region studied. Decay curves from all of the solutions studied at 77°K were found to be exponential in cases where a true glass was formed. Over the range of concentrations studied, the decay times were found to either remain constant or to decrease with increasing concentration. The emission from the mixed crystal of naphthalene in durene consisted of two parts: a short-lived decay from the durene oxidation product and a longer-lived exponential decay from naphthalene. Various theories concerning the causes of the nonexponential decay and the change in the general shape of the decay curves with temperature are discussed. It is suggested that the inhomogeneous magnetic field produced by neighboring triplet molecules is partially responsible for the nonexponential decay; this theory was first proposed by M. Kasha in 1947. However, it appears that the effect is too great to be explained by this mechanism alone, and that purely crystalline phenomena are also very important in determining the type of decay. A discussion of some of these crystal phenomena is included. (*DA*, 1961)

884. PHOTOLUMINESCENT EFFECTS IN CONTACT ELECTROLUMINESCENCE

Morosin, B., Haak, F. A.
***Electrochemical Society, Journal of the,* v. 108, no. 5, pp. 477–478, May 1961**

Mixtures of photoluminescent phosphors with metal particles or powdered materials of high dielectric constant, observed in castor oil cells under ac fields, may give emission which is not intrinsic electroluminescence but photoluminescence. It appears to depend on the intermediate production of ultraviolet or violet light, possibly by local glow discharges. (*PA*, 1961, #17,924)

885. INTERACTION OF ELECTRON ACCEPTORS WITH BASES. VII. VISIBLE ABSORPTION SPECTRA OF AROMATIC AMINE-ACCEPTOR COMPLEXES IN SOLUTION

Foster, R., Thomson, T. J.
***Faraday Society, Transactions of the*, v. 59, no. 485, pt. 5, pp. 1059–1063, May 1963**

Intermolecular complexes of *N, N, N′, N′*-tetramethyl-*p*-phenylenediamine (TMPD), an electron donor, with a series of electron acceptors, were studied. In cyclohexane, intermolecular π–π charge-transfer transitions were indicated. Solutions in MeOH of the weaker acceptor–donor complexes had similar spectra, whereas the stronger acceptor–donor pairs indicated that complete electron transfer had occurred.

886. EXTERNAL PHOTOEFFECT FROM THE SURFACE OF ORGANIC SEMICONDUCTORS

Vilesov, F. I., Zagrubsky, A. A., Garbuzov, D. Z.
***Fizika Tverdogo Tela*, v. 5, no. 7, pp. 2000–2006, July 1963**

Energy spectra of photoelectrons are presented for electronic emission from the surface of anthracene, pentacene, naphthacene, phthalocyanines of Mg, Cu, Al, and Fe, and some other organic compounds. Values of their photoelectric work functions are given. The experimental data are compared with theoretical calculations.

887. SECONDARY ELECTRONIC EMISSION OF SOME POLYMERS

Matskevich, T. L.
***Fizika Tverdogo Tela, Akademiya Nauk SSSR, Otdelenie Fiziko–Matematicheskikh Nauk, Sbornik Statei*, v. 1, no. 2, pp. 277–281, August 1959**

The coefficients of secondary-electronic emission, the coefficients of reflection, and dependence on the energy of primary electrons were measured for polyethylene, 4-bromo-2,5-dimethylstyrene, 2,3-dichloro-4,5-dimethylstyrene, polystyrene, and poly(vinyl alcohol). The results obtained are interpreted.

888. STUDIES ON THE PHOSPHORESCENCE OF POLYSTYRENE

Herold, L. P.-E.
1961
Fordham University, New York, N.Y.
Thesis
(Microfilm available as Mic 61-1570, University Microfilms, Ann Arbor, Mich.)

A bluish green phosphorescence was obtained when a thin film of polystyrene was subjected to an electrical discharge in a helium gas medium at liquid air temperature. It was found that the pressure of the gas carrier in the flask affected the deactivation process. Runs conducted at −196, −78, 0, and 25°C indicated that the intensity of the phosphorescence decreased with rise in temperature. In general, no noticeable effect was observed when the thickness of the polystyrene film was changed, although when extremely thin films were employed, a slight dependence on polystyrene concentration was found. Changing the solvent used to form the film or the nature of the gas in which the film was placed was without effect either on the intensity or the color of the phosphorescence. When polystyrene films containing small additions of either anthracene or methyl-2-anthryl ketone were irradiated, the fluorescence of the two mixtures and phosphorescence of the latter appeared blue rather than light green. The inclusion of other impurities caused no change in the color of the radiation. The visible emission spectrum of the polystyrene glow and afterglow, taken by means of a Gaertner spectrograph, showed a line at 4855 Å and a weaker one at 4340 Å. An explanation is suggested for these experimental observations, based on the supposition that the observed phosphorescence may be due to the decay of polystyrene diradicals.

889. ELECTRONIC SPECTRUM AND BASICITY OF THE CYCLO [3.2.2] AZINES

Gerson, I. F., Heilbronner, E., Joop, N., Zimmerman, H.
***Helvetica Chimica Acta*, v. 46, no. 6, pp. 1940–1951, 1963 (in German)**

The first four absorption bands of the ultraviolet spectrum for these compounds were assigned to the electronic transitions (1) ${}^1A \rightarrow {}^1L_b$, (B_2); (2) ${}^1A \rightarrow {}^1L_A$, (A_1); (3) ${}^1A \rightarrow {}^1B_a$, (A_1); and (4) ${}^1A \rightarrow {}^1B_b$, (B_2). The assignments were made on the basis of molecular orbital theoretical models and experimental polarization data.

890. MAGNETISM OF ORGANIC SUBSTANCES

Liu, T.-M.
***Hua Hsueh Tung Pao*, no. 7, pp. 34–41, 1962**

The paramagnetic properties and the susceptibilities of some conjugated double bond polymers were tabulated. The intensity of the paramagnetic resonance was enhanced by the length of the conjugated double bonds and the presence of uncoupled electron spins, and was independent of the method of preparation and the concentration of the sample. As temperature is decreased from +150 to −196°C, the Curie law is followed, with paramagnetic resonance increasing. The width and the shape of lines were unchanged. The conductivities of the substances containing narrow spectral lines were lower than those of the substances containing wide spectral lines. The conditions for substances that showed wide spectral lines were noted. These facts were helpful for interpreting the structure and the interactions of the electrons in the subgroup of the conjugated system. The susceptibilities of some conjugated high-molecular-weight organic compounds were studied and the data tabulated. The paramagnetism was changed to diamagnetism after the sample was dissolved.

891. SINGLET→TRIPLET ABSORPTION IN HALOGEN SUBSTITUTED TOLUENES

Roy, J. K.
***Indian Journal of Physics and Proceedings of the Indian Association for the Cultivation of Science*, v. 34, no. 7, pp. 331–335, July 1960**

Continuous singlet→triplet absorption in the near ultraviolet due to *o*-bromotoluene, *p*-chlorotoluene, and *m*-fluorotoluene in the liquid state was investigated. It was observed that the region of absorption shifts gradually toward the red with the increase in the atomic weight of the substituent halogen atom. The luminescence spectrum due to *m*-fluorotoluene in the solid state at −180°C was also studied, and the luminescence bands were found to be weaker than those due to chloro- and bromotoluene. (*PA*, 1961, #14,053)

892. RAMAN, INFRARED AND LUMINESCENCE SPECTRA OF SOME TRISUBSTITUTED BENZENES

Deb, K. K., Banerjee, S. B.
***Indian Journal of Physics and Proceedings of the Indian Association for the Cultivation of Science*, v. 34, no. 12, pp. 554–564, December 1960**

Tentative assignments of the vibrational frequencies of the molecules of 2,4- and 3,4-dichlorotoluene and 1,2,4-trichlorobenzene are proposed from an analysis of the Raman and infrared spectra. The Raman spectra of the dichlorotoluenes were investigated at −180°C, and it was observed that some of the intramolecular vibrations are affected and a few low-frequency lines are exhibited by the compounds at this low temperature. Explanation of these changes is offered in terms of association of the molecules. It was also observed that in the solid state at −180°C both the compounds yield luminescence bands and the C=C valence oscillation appears to be coupled with the electronic transition giving rise to these bands. (*PA*, 1961, #14,035)

893. ON THE SINGLET→TRIPLET ABSORPTION IN AROMATIC COMPOUNDS IN GASEOUS STATE

Sirkar, S. C., Roy, J. K.
***Indian Journal of Physics and Proceedings of the Indian Association for the Cultivation of Science*, v. 34, no. 12, pp. 581–583, December 1960**

The near-ultraviolet absorption spectra of benzene and *o*-bromotoluene in the vapor state (at the respective saturation pressures at room temperature) were photographed with a path of about 62 ft. These spectra were compared with those of the substances in the liquid state having equivalent path lengths. It was observed that although benzene in the liquid state with a path length 1.2 cm shows considerable absorption in the 3300–3400 Å region due to singlet→triplet transition, such absorption in the case of the ~~vapor at 12 mm~~ pressure, with a path length of 62 ft, is very much less than that in the liquid. Similar results were observed with *o*-bromotoluene, the path length being 7 mm for the liquid and 62 ft for the vapor at 55 mm pressure. It is pointed out that the singlet→triplet absorption and the corresponding luminescence observed by previous workers in these compounds are enhanced considerably in the state of aggregation of the molecules. (*PA*, 1961. #14,054)

894. FLUORESCENCE SPECTRA OF SOME URANYL SALTS

Narasimham, K. V.
***Indian Journal of Physics and Proceedings of the Indian Association for the Cultivation of Science*, v. 35, no. 6, pp. 282–298, June 1961**

The fluorescence spectra of uranyl acetate, nitrate, sulphate, fluoride I, chloride, potassium uranyl sulphate, and ammonium uranyl sulphate were reinvestigated at room and liquid air temperatures; new analyses are proposed for each spectrum on the basis of a single electronic-allowed transition. (*PA*, 1961, #14,638)

895. INTENSITY OF FLUORESCENCE OF DYES IN SOLUTION

Kishore, J., Machwe, M. K., Krishnan, K. G., Chaudhuri, K. D.
***Indian Journal of Physics and Proceedings of the Indian Association for the Cultivation of Science*, v. 36, no. 8, pp. 415–418, August 1962**

Concentrations of from 2×10^{-7} to 2×10^{-3} g/cc were investigated. An explanation of concentration quenching of fluorescence was obtained.

896. RADIOTHERMOLUMINESCENCE OF POLYETHYLENE AND DISAPPEARANCE OF FREE RADICALS

Shiomi, N., Tahira, S., Yoshida, H., Higashimura, T.
***Institute for Chemical Research, Kyoto University, Bulletin of the*, v. 41, no. 1, pp. 55–60, 1963**

897. STUDIES OF CERTAIN BIOLOGICALLY IMPORTANT POLYANION-ORGANIC CATION COMPLEXES AS ENERGY TRANSFER SYSTEMS

Balazs, E. A., Scheufele, D. S.
October 31, 1962
Institute of Biological and Medical Sciences, Retina Foundation, Boston, Mass.
Scientific Report 3, AFCRL-63-426, AF 19(604)-8476

Visible absorption spectra of Azure A interactions with glucosaminoglycans and sodium polyethylene sulfonates were determined—the latter polyanions with regard to the effects of method of preparation, polymer anionic site to dye ratio, temperature, buffering, centrifugation and chloroform extraction; and the former polyanions with respect to a fixed amount of excess dye and decreasing polyanion concentration. (*STAR*, #N63-15,952)

898. THE KINETICS OF QUENCHING IN LIQUID SCINTILLATORS

Funt, B. L., Hetherington, A.
International Journal of Applied Radiation and Isotopes,
v. 13, pp. 215–221, April 1962

The kinetics of the quenching process were studied for two efficient solvents—monoisopropylbiphenyl and toluene—over a range of solute concentrations. It was found that the Stern-Volmer relationship was applicable, and quenching constants were obtained for carbon tetrachloride, diphenyl mercury, and lead-2-ethylhexanoate in each solvent. The quenching constants were significantly lower in monoisopropylbiphenyl than in toluene. A kinetic scheme for the probable steps in the energy transfer process was formulated, and by the application of steady-state kinetics several experimentally verifiable postulates were obtained. These were tested and confirmed by the experimental data obtained from the variation of quenched constants with solute concentrations. From the results, some useful observations relating to the optimum formulation of loaded liquid scintillators in nuclear radiation detectors can also be made. (*PA*, 1962, #15,607)

899. COMPUTATION OF EFFICIENCIES OF ORGANIC LIQUID SCINTILLATORS

Heller, A.
***IRE Transactions on Nuclear Science*, v. NS-9, no. 3,**
pp. 52–53, June 1962
(Paper presented at the Eighth Scintillation Counter Symposium, Washington, D. C., March 1–3, 1962)

The results of the computation of the scintillation and fluorescence properties of 22 aromatic conjugated systems are presented. Some of these are expected to have superior properties to those in use at present. A new scintillation solute, 1,4-bis-(*p*-isopropylstyryl)-benzene, when used as a secondary solute in a *p*-terphenyl solution in xylene, has an efficiency higher than 80% on the anthracene scale. (*PA*, 1962, #17,471)

900. STRUCTURE FINE DES SPECTRES DE LUMINESCENCE DE MOLÉCULES ORGANIQUES EN SOLUTIONS CRISTALLISÉES (FINE STRUCTURE OF THE LUMINESCENT SPECTRA OF ORGANIC MOLECULES IN CRYSTALLINE SOLUTIONS)

Ciais, A.
Journal de Chimie Physique et de Physicochimie Biologique,
v. 58, no. 2, pp. 190–203, February 1961

Measurements have been made of the luminescence spectra of solutions of benzene, naphthalene, deuterated naphthalene, anthracene, tetracene, phenanthrene, pyrene, fluorene, acenaphthene, and deuterated acenaphthene in solid pentane at 4, 20, and 77°K. Each transition has been found to be made up of several strong lines, whose number depends upon the nature of the solvent and of the solute and also on the concentration and temperature of the solution. These strong lines are accompanied by a larger number of weak lines. Each spectrum may be divided into a number of systems (three to five) within which the interval between two weak lines is an integral multiple of a basic unit. This unit was found to be the same for fluorescent and phosphorescent emission. The structure may be explained by representing the molecules by rotators situated in lattice vacancies of the solvent, and which are affected by the periodic field of the surrounding solvent molecules. If the concentration of the solute is sufficiently low, no quenching of the rotational motion occurs due to interactions between neighboring solute molecules. (*PA*, 1961, #17,917)

901. NIVEAUX QUASI-HYDROGÉNOÏDES DANS LES CRISTAUX MOLÉCULAIRES (QUASI-HYDROGEN TYPE LEVELS IN MOLECULAR CRYSTALS)

Pesteil, P.
Journal de Chimie Physique et de Physicochemie Biologique,
v. 58, no. 7–8, pp. 661–667, July–August 1961

The existence of quasi-H-type levels attributable to excitons or to lattice imperfections is confirmed by spectra studies of C_6H_6, C_6D_6, $C_{10}H_8$, and $C_{10}D_8$ at 20°K, and for $C_{14}H_{10}$ and $C_{14}D_{10}$ at 1.9°K.

902. LES APPROCHES EXPÉRIMENTALES DU COMPORTEMENT SUPRA-MOLÉCULAIRE DES ACIDES NUCLÉIQUES: LEUR LUMINESCENCE DE LONGUE DURÉE (THE SUPRAMOLECULAR BEHAVIOR OF NUCLEIC ACIDS: THEIR LUMINESCENCE OF LONG DURATION)

Douzou, P., Francq, J. C., Hanss, M., Ptak, M
Journal de Chimie Physique et de Physicochemie Biologique,
v. 58, no. 10, pp. 926–933, October 1961

The emission of luminescence of long duration for nucleic acids excited at liquid-N temperature is examined and results are presented. Studies of the spectra and the decline of luminescence contribute to an understanding of energy transfer within polynucleotides.

903. EXTINCTION DE LA FLUORESCENCE DES SOLUTIONS PAR TENSIOACTIVITÉ (QUENCHING OF THE FLUORESCENCE OF SOLUTIONS BY TENSIOACTIVITY [INTERFACIAL TENSION])

Lucatu, E.
Journal de Chimie Physique et de Physicochemie Biologique,
v. 59, no. 2, pp. 128–131, February 1962

A correlation is found between (1) the quenching action of several compounds on the fluorescence intensity of solutions of uranin and rhodamine B, and (2) the interfacial tension between benzene or *n*-heptane and the fluorescent solution containing the quencher. (*PA*, 1962, #9283)

904. ACTION DU RAYONNEMENT γ SUR LES CARACTÉRISTIQUES DES SCINTILLATEURS LIQUIDES (EFFECT OF γ-RADIATION ON THE CHARACTERISTICS OF LIQUID SCINTILLATORS)

Laustriat, G., Klein, J., Coche, A.

Journal de Chimie Physique et de Physiochimie Biologique, v. 59, no. 11–12, pp. 1182–1188, November–December 1962

It is shown that irradiation of the solvent (toluene) by strong doses of γ-radiation causes a decrease in the luminescent yield of liquid scintillators. This effect is caused by the products of radiolysis which influence the luminescence through their quenching properties and through their spectral characteristics (absorption of the solute emission). The nature of these products depends on the conditions of irradiation, notably on the presence of air. (*PA*, 1963, #9470)

905. FLUORESCENCE DIRECTE DE MONOCRISTAUX DE NAPHTALÈNE DOPÉS A L'ANTHRACÈNE (DIRECT FLUORESCENCE FROM MONOCRYSTALS OF NAPHTHALENE DOPED WITH ANTHRACENE)

Martin-Bouyer, M., Meinnel, J.

***Journal de Physique et le Radium*, v. 22, no. 2, pp. 126–128, February 1961**

The specimens were purified by recrystallization, sublimation, and zone fusion, and single crystals were grown by the Bridgman method. The fluorescence spectra, excited by 365-mμ wavelength radiation and characteristic of the anthracene impurity, were measured for anthracene molar concentrations from 1.6 × 10^{-4} to 1.28 × 10^{-2}. The spectra are analyzed and compared with published spectral data on anthracene vapor and crystals. As the concentration is increased, the short-wavelength maxima are reduced in intensity and ultimately suppressed (due to self-absorption). Similar measurements were made using X-ray excitation. No naphthalene fluorescence was observed above 4×10^{-4} molar concentration, due to energy transfer. Radiation damage due to γ-rays and neutrons was observed, causing discoloration and changes in the spectra. (*PA*, 1961, #20,024)

906. SECONDARY ELECTRON EMISSION OF PYROLYTIC GRAPHITE CLEAVED IN A HIGH VACUUM

Whetten, N. R.

***Journal of Applied Physics*, v. 34, no. 4, pt. 1, pp. 771–773, April 1963**

Pyrolytic graphite was cleaved in a high vacuum to obtain clean surfaces, and the secondary electron emission properties of these surfaces were determined. Pyrolytic graphite has a maximum secondary emission yield of 1.0 at 300-ev primary electron energy for electrons incident normal to the basal plane. The most probable energy of the emitted secondaries is 2 ev, with one-half of the secondaries having energy in excess of 8 ev. A maximum secondary emission yield of 0.75 at 350-ev primary energy was measured for normal incident electrons on a face that was perpendicular to the basal plane. The backscattered fraction for pyrolytic graphite was found to be 0.05. No differences were observed in the secondary electron emission properties of single-crystalline pyrolytic graphite and pyrolytic graphite that was less well ordered.

907. INTERMEDIATES IN THE BIOLUMINESCENT OXIDATION OF REDUCED FLAVIN MONONUCLEOTIDE

Hastings, J. W., Gibson, Q. H.

***Journal of Biological Chemistry*, v. 238, no. 7, pp. 2537–2554, July 1963**

Bacterial luciferase from *Achromobacter fischeri* catalyzes a light-emitting reaction involving the oxidation of reduced flavin mononucleotide ($FMNH_2$) in the presence of O_2 and long chain fatty aldehyde. Initiating the reaction with $FMNH_2$ results in the formation of a short-lived enzyme intermediate ($t_{1/2}$ = 10 sec at 10°C). Since excess $FMNH_2$ is oxidized nonenzymatically within 1 sec, no turnover of enzyme occurs; the enzyme intermediate formed may then be considered as a participant in a series of consecutive reactions leading to light emission. In the first step the enzyme reacts with $FMNH_2$ to form a reduced enzyme (Intermediate I) and oxidized flavin. This reduced enzyme then reacts with O_2 to form an intermediate (II) which is stable to both ferricyanide and sodium dithionite. This intermediate can break down (apparently spontaneously) with the emission of a small amount of light. If aldehyde is added, however, the breakdown results in a far greater yield of light from the same amount of intermediate. In the presence of aldehyde a yield as high as 1 photon for 3 molecules of $FMNH_2$ can be obtained. Evidence is presented showing that reduced enzyme (Intermediate I) is subject to inhibition by sodium arsenite, but that neither the unreacted enzyme nor Intermediate II (i.e., after reaction with oxygen) is sensitive to arsenite. The stabilization of this second enzyme (Intermediate II) has been achieved, and light emission can be obtained at a later time by adding aldehyde. Moreover, luminescence occurs in the complete absence of oxygen when Intermediate II and aldehyde are mixed anaerobically.

908. ON THE LUMINESCENCE MINIMUM IN CERTAIN SCINTILLATOR SOLUTIONS

Nosworthy, J. M., Magee, J. L., Burton, M.

***Journal of Chemical Physics*, v. 34, no. 1, pp. 83–89, January 1961**

Several scintillator solutions have been examined for the luminescence minimum previously reported for the case of Co^{60} γ-irradiated cyclohexane + benzene + *p*-terphenyl with oxygen present. The minimum is shown to be dependent on the nature of the solvents and of the quencher. A satisfactory interpretation of the data involves the notion of energy transfer from molecules of the less efficient (common) solvent to the molecules of the more efficient (better) solvent and thence to the scintillator. The latter transfer appears to involve more than one molecule of the solvent. A suggested model of the quenching process explains the existence of two classes of quenchers, one of which does not give a minimum. (For erratum, see Entry #921.)

909. OBSERVED PHOSPHORESCENCE AND SINGLET-TRIPLET ABSORPTION IN *s*-TRIAZINE AND TRIMETHYL-*s*-TRIAZINE

Paris, J. P., Hirt, R. C., Schmitt, R. G.
***Journal of Chemical Physics*, v. 34, no. 5, pp. 1851–1852, May 1961**

910. PHOSPHORESCENCE SPECTRA OF ACENAPHTHENE AT LOW TEMPERATURES

Zmerli, A
***Journal of Chemical Physics*, v. 34, no. 6, pp. 2130–2135, June 1961**

The phosphorescence spectra of acenaphthene, both of single crystals and of solutions in different solvents (polystyrolene, benzene, or EPA), were photographed at low temperatures. At 4 and 77°K unpolarized spectra of the crystal were obtained using a phosphoroscope, and at 20°K the polarized spectra along the three crystallographic axes were photographed without the phosphoroscope. Some peculiarities linked to the existence of two different sets of molecules in the unit cell were observed. Two progressions, here called "normal," connected to each set of molecules were distinguished in the 4 and 77°K spectra, but not in the 20°K spectrum. The interval between the corresponding bands of the two progressions is 28 cm^{-1}. In the 20°K spectrum two new series, here called "nonnormal," and which appear also in the 77°K spectrum, were observed. An attempt at interpretation of these "nonnormal" series is given. (*PA*, 1961, #11,400)

911. ENERGY TRANSFER IN H-BONDED *N*-HETEROCYCLIC COMPLEXES AND THEIR POSSIBLE ROLE AS ENERGY SINKS

El-Bayoumi, M. A., Kasha, M.
***Journal of Chemical Physics*, v. 34, no. 6, pp. 2181–2182, June 1961**

In this research, spectral shifts and energy transfer for hydrogen-bonded molecular complexes are studied, especially those composed of *N*-heterocyclic base pairs. The energy transfer results for the acridine-carbazole hydrogen-bonded complex are reported. Energy transfer in the acridine-carbazole complex may be expected to appear as an increase in the emission yield of acridine (energy acceptor), or as a quenching of the carbazole emission (energy donor), or both. The emission spectra of carbazole alone and in the presence of acridine in a rigid transparent glass solution at 77°K were recorded in different media, using a Perkin-Elmer model 99 double-pass monochromator. The exciting light in all of the experiments consisted of a narrow band in the region of the second absorption band of carbazole. For a solution containing equimolar quantities of carbazole and acridine almost all the exciting light is absorbed by carbazole without appreciable absorption by acridine. Hydrocarbon-glass solution favors the formation of acridine-carbazole hydrogen-bonded complexes. Such complexes seem to act as energy sinks.

912. LUMINESCENCE OF CHROMIUM (III) COMPLEXES

Forster, L. S., De Armond, K.
***Journal of Chemical Physics*, v. 34, no. 6, pp. 2193–2194, June 1961**

Chelates of Cr^{3+} with acetylacetone (ACA) and with 8-hydroxyquinoline, in dilute glassy solutions at −183°C, were excited by wavelengths 3660, 4358, or 5460Å to give an emission band with a peak at 13,200 cm^{-1}. For Cr (ACA)$_3$ the absorption band has a maximum near 19,000 cm^{-1} and a minimum near 21,000 cm^{-1}. The origin of the luminescence is discussed with reference to these and other Cr complexes, and the probable transition is considered to be ^4E–$^4A_2$. (*PA*, 1961, #14,630)

913. ABSORPTION AND LUMINESCENCE ORIGINS IN ANTHRACENE CRYSTALS

Alexander, P. W., Lacey, A. R., Lyons, L. E.
***Journal of Chemical Physics*, v. 34, no. 6, pp. 2200–2201, June 1961**

Observations of the absorption and luminescence spectra at 4°K of zone-refined anthracene crystals and of crystals of various purities have shown that the large difference once supposed to exist between fluorescence and absorption origins in anthracene crystals is not a property of the pure crystal. The purest anthracene showed no absorption from 24,800 to 25,030 cm^{-1}, but less-pure material showed bands in this region due to impurities (e.g., anthraquinone). Free exciton luminescence from pure anthracene crystals is expected to originate at 25,150 cm^{-1} (*b*-polarized). A luminescence origin at 2[illegible]40 cm^{-1} was observed in the purest crystal (compared with [illegible],840 cm^{-1} in an impure crystal), the slight difference from the expected value being attributed to reabsorption. (*PA*, 1961, #14,644)

914. COMPREHENSIVE INVESTIGATION OF THE ELECTRONIC SPECTROSCOPY AND THEORETICAL TREATMENTS OF FERROCENE AND NICKELOCENE

Scott, D. R., Becker, R. S.
***Journal of Chemical Physics*, v. 35, no. 2, pp. 516–531, August 1961**

New data concerning the electronic absorption and emission spectra of ferrocene and the absorption spectrum of nickelocene are presented. Assignment and discussion of the transitions are made, based on the experimental results. No ferrocene emission is observed upon excitation into the lowest energy absorption band. An emission occurs upon excitation into the next higher energy band. These results are interpreted in terms of crossing of the first excited state and the ground state. The luminescence is long lived and is interpreted as phosphorescence paralleling an assigned singlet-triplet absorption at 5280 Å. No nickelocene emission was noted. Assignments of the absorption bands of ferrocene and nickelocene are proposed within the framework of each of the major theoretical approaches. (*PA*, 1961, #12,290)

915. ELECTRONIC SPECTRA AND HYDROGEN BONDING. I. PHENOL AND NAPHTHOLS

Baba, H., Suzuki, S.
***Journal of Chemical Physics*, v. 35, no. 3, pp. 1118–1127, September 1961**

The effect of hydrogen bonding on the electronic absorption spectra of phenol, α-naphthol, and β-naphthol was investigated with particular attention to the relation between the nature of electronic transitions and their behavior in hydrogen-bond formation. The spectra were obtained down to 2000 Å in iso-octane solution in the presence of varying concentrations of dioxane. From the analysis of the observed spectra, the equilibrium constants for the hydrogen bonds and the spectra of the hydrogen-bonded species were determined. The hydrogen-bond energies are given for the ground and excited states of the solute molecules. The experimental results clearly indicate that effects of hydrogen bonding on electronic spectra differ markedly with transitions. Both the frequency shifts and the intensity changes differ in magnitude and even in sign, according to the properties of the transitions concerned. It is shown that the transition at 47,000 cm^{-1} of α-naphthol is displaced to higher frequencies upon formation of the hydrogen bond. Aside from broadening or smoothing of the vibrational structure, no appreciable changes are produced by hydrogen bonding in the spectral patterns of the individual transitions. The behavior of the transitions in hydrogen-bond formation is interpreted on the basis of the electronic structure of the solute molecules. Two factors are shown to be important in accounting for the mechanism of the hydrogen-bonding effect: (1) a change in the electron density at the oxygen atom of the O–H group accompanying an electronic transition, (2) a decrease in the electronegativity of the same oxygen atom resulting from hydrogen-bond formation. (For Part II, see Entry #964.) (*PA*, 1961, #17,329)

916. ANTIFERROMAGNETIC TO FERROMAGNETIC TRANSITIONS IN ORGANIC FREE RADICALS

Edelstein, A. S., Mandel, M.
***Journal of Chemical Physics*, v. 35, no. 3, pp. 1130–1131, September 1961**

A detailed study of the high- and low-temperature portions of the susceptibility curves for picrylaminocarbazyl and Wurster's blue perchlorate was undertaken to investigate co-operative effects. Measurements were made by ESR at 85 Mc for high temperature and 10,000 Mc for low temperature. Temperature varied from 1.5 to 293°K. Essentially, antiferromagnetic behavior was noted at high temperatures, and ferromagnetic at low.

917. LOW-RESOLUTION ANALYSIS OF THE $n \rightarrow \pi^*$ (3000 Å) ABSORPTION SPECTRUM OF *s*-TRIAZINE

Brinen, J. S., Goodman, L.
***Journal of Chemical Physics*, v. 35, no. 4, pp. 1219–1225, October 1961**

The 3000-Å absorption band was examined under low resolution and the long wavelength portion is assigned to the allowed $n \rightarrow \pi^*$ promotion $^1A_2'' \leftarrow {}^1A_1'$ with 0–0 band at 31,574 ± 15 cm^{-1}. Evidence is presented for the onset of a second $n \rightarrow \pi^*$ transition at $\sim 32{,}500$ cm^{-1}. The observed sequence of states contradicts previous predictions based on approximate sp^2 hybridization, and indicates that in the excited states the n orbital has very little s character (~ 0.1). (*PA*, 1961, #17,322)

918. EFFECT OF PRESSURE ON THE LOW-ENERGY ABSORPTION PEAK OF SEVERAL PHTHALOCYANINES

Riggleman, B. M., Drickamer, H. G.
***Journal of Chemical Physics*, v. 35, no. 4, pp. 1343–1344, October 1961**

The effect was measured in nine phthalocyanines in the solid state. In all cases the peak shifted to lower energies. The shifts were not large, but were very sensitive to the metal ion in the phthalocyanine. In general, the amount of shift was greater for ions having larger polarizability. The shift is attributed to perturbation of the excited π-electron state due to dispersion interaction with metal ions in adjacent molecules. (*PA*, 1961, #17,889)

919. MEAN LIFETIME OF THE LOWEST EXCITED SINGLET STATE OF BENZENE

Donovan, J. W., Duncan, A. B. F.
***Journal of Chemical Physics*, v. 35, no. 4, pp. 1389–1391, October 1961**

The lifetime of the first excited $^1B_{2u}$ state of benzene was determined from measurement of decay of fluorescence in the vapor phase. High-frequency electrical excitation, rather than optical excitation, was used. The pressure dependence of the lifetime has been studied under different conditions. The lifetime extrapolated to zero pressure is 0.59 μsec. The pressure dependence is interpreted by a mechanism of collisional deactivation. (*PA*, 1961, #17,330)

920. ELECTRONIC SPECTRA OF SUBSTITUTED ANTHRACENES. EVIDENCES FOR APPEARANCE OF THE ^1L_b TRANSITION

Baba, H., Suzuki, S.
***Journal of Chemical Physics*, v. 35, no. 4, pp 1501–1502, October 1961**

In anthracene this transition is hidden under the stronger ^1L_a transition. It was found, however, in a derivative—β-anthrol—from observations of the absorption and fluorescence spectra in iso-octane and aqueous NaOH solutions. (*PA*, 1961, #19,640)

921. ERRATUM: ON THE LUMINESCENCE MINIMUM IN CERTAIN SCINTILLATOR SOLUTIONS

Nosworthy, J. M., Magee, J. L., Burton, M.
***Journal of Chemical Physics*, v. 35 no. 4, p. 1506, October 1961**

The sentence "Only cyclohexane gives a minimum," appearing in line 6, page 86, *Journal of Chemical Physics*, v. 34, 1961 (Entry #908), should read "Cyclohexane and decalin give minima; *n*-hexane and dodecane do not."

922. EFFECT OF PRESSURE ON THE OPTICAL PROPERTIES OF ORGANIC PHOSPHORS

Gregg, D. W., Drickamer, H. G.
***Journal of Chemical Physics*, v. 35, no. 5, pp. 1780–1788, November 1961**

The effect of pressure to 54 kbar was measured on absorption spectra, emission spectra, and decay rates of four organic phosphors. For fluorescein and dichlorofluorescein the decay rate increases with increasing pressure. The emission spectrum consists of two peaks which approach each other at high pressure. Thus, there appears to be an increased mixing of triplet and excited singlet states at high pressure. For acridine yellow and orange the absorption spectrum shows a dimer and monomer peak. The dimer peak decreases rapidly in intensity with increasing pressure. At high concentrations the component decay rates are largely independent of pressure. At lower concentrations the decay rate becomes slower at higher pressure. Evidently the emission can be associated with the dimer. (PA, 1961, #20,019)

923. SCINTILLATION PROPERTIES OF 9-VINYLANTHRACENE

Heller, A., Katz, D.
***Journal of Chemical Physics*, v. 35, no. 6, pp. 1987–1989, December 1961**

9-Vinylanthracene, for which good scintillation properties were predicted (Entry #578), was found to be a high-grade primary and secondary scintillator, capable of replacing the widely used 1,4-*bis*-(2-(5-phenyl)-oxazolyl)-benzene. (*PA*, 1962, #1158)

924. UNIMOLECULAR DECAY OF THE TRIPLET STATE OF ANTHRACENE IN FLUID AND VISCOUS MEDIA

Jackson, G., Livingston, R.
***Journal of Chemical Physics*, v. 35, no. 6, pp. 2182–2186, December 1961**

The rate of decay of the triplet state of anthracene, dissolved in hexane, tetrahydrofuran, and glycerol, was measured at temperatures ranging from 30 to −70°C. In fluid solvents at ordinary temperatures, the decay appears to be chiefly the result of bimolecular triplet–triplet interaction and of a bimolecular quenching reaction involving an unknown quencher, present in trace amounts even in highly purified solvents. In addition, there appears to be a unimolecular, temperature-independent decay, corresponding to an intrinsic mean life of about 0.01 sec. In glycerol, the first-order rate constant decreases rapidly with decreasing temperature, approaching a limiting half-life of about 0.04 sec at −25°C. This limiting rate appears to be the same as has been previously reported for solutions in EPA at liquid nitrogen temperatures. Similar results were obtained with solutions of dibenzanthracene. (*PA*, 1962, #1159)

925. POLARIZED PHOSPHORESCENCE IN CRYSTALLINE HEXACHLOROBENZENE AT 77°K

Olds, D. W.
***Journal of Chemical Physics*, v. 35, no. 6, pp. 2248–2249, December 1961**

Microphotometer tracings are given for the polarization components of the phosphorescence in the direction of the *b*-axis and perpendicular to it. Commencing with the 0–0 band at 24,322 cm^{-1}, 35 other bands are analyzed up to 20,788 cm^{-1}, using a number of frequencies close to known Raman frequencies, and also one of unknown origin (112 cm^{-1}). It is difficult to deduce the crystal symmetry. (*PA*, 1962, #4185)

926. DELAYED FLUORESCENCE OF ACRIFLAVINE IN RIGID MEDIA

Lim, E. C., Swenson, G. W.
***Journal of Chemical Physics*, v. 36, no. 1, pp. 118–122, January 1, 1962**

Fluorescence of extremely long duration was observed from acriflavine in rigid media. The decay rate of the emission is strongly dependent upon such factors as temperature, duration of excitation, and concentration of the sample. From these and other observations, the delayed fluorescence is interpreted as due to excited singlets formed by recombination of ions and trapped electrons produced initially by photoionization of the dye.

927. FLUORESCENCE OF *s*-TETRAZINE

Chowdhury, M., Goodman, L.
***Journal of Chemical Physics*, v. 36, no. 2, pp. 548–549, January 15, 1962**

The lowest singlet excited state of *s*-tetrazine is (n,π^*), but this is the first known case where fluorescence occurs from this state rather than phosphorescence. The uncorrected emission at 77°K is compared with the absorption curve, and similar curves for the fluorescence and absorption of dimethyl *s*-tetrazine at room temperature are given. The 0–0 band of the *s*-tetrazine emission is at 17,800 cm^{-1}, as compared with 17,100 cm^{-1} for the dimethyl derivative. Emission lifetime is 10^{-5} sec, and the predominant component of the electric vector is parallel to the (n,π^*) singlet absorption, giving positive polarization with respect to the 5460-Å excitation. (*PA*, 1962, #4186)

928. FLUORESCENCE ENERGY TRANSFER AND OXYGEN QUENCHING IN SOLUTIONS OF DIPHENYLOXAZOLE IN CYCLOHEXANE

Weinreb, A.
***Journal of Chemical Physics*, v. 36, no. 4, pp. 890–894, February 15, 1962**

The fluorescent intensity of solutions of diphenyloxazole (PPO) in cyclohexane was measured as a function of concentration for excitation by γ-rays. The fluorescence spectrum of the solutions when excited by UV is also recorded. These UV measurements, together with the results of β-excitation, were used to examine the quenching influence of oxygen on the solute fluorescence and on the energy transfer from cyclohexane. The decay times of the solutions were measured. The results are interpreted to show (1) a tendency of PPO to form molecular complexes in cyclohexane, and (2) a "static" character for the oxygen quenching of cyclohexane. The dependence of transfer probability on solute concentration is discussed. (*PA*, 1962, #7223)

929. MIXED DIMER EMISSION FROM PYRENE CRYSTALS CONTAINING PERYLENE

Hochstrasser, R. M.
***Journal of Chemical Physics*, v. 36, no. 4, pp. 1099–1100, February 15, 1962**

The fluorescence spectrum of pyrene crystals containing perylene is a broad structureless band with a maximum at 5000 Å, intermediate between the spectra of pyrene (4750 Å maximum) and perylene (5750 Å maximum) crystals. The emission is from a type of "mixed dimer," probably from a charge-resonance level. (*PA*, 1962, #8584)

930. OBSERVATION OF ANOMALOUS PHOSPHORESCENCE–FLUORESCENCE INTENSITY RATIO IN EXCITATION OF UPPER ELECTRONIC STATES OF CERTAIN AROMATIC HYDROCARBONS

O'Dwyer, M. F., El-Bayoumi, M. A., Strickler, S. J.
***Journal of Chemical Physics*, v. 36, no. 5, pp. 1395–1396, March 1, 1962**

The ratio of phosphorescence to fluorescence intensity for chrysene and for hexahelicene was found to increase when the molecules were selectively excited to higher energy singlet states. Two possible interpretations of these results are considered. (*PA*, 1962, #10,628)

931. EFFECTS OF RARE-EARTH ION SUBSTITUTION UPON THE FLUORESCENCE OF TERBIUM HEXA-ANTIPYRENE TRI-IODIDE AND SODIUM EUROPIUM TUNGSTATE

Van Uitert, L. G., Soden, R. R.
***Journal of Chemical Physics*, v. 36, no. 7, pp. 1797–1800, April 1, 1962**

The directions and relative ease of transfer of energy between different rare earth hexa-antipyrene aggregates are compared by examining the influences of rare-earth substitutions upon the fluorescence of terbium hexa-antipyrene tri-iodide. Data concerning much shorter range interactions between rare-earth ions are obtained employing the sodium rare-earth tungstates. Energy transfer and quenching effects show systematic relationships to the total orbital angular momentum of the $4f$ subshell electrons of the rare-earth ions. (*PA*, 1962, #10,629)

932. ABSORPTION SPECTRUM OF PHENAZINE SINGLE CRYSTALS AT 77° AND 4.2°K IN THE REGION OF THE $n \rightarrow \pi^*$ TRANSITION

Hochstrasser, R. M.
***Journal of Chemical Physics*, v. 36, no. 7, pp. 1808–1813, April 1, 1962**

The absorption spectrum of the long-wavelength edge of phenazine and 1,2- 3,4-dibenzphenazine was measured at 77 and 4°K. A sharp band system is evident in crystals of each of these molecules. These systems are assigned as n–π^* transitions. For phenazine the band system involved a progression of a 398-cm^{-1} vibration frequency which is attributed to a symmetric ring angular distortion. The band at 22,881 cm^{-1} is assigned as the allowed electronic origin of the transition $(n\pi^*)\ B_{1u} \leftrightarrow A_{1g}$. The spectrum contained a weak component which is attributed to a symmetry forbidden $n \rightarrow \pi^*$ transition lying at less than 96 cm^{-1} below the allowed origin. The analysis of the spectrum suggests that the phenazine molecule is twisted in the $n\pi^*$ excited state. The 0–0 band only appears in the b-polarized spectra and this indicates that crystal induced mixing with higher $\pi\pi^*$ levels is occurring. (*PA*, 1962, #10,601)

933. LOW-TEMPERATURE SOLUTION SPECTRA OF METHYLCYCLOHEXANE AND BENZENE. EFFECT OF OXYGEN AND CARBON TETRACHLORIDE

Tsubomura, H., Lang, R. P.
***Journal of Chemical Physics*, v. 36, no. 8, pp. 2155–2157, April 15, 1962**

Measurements were made of the absorption spectra of some solutions in the form of a low-temperature glass. The absorption band arising from the interaction between oxygen and methylcyclohexane was found to increase at low temperature. The remarkable enhancement of the benzene "MR" series appearing between the B_{2u} bands upon addition of carbon tetrachloride, as found by Ham, was confirmed, but the intensity decreases largely at a higher temperature. (*PA*, 1962, #14,674)

934. EFFECT OF STYRENE MONOMER ON THE FLUORESCENCE PROPERTIES OF POLYSTYRENE

Basile, L. J.
***Journal of Chemical Physics*, v. 36, no. 8, pp. 2204–2210, April 15, 1962**

Fluorescence spectra and lifetimes were studied for polystyrene samples having different average molecular weights and different concentrations of residual styrene monomer. The residual styrene monomer is fluorescent and acts as a typical fluorescent solute in a rigid medium. The fluorescence properties of polystyrene were found to be dependent on both the concentration of residual styrene monomer and, to a lesser extent, the average molecular weight. (*PA*, 1962, #12,633)

935. ULTRAVIOLET SPECTRA OF STILBENE, p-MONOHALOGEN STILBENES, AND AZOBENZENE AND THE TRANS TO CIS PHOTOISOMERIZATION PROCESS

Dyck, R. H., McClure, D. S.
***Journal of Chemical Physics*, v. 36, no. 9, pp. 2326–2345, May 1, 1962**

To improve understanding of the electronic states and photochemical reactions of stilbene, a spectroscopic and photochemical investigation of stilbene, some substituted stilbenes, and azobenzene was carried out. High resolution absorption and fluorescence spectra of the singlet–singlet transition in dilute mixed crystal were analyzed, and from them it is estimated that the potential barrier to *trans-cis* isomerization in the first excited singlet state is about 40 kcal/mole. The absorption spectrum of the first singlet–triplet transition was observed by enhancement with a heavy atom solvent, and is interpreted as showing that the central bond in the lowest triplet state has a very substantial barrier to rotation. An electronic energy level scheme for stilbene was constructed by treating the molecule as one ethylene molecule interacting with two toluene molecules. This treatment suggests that as many as four triplet states may be of lower energy than the first excited singlet and would then be possible pathways for photoisomerization. A study of the deactivation processes of photoexcited stilbene included the temperature dependences of fluorescence and of isomerization efficiencies. The first showed an activated quenching process with a frequency factor of 10^{12}, which makes it a less forbidden process than is common for singlet–triplet crossings. The second showed that the activated process has the major isomerization yield. In p-bromostilbene an unactivated process has the major isomerization yield, indicating that there is an atomic number effect on the rate of the unactivated process. Thus, the direct isomerization in the first excited singlet or first excited triplet states was ruled out; two other paths, one with a small activation energy and the other apparently a singlet to excited triplet crossing, were found. (*PA*, 1962, #14,675)

936. SPIN EXCHANGE BETWEEN EXCITONS AND FREE RADICALS

McConnell, H. M., Griffith, H. O., Pooley, D.
***Journal of Chemical Physics*, v. 36, no. 9, pp. 2518–2519, May 1, 1962**

An X-irradiated single crystal of $(\phi_3PCH_3)^+ (TCNQ)_2^-$ gave ESR spectra showing that the relative triplet concentration at −115°C is greater than at −150°C. The broadening of the free radical signal is attributed to exciton–free radical spin exchange. There is evidence of mobile triplet excitons. (*PA*, 1962, #16,634)

937. INTERMOLECULAR PROTON TRANSFER IN THE EXCITED HYDROGEN-BONDED COMPLEX IN NON-POLAR SOLVENT AND FLUORESCENCE QUENCHING DUE TO HYDROGEN BONDING

Mataga, N., Kaifu, Y.
***Journal of Chemical Physics*, v. 36, no. 10, pp. 2804–2805, May 15, 1962**

In the course of the study of the hydrogen-bonding effect of triethylamine on the fluorescence spectra of some naphthalene derivatives such as naphthols and naphthylamines, an anomalously large red shift of the fluorescence spectra caused by hydrogen bonding in the case of β-naphthol was found. A short phenomenological description of these spectral changes is given, based on the charge transfer model of the hydrogen bond. In essence, it is argued that due to the strong charge transfer to the O–H antibonding orbital, the equilibrium O–H distance will become longer, and the curvature of the potential surface may, in the excited state, become remarkably smaller than those in the ground state. (*PA*, 1962, #19.568)

938. SURFACE IONIZATION ENERGIES OF ORGANIC COMPOUNDS: PHTHALOCYANINES

Pope, M.
***Journal of Chemical Physics*, v. 36, no. 10, pp. 2810–2811, May 15, 1962**

Measurements of I_s of the organic compounds metal-free copper and magnesium phthalocyanine are reported. Few I_s measurements have previously appeared in the literature. The values obtained by Kearns and Calvin agree remarkably well with those of the present study, as shown by the following table of phthalocyanine surface-ionization energies:

Compound	I_s (ev)	Source
Metal-free phthalocyanine	5.15±0.05	K and C
Metal-free phthalocyanine	5.20±0.0 0.05	This paper
Nickel phthalocyanine	4.95±0.05	K and C
Ferric phthalocyanine	4.95±0.05	K and C
Copper phthalocyanine	5.00±0.0 0.05	This paper
Magnesium phthalocyanine	4.96±0.0 0.05	This paper

An unusual technique was used to measure I_s. The compounds were available in fine grained form, and the powder was introduced into an argon-filled Millikan apparatus fitted with quartz windows. The capacitor plates of the apparatus were charged to 1500 v (plate separation 0.7 cm), the upper plate being negative. Crystals of about 2×10^{-4} cm radius falling between these plates were exposed to light from a 1000-w Hg-xenon lamp passed through a 250-mm grating monochromator. At the threshold wavelength, the crystals stopped falling and started rising, indicating that electrons had been ejected from the crystals, leaving them positively charged. The ejection of one or two electrons was easily detected. Since there was probably a layer of argon atoms surrounding the crystals through which the ejected electrons had to pass, the measured I_s should represent an upper limit.

939. ANALYSIS OF THE EPR SPECTRUM OF *N,N'*-TETRAMETHYLBENZIDINE POSITIVE ION

Galus, Z., Adams, R. N.
***Journal of Chemical Physics*, v. 36, no. 10, p. 2814,**
May 15, 1962

940. THERMOLUMINESCENCE FROM GAMMA-IRRADIATED BIOCHEMICALS. INVESTIGATION OF EMISSION SPECTRA

Weinberg, C. J., Nelson, D. R., Carter, J. G.,
Augenstine, L. G.
***Journal of Chemical Physics*, v. 36, no. 11, pp. 2869–2879,**
June 1, 1962

Crystalline powders of the aromatic amino acids and the enzyme trypsin were exposed at 77°K to Co^{60} γ-rays, and the spectral distribution (between 3000 and 6500 Å) of the thermoluminescence emitted upon subsequent heating was determined using band-pass filters. At a temperature corresponding to a particular peak in a plot of emission intensity vs. T, a large fraction of the emission (except from phenylalanine) consisted of one characteristic spectral component. In general, the proportion of emission at the longer wavelengths increased with increasing temperature. The thermal-activation energies of thermoluminescence, estimated from plots of $\ln I_T$ vs. $1/T$ (about 0.2 ev for the amino acids and 0.1 ev for trypsin), are lower than similar determinations at comparable temperatures for alkali halide crystals. The γ-ray-induced thermoluminescence from amino acid crystals is composed of longer wavelengths than the UV-excited fluorescence (at room temperature) or long-lived phosphorescence (at 77°K). The possible limitations within which lattice imperfections might account for these effects are discussed briefly. The spectral results for trypsin provide additional evidence that, in accord with previous predictions, at least some of the electronic rearrangements arising from γ-ray interaction become preferentially localized in only a restricted number of configurations. The metastable species which persist at 77°K likely depend upon the native conformation of the protein, and the available evidence suggests that the decay of an excited triplet state of tryptophan accounts for the majority of the trypsin emission. Even so, the activation energies and spectra indicate that the initial trapping and untrapping do not occur at the aromatic amino acid residues. Accordingly, mechanisms are considered whereby electronic rearrangements at other sites in trypsin could lead to the excitation of an aromatic residue followed by phosphorescence from a tryptophan residue. (*PA*, 1962, #14,758)

941. RADIATIONLESS TRANSITIONS AND RADIATIVE LIFETIME OF $^3B_{1u}$ STATE OF BENZENE

Lim, E. C.
***Journal of Chemical Physics*, v. 36, no. 12, pp. 3497–3498,**
June 15, 1962

Due to the previous discrepancies in the radiative lifetime of $^3B_{1u}$ state of benzene, redetermination of the absolute fluorescence and phosphorescence quantum yields of benzene was carried out. As a result, the lifetime can be given as 28 ± 2 sec. Radiationless transitions are considered; it is thought that the $S_1 \rightarrow S_0$ radiationless transition is of much less importance than the $S_1 \rightarrow T_1$ radiationless transitions or the $S_1 \rightarrow S_0$ radiative transition.

942. POLARIZATION OF THE SPECTRA OF CRYSTALLINE AZOBENZENE AND MIXED CRYSTALS OF AZOBENZENE IN STILBENE AT 77° AND 4.2°K IN THE REGION OF THE LOWEST $n \rightarrow \pi^*$ TRANSITION

Hochstrasser, R. M., Lower, S. K.
***Journal of Chemical Physics*, v. 36, no. 12, pp. 3505–3506,**
June 15, 1962

In the measurements the observed dichroic ratio (I_a/I_b = 3.8:1) proves that the transition moment of the lowest energy absorption band is in the molecular plane and makes an angle of 16°C to the L-axis. The theory is discussed, and the agreement between theory and experiment is satisfactory. (*PA*, 1962, #18,816)

943. VARIATION WITH EXCITING WAVELENGTH OF THE FLUORESCENCE EFFICIENCIES OF SOME ALKYL BENZENES

Kato, S., Lipsky, S., Braun, C. L.
***Journal of Chemical Physics*, v. 37, no. 1, pp. 190–191,**
July 1, 1962

Fluorescence yields of benzene, toluene, *p*-xylene, and mesitylene were measured in the pure state, in dilute solution in cyclohexane, and in the vapor phase. Excitation involving higher electronic states than the lowest is less efficient and some loss occurs during internal conversion. Dilution has some effect in improving the efficiency, but in the vapor phase the wavelength dependence of fluorescence efficiency is even more marked. (*PA*, 1962, #19,569)

944. ELECTRON MAGNETIC RESONANCE OF TRIPLET STATES AND THE DETECTION OF ENERGY TRANSFER IN CRYSTALS

Brandon, R. W., Gerkin, R. E., Hutchison, C. A., Jr.
***Journal of Chemical Physics*, v. 37, no. 2, pp. 447–448,**
July 15, 1962

Using electron resonance, observations have been made of transfer of energy in single crystals from optically excited phenanthrene molecules to naphthalene molecules, with creation of triplet states in the latter. This transfer has been observed in single crystals of the two species in biphenyl. Observations of magnetic resonance of triplet states of phenanthrene and of naphthalene occurring together and separately as solutes in biphenyl crystals have been made at the boiling point of liquid nitrogen both (1) at high fields using 2.3×10^{10} sec^{-1} radiation, and (2) at fields of 75 to 4 gauss using radiation of appropriate frequencies. The ratios of (1) the intensities of the resonance signals of the crystalline solutions in the presence of a high-frequency cutoff filter between the light source and the crystalline solution to (2) the intensities in the absence of such a filter are reported. The observed values of the parameters D and E for naphthalene and phenanthrene in biphenyl and other solvents are tabulated.

945. PHOTOSENSITIZATION BY BENZENE VAPOR: BIACETYL. THE TRIPLET STATE OF BENZENE

Ishikawa, H., Noyes, W. A., Jr.
***Journal of Chemical Physics*, v. 37, no. 3, pp. 583–591,**
August 1, 1962

Biacetyl strongly quenches the fluorescence of benzene vapor. There is a resulting dissociation of biacetyl which occurs presumably because the second excited singlet state of biacetyl is produced by energy transfer from the benzene. Emission by biacetyl also occurs, but the ratio of phosphorescence to fluorescence is very large and may be infinity. The triplet state of biacetyl seems to be produced preferentially by energy transfer from a triplet state of benzene. Emission efficiencies are such that nearly every singlet-state molecule of benzene which does not fluoresce must undergo an intersystem crossover to the triplet state. Since this crossover predominates over fluorescent emission. the life of the singlet state of benzene is presumably determined mainly by the crossover. The effective cross section for self-quenching of the singlet state of benzene is about 0.036×10^{-16} cm^2, while the effective cross section for quenching by biacetyl is about 2.5×10^{-16} cm^2. Since the life of the triplet state of benzene in the gas phase is not known, cross sections for reactions of this state may not be calculated. (*PA*, 1962, #20,844)

946. POLARIZATION OF TRIPLET→SINGLET TRANSITIONS IN POLYACENES

Krishna, V. C., Goodman, L.
***Journal of Chemical Physics*, v. 37, no. 4, pp. 912–914,**
August 15, 1962

The polarization of $T \rightarrow S$ emission of several polyacenes was measured in rigid glassy solids. It is concluded that in polyacenes the $\pi \rightarrow \pi^*$ triplet-singlet transition probability is due to spin-orbit interaction involving (π, σ) configurations. The interaction of the (π, π^*) singlets with (π, π^*) triplets is estimated to produce less than 10% of the total $S \rightarrow T$ transition probability. (*PA*, 1962, #20,857)

947. LOCATION OF THE LOWEST TRIPLET LEVEL IN AZULENE

Wa[illegible], W. R.
***Journal of Chemical Physics*, v. 37, no. 4, pp. 923–924,**
August 1[illegible], 1962

Previous attempts to locate the position of the lowest triplet state of this molecule were unsuccessful. Energy transfer was suggested for obtaining the position of triplet levels not accessible by direct excitation. Porter (1961) showed that this type of energy transfer

$$A^*(\text{triplet}) + B(\text{singlet}) = A(\text{singlet}) + B^*(\text{triplet})$$

is highly efficient when the energy gap between the donor and acceptor levels is relatively large and is nearly diffusion controlled. This technique was used to try to detect the position of the lowest triplet level in azulene. Anthracene was used as donor and the usual flash photolytic technique employed. There is strong evidence that the triplet level of azulene is considerably below that of anthracene (14,700 cm^{-1}) and also well below the first singlet state in azulene (14,650 cm^{-1}). (*PA*, 1962, #22,984)

948. STIMULATED EMISSION IN A PHOTOSENSITIZED RIGID-GLASS SOLUTION

Dolan, E., Albrecht, A. C.
***Journal of Chemical Physics*, v. 37, no. 5, pp. 1149–1150,**
September 1, 1962

A glass of 10^{-3} *M* tetramethylparaphenylenediamine in 2-methyl pentane was photooxidized and then continuously illuminated at 77°K with red or infrared light. The stimulated emission was much richer in the phosphorescence radiation (470 mμ) than when stimulation was by ultraviolet light. The processes and lifetimes are discussed. The stimulated emission is believed to involve optical excitation of a trapped electron to an excited state of enhanced mobility. (*PA*, 1963, #959)

949. RELATIVE IMPORTANCE OF EXCITON DELOCALIZATION AND ELECTRON DELOCALIZATION IN POLYENE SPECTRA

Murrell, J. N.
***Journal of Chemical Physics*. v. 37, no. 5, pp. 1162–1163,**
September 1, 1962

An experimental test was made of the relative importance of these two effects. Since there is no first-order exciton interaction between triplet states, any difference between the positions of the triplet states of ethylene and butadiene must be due to electron interaction. Using the author's theoretical calculations and the observed experimental data, it is shown that electron delocalization is responsible for the triplet-state stabilization of 1 ev in going from ethylene to butadiene. (*PA*, 1962, #22,994)

950. EFFECT OF PRESSURE ON CYANINE SPECTRA

Samara, G. A., Riggleman, B. M., Drickamer, H. G.
***Journal of Chemical Physics*, v. 37, no. 7, pp. 1482–1488,**
October 1, 1962

The effect of high pressure was measured on the electronic spectra of a number of cyanine dyes dissolved in cellulose acetate. In general, a red shift was observed with pressure, which varied in magnitude with the chain length and electronegativity of the end group. The results are discussed in terms of Olszewski's resonance barrier model. The peaks tended to broaden with increasing pressure, and to decrease in height. There was no significant change in the total area under the peak. For a few cyanines the spectra of the crystals were also measured to study the effect of pressure on the Davydov splitting. The degree of splitting increased with increasing pressure, as was to be expected. There was a redistribution of intensity among the different branches with increasing splitting. (*PA*, 1962, #22,988)

951. CRYSTAL SPECTRUM OF COPPER ACETYLACETONE

Ferguson, J., Belford, R. L., Piper, T. S.
***Journal of Chemical Physics*, v. 37, no. 7, pp. 1569–1571, October 1, 1962**

Curves are shown for the polarized absorption spectrum between 11,000 and 22,000 cm^{-1} of single crystal copper acetylacetone at 30 and 300°K. The interpretation of the three observed absorption bands is discussed. (*PA*, 1963, #3027)

952. ELECTRON AND NUCLEAR MAGNETIC INTERACTION IN TRIPLET STATES OF VARIOUS ORGANIC PHOSPHORS

Smaller, B.
***Journal of Chemical Physics*, v. 37, no. 7, pp. 1578–1579, October 1, 1962**

A series of measurements was made on the triplet state of various organic phosphors. The experimental arrangement utilized the conventional EPR equipment operating at 9350 Mc with an Osram HBO 500 mercury lamp illuminating the sample *in situ* to produce the phosphorescent state. The samples were diluted in EPA or methanol to form a glass at 77°K. Observations were made on the "forbidden," $\Delta M = \pm 2$, transition with the RF field perpendicular to the static field.

The following results were obtained for zero field splitting and forbidden transition linewidth for triplet states of various phosphors:

	$D' \times 10^2$ cm^{-1}	ΔH oersteds
Benzene	15.93	18.1
Naphthalene	10.49	11.2
Anthracene	7.70	11.9
Diphenyl	11.30	12.6
Terphenyl	9.61	9.1
Triphenylene	13.53	7.9
Phenanthrene	13.35	12.2
Chrysene	10.52	10.1
Coronene	9.71	7.0
Pyrene	9.29	11.5
3,4-Benzpyrene	7.58	10.2
Fluorene	10.96	13.7
Benzoic acid	13.85	15.8
Hydroquinone	13.21	11.5
Aniline	13.17	45.0
Diphenylamine	9.94	21.8
Indole	12.77	16.5
Quinoline	10.68	14.9
Carbazole	10.44	11.1

The advantage of paramagnetic resonance detection over optical detection systems for the determination of relative concentration of triplet states is obvious in cases where phosphorescent spectra overlap or where radiationless decay to the ground state is predominant. The technique, because of its unambiguity in identification of triplet states, has been used in the study of energy transfer between excited states and enhancement of photoproduction of free radicals.

953. EFFECT OF ADDED QUENCHERS IN ORGANIC SCINTILLATOR SOLUTIONS: AROMATIC HALIDES

Kropp, J. L., Burton, M.
***Journal of Chemical Physics*, v. 37, no. 8, pp. 1742–1751, October 15, 1962**

Luminescence-intensity measurements, as affected by quencher concentration, solvent and scintillator, yield information on quenching constants, on specific rates of quenching, on mechanism of quenching, on contrast between quenching of solvent and quenching of scintillator, and on contrast between quenching in benzene as solvent and quenching in cyclohexane as solvent. For a number of aromatic bromides (and for iodobenzene), excitation transfer appears to be involved in the quenching process; in those cases the specific rates are higher than may be expected for simple diffusion-controlled reactions. Typical specific rates (k_q) are $\simeq$ or $>$ 2.5×10^{10} M^{-1} sec^{-1} in benzene. The donor states from which excitation is transferred are not identified. In cyclohexane, calculated k_q values are very much higher, implying that the mechanism of the quenching process is quite different in such cases. Some of the results can be explained in terms of the theory of solvent domains; the data for cyclohexane suggest that the mechanism of deposition and localization of energy must also be carefully considered. (*PA*, 1963, #1699)

954. EFFECT OF ADDED QUENCHERS IN ORGANIC SCINTILLATOR SOLUTIONS: ORGANOMETALLICS

Kropp, J. L., Burton, M.
***Journal of Chemical Physics*, v. 37, no. 8, pp. 1752–1756, October 15, 1962**

Quenching constants (γ_s and γ_x) are given for a variety of perphenyl metals (Si, Ge, Sn, Pb, Sb, and Hg) and for mercury dimethyl acting on benzene and cyclohexane solvents and p-terphenyl and DPA scintillators. Specific rates are calculated for the quenching processes and are found to divide into the following classes: $< 7 \times 10^9$ M^{-1} sec^{-1}, corresponding to spin-perturbation-induced quenching (with a probability factor less than unity, according to Umberger-LaMer calculations); and $\geqq 3 \times 10^{10}$ M^{-1} sec^{-1} (exceeding such calculated values), corresponding to highly favored excitation-transfer processes. The latter high values can be explained in terms of the domain theory of liquid scintillator solutions. Specific rates in the intermediate range for GePh$_4$, and perhaps for SiPh$_4$, acting on solvents are consistent with resistance to high-energy irradiation and with attendant probability that long-lived excited states of such quenchers actually transfer excitation to the scintillator. Anomalously high quenching constants and specific rates for quenching (as well as an anomalous relationship between quenching constants for aerated and deaerated solutions) in the case of cyclohexane suggest that a proper view of energy deposition should be an initial nonlocalized excitation of the system, followed by competitive localization of excitation in one of several particular species, i.e., cyclohexane (which may immediately decompose if an excited state is directly produced), quencher, or scintillator.

955. LUMINESCENCE DECAY TIMES: CONCENTRATION EFFECTS

Yguerabide, J., Burton, M.
Journal of Chemical Physics, **v. 37, no. 8, pp. 1757–1774, October 15, 1962**

The optical properties (e.g., absorption spectrum, fluorescence spectrum, luminescence decay) of solutions of 2,5-diphenyloxazole (PPO) and *p*-terphenyl in benzene and cyclohexane are reported as functions of solute concentration. The absorption spectra of the solutions, when plotted as extinction coefficient vs. wavelength, are unaffected by scintillator concentration, but the fluorescence spectrum of PPO solutions is affected in both intensity and shape. The luminescence decay of all solutions studied is nonexponential and can be resolved into the sum of two exponential decays. The fluorescence spectra and decay curves are affected by oxygen. The interactions between excited and unexcited molecules and between unexcited molecules themselves and the effect which these interactions have on the optical properties of luminescent solutions are examined. The experimental results can be adequately explained by a mechanism which involves formation of transient dimers by an interaction between excited and unexcited molecules in addition to excitation of solute domains of unexcited solute molecules. It is shown that cage effects alone cannot account for the luminescent properties of the systems studied. (*PA*, 1963, #1701)

956. FLUORESCENCE QUENCHING OF A SCINTILLATION SOLUTION BY OXYGEN

Berlman, I. B., Walter, T. A.
Journal of Chemical Physics, **v. 37, no. 8, pp. 1888–1889, October 15, 1962**

A new method of comparing the magnitude of quenching by oxygen for each of a series of solute molecules in cyclohexane solution is presented. It consists of plotting the ratio L_0/L vs. the mean decay time τ of the solute in a deaerated solution; L_0 is the fluorescence yield from a deaerated, L the yield from an aerated solution. The results for 10 fluors give a linear relation between L_0/L and τ, and this result, together with the large quenching constant per unit oxygen concentration, is interpreted as supporting the theory that oxygen quenching is a diffusion-controlled process. (*PA*, 1963, #3810)

957. RAPID TRIPLET EXCITATION MIGRATION IN ORGANIC CRYSTALS

Nieman, G. C., Robinson, G. W.
Journal of Chemical Physics, **v. 37, no. 9, pp. 2150–2151, November 1, 1962**

Experiments on fluorescence and phosphorescence with three-component isotopic mixed crystals (e.g., 99.2% C_6D_6, 0.4% C_6H_5D, 0.4% C_6H_6) at low temperatures (4.2°K) suggest that in π-electron organic crystals the interaction matrix element associated with the triplet state may well be of the same order as that for the lowest singlet state. The large matrix element coupled with the long triplet lifetime has important consequences in several spheres, including biology, e.g., in connection with energy transfer via the triplet state in photosynthesis. (*PA*, 1963, #3058)

958. QUENCHING AND ENERGY TRANSFER BY THE SAME SUBSTANCE

Furst, M., Kallmann, H. P.
Journal of Chemical Physics, **v. 37, no. 10, pp. 2159–2161, November 15, 1962**

The quenching by *o*-terphenyl of the γ-ray-induced fluorescence of *o*-xylene/9,10-diphenylanthracene solutions does not give the usual linear dependence of I_0/I on quencher concentration. The effect is ascribed to a quencher concentration-dependent energy transfer from the solvent to *o*-terphenyl which has a finite transfer probability to the fluorescent solute. This interpretation is confirmed by the enhancement of energy transfer caused by the addition of *o*-terphenyl to a solution of a fluorescent solute in tri-*n*-butylphosphate, a solvent having a very low transfer efficiency. (*PA*, 1963, #1702)

959. FLUORESCENCE POLARIZATION OF SOME PORPHYRINS

Gouterman, M., Stryer, L.
Journal of Chemical Physics, **v. 37, no. 10, pp. 2260–2266, November 15, 1962**

Fluorescence-polarization data on porphyrins are reported. The results can be readily interpreted in terms of the theory of polarization spectroscopy and the theory of the electronic and vibrational structure of these molecules. It is shown how these two theories combine to interpret most of the data, but some anomalies remain. The results hint at the richness of data that may be expected from fluorescence-polarization experiments when techniques are developed further. (*PA*, 1963, #2650)

960. PORPHYRIN CHARGE-TRANSFER COMPLEXES WITH SYM-TRINITROBENZENE

Gouterman, M., Stevenson, P. E.
Journal of Chemical Physics, **v. 37, no. 10, pp. 2266–2269, November 15, 1962**

Absorption spectra of porphyrins in solution with trinitrobenzene indicate formation of a fairly strong one-to-one charge-transfer complex. The ΔF and ΔH values are given for etioporphyrin and tetraphenylporphin; a rough ΔF value was obtained for Zn tetraphenylporphin. It was also found that trinitrobenzene strongly quenches the porphyrin fluorescence. (*PA*, 1963, #2651)

961. POLARIZATION OF THE LUMINESCENCE OF PHENANTHRENE

Azumi, T., McGlynn, S. P.
***Journal of Chemical Physics*, v. 37, no. 10, pp. 2413–2420, November 15, 1962**

The polarization of the luminescence emitted when a randomly oriented array of phenanthrene molecules is excited with polarized light is discussed. Considerable attention is devoted to various correction methods in an effort to establish a correct zero-polarization base line. The polarization of the fluorescence excitation spectrum, the fluorescence spectrum, and the phosphorescence spectrum of phenanthrene was determined. The polarization of the fluorescence spectrum validates Platt's assignment of the first four singlet electronic states of phenanthrene as ^1L_b, ^1L_a, ^1B_b, and ^1C_b, in order of increasing energy. The possible occurrence of one or two other electronic states in the same energy interval, as suggested by Zimmermann and Joop, is discussed. The phosphorescence emission is primarily polarized out of plane. The results further suggest that either two perturbing singlet states are mixed into the lowest triplet state, or that two perturbing triplet states are mixed into the singlet ground state by spin-orbital coupling; the Platt assignment of ^3L_a for the lowest triplet state is supported. It has been found that polarization measurements are of considerable help in vibrational analysis, and may in certain cases uniquely determine vibrational types. A vibrational analysis of the fluorescence spectrum, phosphorescence spectrum, and ^1L_b absorption band is presented. (*PA*, 1963, #3062)

962. ELECTRONIC SPECTRUM OF 2,2′-PARACYCLOPHANE

Ron, A., Schnepp, O
***Journal of Chemical Physics*, v. 37, no. 11, pp. 2540–2546, December 1, 1962**

The polarized absorption and fluorescence spectra of single crystals of 2,2′-paracyclophane at 20°K were recorded in the region 3300–3100 Å. The spectra consist of narrow lines of which 87 could be measured in absorption and nine in emission. Single crystals having two different planes developed could be prepared sufficiently thin for measurements. The spectra obtained could be divided into two components, one characteristic of a transition moment parallel, and the other perpendicular to the unique axis of the tetragonal crystal. These polarization directions are characteristic of molecular directions since in this case no Davydov splitting is to be expected in view of the high symmetry of the crystal. The absorption system is analyzed satisfactorily as representing the forbidden component of the benzene $^1A_{1g} \rightarrow {}^1B_{2u}$ transition in the "dimer" molecule. A totally symmetric progression-forming frequency of 240 cm⁻¹ is assigned as the intermoiety vibration. The appearance of a weak 0–0 transition is interpreted as due to a small-amplitude twist of the moieties relative to one another. (*PA*, 1963, #4773)

963. ABSORPTION SPECTRUM OF Pu^{3+} IN LANTHANUM TRICHLORIDE AND LANTHANUM ETHYLSULFATE

Lämmermann, H., Conway, J. G.
***Journal of Chemical Physics*, v. 38, no. 1, pp. 259–269, January 1, 1963**

The polarized absorption spectrum and some Zeeman effect studies were conducted on crystals of lanthanum trichloride and lanthanum ethylsulphate containing 0.1 and 5 mole % of Pu^{3+} at various low temperatures. The ground-state levels as well as several excited states are well characterized. Attempts at fitting the positions of levels to 5*f* hydrogenic free-ion states give good agreement for $F_2 = 245$ cm^{-1} and $\zeta = 2290$ cm^{-1}. (*PA*, 1963, #8601)

964. ELECTRONIC SPECTRA AND HYDROGEN BONDING. II. ANTHROLS

Suzuki, S., Baba, H.
***Journal of Chemical Physics*, v. 38, no. 2, pp. 349–353, January 15, 1963**

(For Part I, see Entry #915.) An investigation was made of the effect of hydrogen bonding on the absorption and fluorescence spectra of α- and β-anthrols. It is shown that, when a hydrogen bond is formed between the anthrols and dioxane, each electronic band exhibits a characteristic behavior which supplies a substantial clue as to the origin of the band. The behavior in hydrogen bonding of the low-frequency absorption of β-anthrol clearly indicates that the absorption consists of two overlapping electronic transitions: one at lower frequencies, which was previously assigned to the ^1L_b transition, shows a large red shift (340 cm⁻¹) upon formation of the hydrogen bond, whereas the other transition, ^1L_a, shows only a small red shift (60 cm⁻¹). The results of experiments on both the absorption and fluorescence spectra show that the proton-donating power of the anthrols is evidently greater in the first excited state than in the ground state. (*PA*, 1963, #8287)

965. FLUORESCENCE DECAY TIMES OF RARE-EARTH CHELATES

Bhaumik, M. L., Lyons, H., Fletcher, P. C.
***Journal of Chemical Physics*, v. 38, no. 2, pp. 568–569, January 15, 1963**

Fluorescence lifetimes at 300 and 90°K of the hydrated chlorides are compared with those of the chelates with benzoylacetone (Eu and Sm), acetylacetone (Tb), and dibenzoylmethane (Sm). Possible mechanisms are discussed to account for the much longer decays of the chelates. (*PA*, 1963, #11,001)

966. OPTICAL ABSORPTION SPECTRUM OF METAL-FREE PHTHALOCYANINE SINGLE CRYSTALS

Heilmeier, G. H., Warfield, G.
***Journal of Chemical Physics*, v. 38, no. 4, pp. 893–897, February 15, 1963**

The optical absorption spectrum of the molecular crystal metal-free phthalocyanine was investigated in the region 25,000 to 3500 Å. The spectrum of the phthalocyanine molecule retains much of its identity in the crystal, as evidenced by the similarity in the regions of main absorption. This is a consequence of the weak intermolecular binding forces. The crystal absorptions in the region 8000 to 5000 Å, and below 4000 Å, can be attributed to excitations from the highest filled molecular orbital to the vibrationally broadened and shifted excited states of the molecule which occur in the crystal field. Vibrational structure was observed which was attributed to a symmetrical breathing vibration of the peripheral benzene rings and, quite possibly, a similar vibration of the entire phthalocyanine molecule. (*PA*, 1963, #10,971)

967. PHOSPHORESCENCE LIFETIME STUDIES IN SOME ORGANIC CRYSTALS AT LOW TEMPERATURES

Olness, D., Sponer, H.
***Journal of Chemical Physics*, v. 38, no. 7, pp. 1779–1782, April 1, 1963**

Triplet–singlet decay curves from naphthalene, phenanthrene, chrysene, durene, and hexamethylbenzene have been studied in the crystalline phase at temperatures of 4°K and higher, and for comparison in rigid glass solutions at 77°K. The decay from true dilute solutions was found to follow an exponential law. At 4°K, the phosphorescence emission from crystals of naphthalene, phenanthrene, and chrysene followed an exponential law, while that from durene and hexamethylbenzene was always nonexponential. Various theories are discussed concerning the causes of the nonexponential decay and the change in the general shape of the decay curves with different modes of sample preparation and with temperature.

968. DOUBLE-PHOTON EXCITATION OF FLUORESCENCE IN ANTHRACENE SINGLE CRYSTALS

Singh, S., Stoicheff, B. P.
***Journal of Chemical Physics*, v. 38, no. 8, pp. 2032–2033, April 15, 1963**

While investigating the fluorescence of various solids excited by the 6940-Å radiation from a pulsed ruby maser, an unusually intense blue fluorescence from single crystals of anthracene was observed. A study of its spectrum revealed this to be the well-known λ4300-Å emission arising from the transition $^1B_{2u} \rightarrow {}^1A_g$, and intensity measurements proved that excitation took place by a two-photon absorption process.

Since the authors' interpretation of the process leads to new information about the energy levels of the anthracene molecule and may well be of general interest in similar spectroscopic studies, detailed results are published.

In the experiments, unpolarized maser radiation passed through a red filter and was focused on the sample. Light leaving the sample passed through a filter of $CuSO_4$ solution to remove the maser radiation; the transmitted light was dispersed by a monochromator and focused on a calibrated photomultiplier. The maser signal was monitored by reflecting a small part of the radiation with a beam splitter onto a phototube. Both signals were displayed on a dual-beam oscilloscope. The time constants of the detectors were about 10^{-3} sec for intensity measurements and $< 10^{-6}$ sec for lifetime measurements. For photographing the spectrum, the monochromator was replaced by a grating spectrograph. Several single crystals from 100 μ to 2 mm in thickness were used. They were cleaved and polished, and enclosed with helium in quartz capsules for study at 77° and at 300°K. The maser radiation was incident normal to the *ab* crystal plane.

Plots are presented for the fluorescence spectra of anthracene single crystals at 77° and 300°K, excited by a ruby maser. Each point represents the fluorescence intensity measured photoelectrically for a single maser flash. The maser radiation incident on the crystal at 77°K was only half that with the crystal at 300°K. The intensity dependence of the two main maxima in the fluorescence of anthracene crystals at 77°K on the incident maser beam intensity is also plotted.

969. ELECTROLUMINESCENCE IN ORGANIC CRYSTALS

Pope, M., Kallmann, H. P., Magnante, P.
***Journal of Chemical Physics*, v. 38, no. 8, pp. 2042–2043, April 15, 1963**

Electroluminescence has been observed in single crystal anthracene, and in single crystal anthracene with about 10^{-1} mole % tetracene as an impurity. The luminescence in the case of anthracene was the usual anthracene fluorescence; in the case of anthracene with tetracene impurity, it was that of tetracene.

The crystals were 10 to 20 μ thick and were prepared by sublimation and from solution. Two electrode configurations were used, the results differing markedly. In one, silver paste (epoxy base) electrodes were used, the area of one electrode being made smaller than the opposite electrode. In a typical case, the small electrode was 1 mm in diameter compared with an 8-mm-D opposing electrode. In the second configuration, the electrodes were 0.1 M solutions of NaCl, 0.1 cm^2 in area, and were symmetrically disposed on both sides of the crystals. The field was applied along the c' direction of the crystal. Experiments were carried out either with no current limiting resistor or with one of 10^5 Ω, when current measurements were made. Light was detected with a photomultiplier using a DuMont 6292 tube.

970. COMPREHENSIVE SPECTROSCOPIC INVESTIGATION OF POLYNUCLEAR AROMATIC HYDROCARBONS. ABSORPTION SPECTRA AND STATE ASSIGNMENTS FOR THE TETRACYCLIC HYDROCARBONS AND THEIR ALKYL-SUBSTITUTED DERIVATIVES

Becker, R. S., Singh, I. S., Jackson, E. A.
***Journal of Chemical Physics*, v. 38, no. 9, pp. 2144–2171, May 1, 1963**

The absorption spectra have been investigated and state assignments made for benz(*a*)anthracene, benzo(*c*)phenanthrene, chrysene, triphenylene, naphthacene, and pyrene. These results are compared with existing theoretical and experimental studies. The identification of electronic transitions has been made for all monomethyl derivations of the above hydrocarbons except naphthacene. The study extends over the spectral region 16,500–52,500 cm^{-1}. In addition, vibrational analyses are proposed for all cases considered. Certain dimethyl-, alkyl- and fluorosubstituted derivatives have been studied. General spectral characteristics are included.

971. DELAYED FLUORESCENCE OF SOLID SOLUTIONS OF POLYACENES

Azumi, T., McGlynn, S. P.
***Journal of Chemical Physics*, v. 38, no. 11, pp. 2773–2774, June 1, 1963**

A delayed fluorescence has been observed from various un-degassed and degassed rigid-glass solutions of some polyacenes at 77°K. A solution of polyacene is cooled by liquid nitrogen and irradiated by a 150-w Xe lamp at the wavelength of its excitation maximum. The long-lived emissions (delayed fluorescence and phosphorescence) are recorded by an Aminco–Keirs spectrophosphorimeter. The delayed fluorescence has the same spectral distribution as ordinary fluorescence and decays about four to five times faster than the phosphorescence. This phenomenon has been observed for naphthalene, phenanthrene, and hexahelicene, but not for anthracene, 1,2-benzanthracene, pyrene, and chrysene.

A series of delayed emission spectra of phenanthrene recorded by varying the intensity of the exciting light is presented. The ratio of the intensity of the delayed fluorescence to the square of the intensity of phosphorescence is shown to be constant within 1% for the whole series of reproduced spectra. This experimental fact indicates that two triplet molecules produce the one singlet excited molecule which is responsible for the delayed fluorescence. The possible mechanisms for such forming of one singlet excited molecule are discussed. A plausible mechanism involves a direct resonance interaction. This note contains direct experimental evidence of an exciton–exciton interaction. (For Part II, see Entry #981.)

972. POLARIZED ABSORPTION SPECTRA OF PURINES AND PYRIMIDINES

Stewart, R. F., Davidson, N.
***Journal of Chemical Physics*, v. 39, no. 2, pp. 255–266, July 15, 1963**

Polarized absorption spectra in the molecular planes for thin sections (0.1 μ and up) of single crystals of 1-methylthymine, 9-methyladenine, and their 1:1 hydrogen-bonded complex (the AT dimer) have been obtained. For 1-methylthymine, the first absorption band ($\lambda_{max} \approx 275\ m\mu$) is polarized close to the N_1–C_4 axis, and the second UV band ($\lambda_{max} < 230\ m\mu$) is polarized approximately perpendicular to the first. For 9-methyladenine, the crystal structure is not known, but the data for the AT dimer can be interpreted by assuming that the intense long-wavelength band ($\lambda_{max} \approx 275$) is short-axis ($C_6$–$C_5$) polarized. There is a weak band with $\lambda_{max} \approx 255$ which is then long-axis polarized, and probably the second strong band ($\lambda_{max} < 230$) is also long-axis polarized. All of the crystal spectra, and especially the AT dimer, are hypochromic with respect to the solution spectra. The 9-methyladenine spectrum is markedly red-shifted in the crystals. The intensity changes and spectra shifts probably cannot be explained by a dipole–dipole exciton interaction. The spectrum of the AT dimer perpendicular to the molecular planes begins at about 300 $m\mu$ and is still rising at 230 $m\mu$; it is attributed to n–π^* transitions.

973. FLUORESCENCE OF EUROPIUM THENOYLTRIFLUOROACETONATE. I. EVALUATION OF LASER THRESHOLD PARAMETERS

Winston, H., Marsh, O. J., Suzuki, C. K., Telk, C. L.
***Journal of Chemical Physics*, v. 39, no. 2, pp. 267–271, July 15, 1963**

A crystalline form of europium thenoyltrifluoroacetonate (EuTTA) with a melting point of 164–166°C has been prepared. Measurements of absorption and emission spectra, fluorescence lifetime, and relative quantum yield have been made on solutions of EuTTA in acetone, toluene, and ethanol. From these measurements, the required laser threshold concentration of excited EuTTA molecules in acetone at room temperature for a laser cavity with an optical loss of 1%/cm is calculated to be $2.3 \times 10^{17}\ cm^{-3}$.

974. FLUORESCENCE OF EUROPIUM THENOYLTRIFLUOROACETONATE. II. DETERMINATION OF ABSOLUTE QUANTUM EFFICIENCY

Gudmundsen, R. A., Marsh, O. J., Matovich, E.
***Journal of Chemical Physics*, v. 39, no. 2, pp. 272–274, July 15, 1963**

The absolute quantum efficiency of the fluorescence of europium thenoyltrifluoroacetonate in acetone has been measured by a calorimetric method, and substantiated by comparing the output against that from acridone. The quantum efficiency of the fluorescence, which peaks at 6122 A, from acetone solutions at 2[illegible]C is 0.56 ± 0.08.

975. FLUORESCENCE LIFETIME OF THE EUROPIUM DIBENZOYLMETHIDES

Metlay, M.
***Journal of Chemical Physics*, v. 39, no. 2, pp. 491–492, July 15, 1963**

The fluorescence lifetimes of EuD$_3$ and EuD$_4$ are reported. EuD$_3$ and EuD$_4$ were prepared by the method of Whan and Crosby. Two independent samples of EuD$_4$ were made, and a portion of each was heat treated to form EuD$_3$. Fluorescence was excited by light from a GE FT130 flashtube through a Corning 7-60 filter. The emitted light was passed through a monochromator set at 6100 Å with a band pass of 65 Å, to a photomultiplier tube. The output of the tube was displayed on an oscilloscope and photographed. The observed lifetimes are tabulated. In an attempt to understand the reasons for the marked differences in lifetime exhibited by EuD$_3$ and EuD$_4$, a brief study was made of the nature of the fourth dibenzoylmethane in EuD$_4$.

976. EXCITATION OF π ELECTRONS IN POLYSTYRENE AND SIMILAR POLYMERS BY 20-kev ELECTRONS

Swanson, N., Powell, C. J.
***Journal of Chemical Physics*, v. 39, no. 3, pp. 630–634, August 1, 1963**

Excitation of the π-electrons in thin films of polystyrene and some similar polymers has been observed in the characteristic energy loss spectra of 20-kev electrons scattered at zero angle. The observed energy loss of approximately 7 ev corresponds to the strong UV absorption near 1800 Å in benzene and its derivatives. An energy loss of 6.97 ± 0.10 ev was measured in films of atactic and isotactic polystyrene, styrene ethylene copolymer, and poly 2,3,4,5,6-pentadeuterostyrene, and an energy loss of 7.25 ± 0.15 ev was measured in poly 2,3,4,5,6-pentafluorostyrene. These energy losses appeared as sharp peaks superimposed on a very broad and more intense loss peak with a maximum at 21.3 ± 0.3 ev in all the electron energy loss spectra obtained. The results for the energy loss attributed to the π-electrons are correlated with relevant UV absorption data. A discernible decrease in the measured ~7-ev loss occurred during electron bombardment of the specimens, and is attributed to film contamination and breakdown. The angular distribution of the intensity of each loss in isotactic polystyrene about zero scattering angle was also measured.

977. RADIATIONLESS TRIPLET–SINGLET TRANSITIONS IN NAPHTHALENE

Hadley, S. G., Rast, H. E., Jr., Keller, R. A.
***Journal of Chemical Physics*, v. 39, no. 3, pp. 705–711, August 1, 1963**

The fluorescent intensity, phosphorescent intensity, and phosphorescent lifetime of naphthalene and naphthalene-D$_8$, dissolved in durene, were measured as a function of temperature from 77 to 325°K. These measurements indicate that radiationless transitions from the first excited single state are temperature independent, but radiationless transitions from the lowest triplet are strongly temperature dependent. Analysis of the data for the decay of the triplet state indicates that only one activated state is responsible for this temperature dependence. The activation energy and pre-exponential factor for decay from this state are 3559 ± 79 cm^{-1} and $(4.2 \pm 1.5) \times 10^7$ sec^{-1} for naphthalene, and 3362 ± 35 cm^{-1} and $(1.30 \pm 0.24) \times 10^7$ sec^{-1} for naphthalene-D$_8$. These data can be interpreted as corresponding to the excitation of one of the intramolecular C–C stretching modes to its second excited state or a combination of two C–C fundamentals.

978. DELAYED FLUORESCENCE AND POSSIBLE ONE-ELECTRON PHOTO-IONIZATION OF DYES IN RIGID MEDIA

Lim, E. C., Wen, W.-Y.
***Journal of Chemical Physics*, v. 39, no. 3, pp. 847–848, August 1, 1963**

Singlet–singlet emission of extremely long duration from rigid solutions of acriflavine has been reported previously. The emission, which is observed at the temperature of liquid nitrogen, has been interpreted as the emission from the excited singlets of the dye formed by recombination of radical ions and electrons produced initially by one-electron photoionization of the dye molecules.

The purpose of the present note is to establish the generality of such emission among various dyes, and to report on the dye-induced photoreduction of metal ions which appears to offer an indirect support to the proposed emission mechanism.

The dyes employed in the present study are 3,6-diamino and 3,6-dimethylamino acridines (proflavine, acridine orange, and their various 10-alkyl derivatives), carbocyanine dyes (3,3′-dialkyl-thiazolinocarbocyanine iodide, 3,3′-dialkyl-oxacarbocyanine iodide, 3,3′-dialkyl-thiacarbocyanine iodide, and related dyes), and acidic (cationic) and basic (anionic) forms of fluorescein, with two of the acridine dyes, acriflavine and ethyl proflavine (3,6-diamino-10-ethyl-acridinium chloride), receiving most of the attention.

979. FLUORESCENCE SPECTRAL STUDY OF WAVELENGTH SHIFTERS FOR SCINTILLATION PLASTICS

Sandler, S. R., Tsou, K. C.
***Journal of Chemical Physics*, v. 39, no. 4, pp. 1062–1067, August 15, 1963**

An investigation of the fluorescence spectra of a series of 1,3,5-triaryl-2-pyrazoline indicated that substituents in the 3-phenyl ring shifted the fluorescence-emission wavelength linearly with Brown's σ_p^+. On the basis of this evidence, the excited state is thought to have a partial positive charge located on carbon 3 of the pyrazoline ring. The shift in the absorption spectral bands of 1,3,5-triphenyl-2-pyrazoline with concentration is presented as evidence of a dimer or an associated complex. The fluorescence quenching at higher concentrations may be due to the energy dissipating effect of the dimers or complexes. The high extinction coefficient of the ultraviolet maximum and yet the similarity of the fluorescence intensity of 4,4′-bis-[5-(1,3-diphenyl-2-pyrazolinyl)] benzene to 1,3,5-triphenyl-2-pyrazoline are explained on the basis of an internal quenching mechanism. The efficiencies of these two compounds as wavelength shifters in plastic scintillators are approximately equal.

980. RADIATIVE TRANSITION PROBABILITIES WITHIN $4f^n$ CONFIGURATIONS: THE FLUORESCENCE SPECTRUM OF EUROPIUM ETHYLSULFATE

Axe, J. D., Jr.
Journal of Chemical Physics, v. 39, no. 5, pp. 1154–1160, September 1, 1963

The relative intensities of the transitions occurring in the fluorescence spectrum of $Eu(C_2H_5SO_4)_3 \cdot 9H_2O$ have been measured at 77 and 4°K. The strengths of both the "forbidden" electric dipole transitions and magnetic dipole transitions which were observed are compared to theoretical expressions and the results are discussed. The results are in reasonable agreement with recent phenomenological treatments of crystal-field-induced dipole radiation, and suggest that g-orbital configurational mixing contributes significantly to the process.

981. DELAYED FLUORESCENCE OF SOLID SOLUTIONS OF POLYACENES. II. KINETIC CONSIDERATIONS

Azumi, T., McGlynn, S. P.
Journal of Chemical Physics, v. 39, no. 5, pp. 1186–1194, September 1, 1963

(For Part I, see Entry #971.) Delayed fluorescence has been observed at 77°K from rigid-glass solutions of some aromatic hydrocarbons and their halo derivatives. The intensity of the delayed fluorescence is proportional to the square of the phosphorescence intensity. The decay of delayed fluorescence in all cases may be represented as the sum of two first-order processes; the lifetime of the longer-lived component varies between ½↔⅕ that of the phosphorescence, while the lifetime of the shorter-lived components varies between 1/10↔1/50 that of phosphorescence. The intensity of delayed fluorescence observed from a solution of a given compound varies as the ratio $\phi_f\phi_p^2/k_3^{*2}$, where ϕ_f and ϕ_p are fluorescence and phosphorescence quantum yields, respectively, and where k_3* is the emissive phosphorescence rate constant. Phosphorescence decay exhibits a slight nonexponentiality only in the case of those solutions where the delayed fluorescence is especially strong. Delayed fluorescence is spectrally identical with ordinary fluorescence. The above facts may only be interpreted, within the limits of spectrograph resolution available, by a kinetic mechanism which involves a triplet–triplet annihilation process, this mutual annihilation resulting in the eventual production of the singlet excited state of one of the partners. Some ancillary hypotheses are required to interpret the shorter-lived component of the delayed fluorescence, and a kinetic flow sheet representative of the energy-transfer processes involved in the production of delayed fluorescence is proposed.

982. POLARIZATION OF THE $\pi^* \rightarrow \pi$ AND $\pi^* \rightarrow n$ PHOSPHORESCENCE SPECTRA OF *N*-HETEROCYCLICS

El-Sayed, M. A., Brewer, R. G.
Journal of Chemical Physics, v. 39, no. 7, pp. 1623–1628, October 1, 1963

Phosphorescence polarization measurements have been performed by the method of photoselection. Since this technique requires a knowledge of the polarization of at least two perpendicularly polarized absorption bands, the method can be fully exploited in the case of the *N*-heterocyclics where the (n, π^*) and (π, π^*) absorptions are perpendicular to each other. The results on pyrazine (1,4-diazabenzene) show that the $\pi^* \rightarrow n$ emission is polarized along the N···N axis, in agreement with previous work. The polarization is uniform throughout the 600-cm^{-1}[$\nu_a(a_g)$] progression and does not alternate as does the intensity or the vibrational frequency. This behavior might arise from a resonance-type interaction which produces a progression with mixed Franck–Condon characteristics Quinoxaline (1,4-diazanaphthalene) is found to have a $\pi^* \rightarrow \pi$ phosphorescence spectrum which is highly polarized out of plane. Approximate calculations show that the (n, π^*) singlet state in quinoxaline is at least as important as the (σ, π^*) states in mixing with the emitting (π, π^*) triplet state. The general conclusion reached is that in nitrogen heterocyclics when the phosphorescent state is of the (n, π^*) type, the mixing singlet is of the (π, π^*) type, or in-plane Rydberg state, whereas if the emitting triplet state is of the (π, π^*) type, the mixing singlet might be of the (n, π^*), (σ, π^*), and/or perpendicularly polarized Rydberg state.

983. FLUORESCENCE OF NAPHTHACENE VAPOR

Williams, R., Goldsmith, G. J.
Journal of Chemical Physics, v. 39, no. 8, pp. 2008–2011, October 15, 1963

The absorption spectrum of naphthacene vapor is similar to that in solution. There is an absorption band with pronounced vibrational structure running about 5000 to 3500 Å, and a second stronger band from 2700 Å to shorter wavelengths. An examination has been made of the fluorescence spectrum of the vapor at low pressures, such that molecules have no collisions during the lifetime of the excited state. By selective excitation with either the 3650- or the 2537-Å line of the mercury lamp, it is possible to excite molecules into either the first or the second excited singlet state. The fluorescence emission appears to be from the first excited singlet state in both cases, even though the molecules suffer no intermolecular collisions in the excited state.

984. FLUORESCENCE OF CATECHOL AMINES AND RELATED COMPOUNDS CONDENSED WITH FORMALDEHYDE

Falck, B., Hillarp, N. A., Thieme, G., Torp, A.
***Journal of Histochemistry and Cytochemistry*, v. 10, pp. 348–354, 1962**

The amines included in a dried protein film were exposed to HCHO vapor. Primary amines having OH groups at the 3 and 4 positions fluoresced intensely, secondary amines weakly. The course of the reactions with HCHO is considered.

985. THE FLUORESCENCE SPECTRUM OF NAPHTHALENE VAPOR IN THE 3100 Å REGION

Hollas, J. M.
***Journal of Molecular Spectroscopy*, v. 9, no. 2, pp. 138–169, August 1962**

The fluorescence spectra of naphthalene-H_8 and naphthalene-D_8 were photographed in the 3100-Å region using a spectrograph with a resolution of about 0.5 cm^{-1}. Three mercury lines in the region of 3125 Å were used for excitation, and spectra were obtained at a pressure of ~0.1 mm Hg (when emission occurs before many collisions between molecules have taken place) and with helium added to a pressure of 5 mm Hg (when vibrational deactivation occurs before emission). The low-pressure spectra are extensive and were used in making vibrational assignments. The high-pressure spectra are less extensive but contain further useful information; rotational contours in these spectra were used to support vibrational assignments. An understanding of the mechanism of the fluorescence has enabled an assignment of the 72 cm^{-1} sequence interval to be made in both naphthalene-H_8 and -D_8. The contours of the 72 cm^{-1} sequence members show evidence for coriolis interaction in support of their assignments. The vibrations involved in some other sequences have been ascertained from the low-pressure spectra. Combination bands are assigned which confirm the existence of the a_g vibrations with frequencies of about 516 and 493 cm^{-1}, respectively, in naphthalene-H_8 and -D_8. (*PA*, 1962, #20,856)

986. QUANTUM EFFICIENCIES OF FLUORESCENCE OF ORGANIC SUBSTANCES: EFFECT OF SOLVENT AND CONCENTRATION OF THE FLUORESCENT SOLUTE

Melhuish, W. H.
***Journal of Physical Chemistry*, v. 65, no. 2, pp. 229–235, February 1961**

The absolute quantum efficiencies of fluorescence of deaerated solutions of several organic fluorescent substances in petroleum ether (b.p. 60–80°C), ethanol (99%) and benzene at 25°C were measured with a rhodamin B quantum counter. An equation was derived for correcting the observed efficiencies of fluorescence for reabsorption of fluorescence and shifts in the region of absorption away from the quantum counter. Absolute quantum efficiencies of fluorescence extrapolated to zero concentration, bimolecular self-quenching constants, and oxygen-quenching constants were measured at 25°C. Quinine bisulfate, 5×10^{-3} M in 1 N H_2SO_4, is proposed as a standard with an absolute quantum fluorescence efficiency of 0.51 at 25°C.

987. THE FLUORESCENCE AND PHOSPHORESCENCE OF TRIFLUOROACETONE VAPOR

Ausloos, P., Murad, E.
***Journal of Physical Chemistry*, v. 65, no. 9, pp. 1519–1521, September 1961**

The fluorescence and phosphorescence of trifluoroacetone have been investigated at 2652, 2804, 3025, 3130 and 3341 Å. The effects of concentration and temperature on the yields of triplet- and singlet-state emissions are comparable to those observed for acetone. The emissions from 2-butanone and 2-pentanone have been investigated briefly. Both compounds phosphoresce very weakly, and their fluorescence yields are nearly identical with those observed for acetone and trifluoroacetone.

988. CORRELATION OF THE RELATIVE PULSE HEIGHT OF ORGANIC SCINTILLATORS WITH POLARITY AND RESONANCE EFFECTS

Sandler, S. R., McGonigal, P. J., Tsou, K. C.
***Journal of Physical Chemistry*, v. 66, no. 1, pp. 166–171, January 1962**

A linear correlation was found between the relative pulse height of plastic scintillators and the ionization potential and Hammett or Taft substituent constants of the solvent and fluor. Some aspects of the scintillation mechanism are discussed. (*PA*, 1962, #6626)

989. OXYGEN QUENCHING OF FLUORESCENCE IN SOLUTION: AN EXPERIMENTAL STUDY OF THE DIFFUSION PROCESS

Ware, W. R.
***Journal of Physical Chemistry*, v. 66, no. 3, pp. 455–458, March 1962**

Unusually large Stern–Volmer constants for the quenching of fluorescence of aromatic hydrocarbons by oxygen in solution are well known. The rate constants for the quenching reaction were determined by fluorescence lifetime measurements for several hydrocarbons in a series of solvents covering a wide range of viscosities. The diffusion coefficient for oxygen in several solvents was also determined. The rate constants are consistent with a diffusion-controlled reaction when the unusually large diffusion coefficient for oxygen is taken into account. (*PA*, 1962, #9282)

990. THE LUMINESCENCE OF FLUORESCEIN DYES

Forster, L. S., Dudley, D.
***Journal of Physical Chemistry*, v. 66, no. 5, pp. 838–840, May 1962**

The fluorescence and phosphorescence yields and triplet-state lifetimes were determined for a number of halogenated fluorescein dyes in EPA solutions. The lifetimes decrease progressively as the number of halogen atoms is increased in both the bromine and iodine series of derivatives, and the lifetime is always less in the iodine than in the corresponding bromine derivative. The results indicate that the diminution of the fluorescence yield that accompanies bromine and iodine substitution is not due primarily to an increase in intersystem crossing but rather to increased internal conversion from the excited singlet state to the ground state. (*PA*, 1962, #15,608)

991. TRIPLET-SINGLET EMISSION IN FLUID SOLUTION

Parker, C. A., Hatchard, C. G.
***Journal of Physical Chemistry*, v. 66, no. 12, pp. 2506–2513, December 1962**

Using a photoelectric spectrophosphorimeter of novel design, the long-lived luminescence from solutions of two dyestuffs and two aromatic hydrocarbons has been investigated. Solutions of eosin and proflavine hydrochloride in ethanol or glycerol give rise to two bands of long-lived luminescence which are attributed, respectively, to the triplet–singlet radiative transition and to delayed fluorescence arising from triplet–upper-singlet thermal activation. A study of the band intensities as a function of temperature and solvent can provide information about the probabilities of the three intersystem crossing processes. Triplet–singlet emission has been observed from phenanthrene in ethanol at room temperature. At lower temperatures a weak delayed fluorescence also is emitted. Phenanthrene solutions containing trace quantities of anthracene give sensitized anthracene delayed fluorescence. Solutions of pure anthracene also give anthracene delayed fluorescence. The observations of delayed fluorescence from the hydrocarbons are discussed only briefly. (*PA*, 1963, #11,800)

992. RESONANCE TRANSFER OF EXCITATION ENERGY BETWEEN NUCLEOSIDES AND ACRIDINE ORANGE

Basu, S., Greist, J.
***Journal of Physical Chemistry*, v. 67, no. 6, pp. 1394–1395, June 1963**

The efficiency of excitation-energy transfer from the donor M_1 (nucleoside) to the acceptor M_2 (acridine orange), i.e., the number of M_2 molecules excited by transfer calculated for one excited M_1 molecule, was determined by comparison of the fluorescence intensity of M_2 on excitation by ultraviolet radiation in the absorption band of the donor (350 mμ) and in a band where the acceptor absorbs but the donor is transparent (450 mμ). If the fraction of 350-mμ light absorbed in M_1 equals α_{11} and that in M_2 equals α_{21}, then the transfer efficiency, T_{12} is given by the relation

$$T_{12} = \frac{I_{21}/I_{22} - \alpha_{21}}{\alpha_{11}}$$

where I_{21} and I_{22} are the respective fluorescence intensities of M_2 under equal flux of exciting photons. The efficiencies T_{12} calculated for four different nucleoside–acridine orange systems are summarized as

Nucleoside	T_{12} (%)
Inosine	40
Adenosine	35
Uridine	31
Thymidine	28

993. THE ABSORPTION SPECTRUM OF BIPHENYL SINGLE CRYSTAL

Rao, A. V. K.
***Journal of Scientific and Industrial Research*, India, v. 21B, p. 231, 1962**

Measurements with various experimental conditions are reported.

994. PREVENTION OF SPONTANEOUS LUMINESCENCE OF LUMINOL

Arai, M.
***Kagaku Keisatsu Kenkyusho Hokoku*, v. 63, pp. 24–26, 1962**

Spontaneous luminescence is prevented by adding either hydroquinone or 4-carboxyindazole. Durability of hydroquinone prevention is noted.

995. FLUORESCENT BRIGHTENING AGENTS OF THE BIS-BENZOXAZOLYLETHYLENE SERIES CONTAINING SUBSTITUTED HYDROXYMETHYL GROUP

Maruyama, T., Kuroki, N., Konishi, K.
***Kogyo Kagaku Zasshi*, v. 66, no. 2, pp. 789–792, 1963**

996. EFFECT OF VARIOUS PHYSICAL INFLUENCES ON THE LUMINESCENT PROPERTIES OF DEOXYRIBONUCLEIC ACID *IN VITRO*

Khodas, M. Y.
***Laboratornoe Delo*, v. 9, no. 7, pp. 21–25, 1963**

997. THE CORRELATION BETWEEN THE PHYSIOLOGICAL STATE AND AVERAGE LENGTH OF FLUORESCENCE OF BACTERIOCHLOROPHYLL IN THE CELLS OF PHOTOSYNTHESIZING BACTERIA

Rubin, A. B., Osnitskaya, L. K.
***Mikrobiologiya*, v. 32, no. 2, pp. 200–203, March 1963**

The average fluorescence length of bacteriochlorophyll in the cells of purple sulphur bacteria is five to six times less than in the solution; this fact is apparently due to photosynthetic inactivation of the light-excited pigment molecules. The nature of these processes is ascertained.

At the logarithmic growth stage of *Chromatium vinosum* cells, the efficiency of utilization of the absorbed light energy in primary photosynthetic processes is higher than prior to this stage or at the growth extinction stage.

Several factors influencing the metabolic state of the cells do not affect the inactivation processes of the excited bacteriochlorophyll molecules during photosynthesis.

998. PARAMAGNETIC RESONANCE IN PHOSPHORESCENT AROMATIC HYDROCARBONS. I. NAPHTHALENE

van der Waals, J. H., de Groot, M. S.
Molecular Physics, v. 2, no. 4, pp. 333–340, October 1959

Formerly Hutchison and Mangum have observed electron spin resonance in the lowest triplet state of naphthalene. An analysis of their results is given on the basis of spin–spin interaction between the two unpaired electrons. In addition to the lines observed by these authors, another transition, which corresponds to $\Delta M = \pm 2$ in the atomic case, must occur at low field strength. This transition has been observed in a mixed crystal as well as in rigid glass solution.

999. PARAMAGNETIC RESONANCE IN PHOSPHORESCENT AROMATIC HYDROCARBONS. II. DETERMINATION OF ZERO-FIELD SPLITTING FROM SOLUTION SPECTRA

de Groot, M. S., van der Waals, J. H.
Molecular Physics, v. 3, no. 2, pp. 190–200, March 1960

Electron paramagnetic resonance spectra are given of glassy solutions of triphenylene, 1,3,5-triphenylbenzene, coronene, and naphthalene excited into their lowest triplet state by ultraviolet irradiation at liquid-nitrogen temperature. For each substance two spectra were measured: one with the RF magnetic field parallel to the constant field, the other with the fields at right angles.

A method is suggested for analyzing the spectra of those molecules having a trigonal symmetry axis, and values of the zero-field splitting parameter are derived. A complete treatment for molecules of lower symmetry has not been given, but it is shown that the results obtained on a glassy solution of naphthalene are in agreement with those obtained by Hutchison and Mangum with single crystals.

1,000. THE CRYSTAL SPECTRA OF VERY WEAK TRANSITIONS. I. MEASUREMENTS OF THE NAPHTHALENE 3200 Å SYSTEM AT 4°K

Craig, D. P., Lyons, L. E., Walsh, J. R.
Molecular Physics, v. 4, no. 2, pp. 97–112, March 1961

The weak absorption system of crystalline naphthalene at 3200 Å was measured at 4°K in polarized light. Previous work at 20°K is supplemented by a number of newly recorded absorption lines, and by re-measurement of the frequencies of all lines at the lower temperature. The spectrum is compared with vapor spectrum and corresponding bands are identified, so far as possible. Exciton resonance effects are analyzed and discussed. The analysis discloses that the important b_{3g} vibrations of upper state frequencies 438 and 911 cm^{-1} are both reduced by 5% in the crystal, and smaller changes are identified in other vibrations. Comparison with the vapor spectrum shows that vibrationally induced bands, even when relatively strong, are little influenced by intermolecular forces, whereas very weak pure electronic bands give evidence of much greater effects. (For Part II, see Entry #607.) (*PA*, 1961, #14,592)

1,001. THE EFFECT OF DEUTERIUM AND CHLORINE SUBSTITUTION ON TRIPLET → SINGLET TRANSITION PROBABILITIES IN NAPHTHALENE

de Groot, M. S., van der Waals, J. H.
Molecular Physics, v. 4, no. 2, pp. 189–190, March 1961

Measurements are reported for the effect of substitution in aromatic molecules on the radiative transition probability from the triplet phosphorescence state (T) to the ground (S_0) state. This is done by irradiating a glassy solution of the phosphorescent substance, at 77°K, in a microwave cavity. The relative concentration of molecules in their triplet state is determined from the (integrated) intensity of the magnetic resonance signal. After the exciting light has been switched off, the corresponding phosphorescence intensity and decay time are measured by means of a photomultiplier and a recording instrument. Some preliminary results on naphthalene ($C_{10}H_8$), deuteronaphthalene ($C_{10}D_8$), and β-chloronaphthalene ($C_{10}H_7Cl$) are tabulated. Further experiments with greater accuracy are planned.

1,002. RETARDATION OF SINGLET AND TRIPLET EXCITATION MIGRATION IN ORGANIC CRYSTALS BY ISOTOPIC DILUTION

El-Sayed, M. A., Wauk, M. T., Robinson, G. W.
Molecular Physics, v. 5, no. 2, pp. 205–208, March 1962

Measurements with a 2-m grating spectrograph on a $C_{10}D_8$ crystal containing 0.5% $C_{10}H_8$ between 4.2 and 77°K are reported. Above 20°K the $C_{10}H_8$ fluorescence vanishes and is replaced by that of a 100% $C_{10}D_8$ crystal. At 4.2°K, line-like phosphorescence with a lifetime of 2.6 sec comes from the $C_{10}H_8$ sites. In the impure section from zone-refining a phosphorescence having a lifetime of $\gg 2.6$ sec occurs from impurities only at both 4.2 and 77°K. Other data from both pure and impure sections are presented, and eight conclusions drawn. It is suggested that in dilute crystals impurity singlet and triplet states are populated by long-range tunneling of the excitation. At 4.2°K the tunneling of triplet excitation from $C_{10}H_8$ centers to impurity centers occurs in a time short compared with 2.6 sec. The time for tunneling of the singlet excitation to impurity centers is long compared with the fluorescence lifetime of 10^{-6} sec. The relatively lower values of the ratio of the quantum yields of phosphorescence to fluorescence may be due to quenching at physical defects during long-range migration.

1,003. ON THE FLUORESCENCE SPECTRUM AND DECAY TIME OF NAPHTHALENE

Berlman, I. B., Weinreb, A.
Molecular Physics, v. 5, no. 4, pp. 313–319, July 1962

The effect of temperature, solvent, concentration of solute, and quenching by oxygen on the decay time and fluorescence spectrum of naphthalene was investigated. At high solute concentrations (>0.1 *M*) an anomaly in the emission spectrum is interpreted as being due to transient dimers, whereas at lower solute concentrations (<0.1 *M*) no evidence was found to support the assumption of transient dimers. The decay time of naphthalene in paraffin oil when excited by a pulsed beam of electrons is unaccountably longer than that of naphthalene in a less viscous medium. (*PA*, 1963, #138)

1,004. THE CRYSTAL SPECTRUM OF NAPHTHALENE IN THE REGION 3200 Å TO 2200 Å

Bree, A., Thirunamachandran, T.
***Molecular Physics*, v. 5, no. 4, pp. 397–405, July 1962**

The absolute intensity of absorption in the naphthalene crystal spectrum was measured at room temperature. Measurements on the intense system at 2200 Å and on the system of medium intensity at 2850 Å were recorded for the first time along both the *a* and *b* crystal axes and indicate that the transitions are polarized along the long and short molecular axis, respectively. The assignment of the weak system at 3200 Å as arising from a long-axis transition is confirmed. (*PA*, 1963, #934)

1,005. A SIMULTANEOUS ELECTRONIC TRANSITION OF THE OXYGEN-NAPHTHALENE COMPLEX

Dijkgraaf, C., Sitters, R., Hoijtink, G. J.
***Molecular Physics*, v. 5, no. 6, pp. 643–644, November 1962**

From the experimental value of the $^3\Sigma \rightarrow {}^1\Delta$ transition energy previously obtained, it is reasonable to expect a second absorption 7940 cm^{-1} above the 0–0 band of the induced singlet–triplet absorption. For most molecules the singlet–triplet separation is too small to make this absorption observable. The naphthalene molecule, however, is known for its large singlet–triplet separation. From the spectrum for naphthalene presented in the article, a second absorption is observed with a maximum at 29,000 cm^{-1} which is 8000 cm^{-1} higher than the 0–0 band of the singlet–triplet transition. This absorption has not been observed in the spectrum of naphthalene induced by heavy atom molecules, so that the possibility of a second induced singlet–triplet transition may be disregarded. The intensity of the 29,000 cm^{-1} band did not alter after rigorous purification of the naphthalene. The optical density of this maximum was found to be proportional to the concentration of the naphthalene and to be linear in the pressure of the oxygen.

1,006. EFFECT OF SYMMETRY OF VISIBLE-BAND INTENSITIES OF CUPRIC CHELATES

Belford, R. L., Yeranos, W. A.
***Molecular Physics*, v. 6, no. 2, pp. 121–138, March 1963**

Using the probable symmetry of several cupric chelates dissolved in CHCl$_3$ or C$_5$H$_5$N, some rational trends in the electric dipole intensity of the copper *d–d* absorption bands are inferred. It is postulated that the centric molecules show only weak ($\epsilon < 50$) vibrationally induced transitions, but that the acentric molecules should have higher transition moments. The intensity in each case should increase when the compound is monopyridinated. Spectra of solutions of two series of chelates chosen for their symmetry variations have been measured; the spectra are in accord with the predictions. Judiciously used, intensity of visible absorption bands of a new cupric species can provide useful evidence about its geometry; more frequent use of this evidence is recommended.

1,007. THE VARIATION OF THE FLUORESCENCE OF ORGANIC SOLUTIONS AFTER IRRADIATION WITH ULTRAVIOLET LIGHT AND β-RADIATION

Herforth, L., Hilbig, H.
***Monatsberichte der Deutschen Akademie der Wissenschaften zu Berlin*, v. 2, pp. 271–277, 1960**

The substances anthracene, *p*-terphenyl, tetraphenylbutadiene, 1,4-diphenylbutadiene, stilbene, and 1,4-diphenylbutene dissolved in C_6H_6 and PhCl were examined. Irradiation with 0.7 to 4.2 × 10^{-4} rad of β-rays caused a 10% decrease in fluorescence when the substances were dissolved in C_6H_6. Only 0.2 to 0.8 × 10^{-4} rad were required for a 10% decrement in PhCl. The last three compounds showed a 10% decrease in fluorescence when ultraviolet radiation was applied, which was only 10^{-3} as much as that required to decrease the fluorescence of anthracene by 10%.

1,008. THE TEMPERATURE DEPENDENCE OF ENERGY TRANSFER IN NAPHTHALENE AND ANTHRACENE CRYSTALS [ABSTRACT]

Wolf, H. C.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 13–16
National Research Council, Ottawa, Canada, 1962

It has previously been shown that the transfer of electronic excitation energy in mixed crystals from the host crystal to the guest molecules, as observed by sensitized fluorescence, is partially quenched at low temperatures. The temperature dependence of fluorescence spectra from naphthalene, anthracene, and other crystals containing different admixtures is investigated here in order to better understand the mechanism of this energy transfer process.

The temperature dependence of energy transfer is concluded to be mainly the result of a competition between different traps.

The present observations on energy transfer and temperature dependence suggest a diffusion process of excitons as a mechanism responsible for the energy transfer. No influence of temperature or of lattice defects other than the traps mentioned above was noticed on the lifetime or free path of the excitons.

1,009. TRANSFER OF EXCITATION ENERGY IN NAPHTHALENE-TETRACENE SOLID SOLUTIONS [ABSTRACT]

Reed, C. W., Lipsett, F. R.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 17–19
National Research Council, Ottawa, Canada, 1962

The system of crystalline naphthalene with added tetracene has been studied with the aim of elucidating some of the processes involved when excitation energy transfer takes place from naphthalene to tetracene. Previous work on the same system by Lipsett and Dekker was limited to the establishment of an exciton transfer mechanism rather than the photon cascade process, and its concentration dependence was shown.

The present work was carried out on single and polycrystalline samples of millimeter thicknesses and thicknesses of 0.1 to 10 μ (grown between quartz discs). The efficiency of excitation energy transfer from naphthalene to tetracene has been measured by studying the polarized fluorescences of naphthalene and tetracene as a function of wavelength of the exciting light, temperature, concentration of tetracene, and also concentration of the impurity β-methyl naphthalene (which is normally present in naphthalene and contributes strongly to the so-called intrinsic fluorescence of naphthalene). For a given concentration of tetracene, it was found that the energy transfer decreased steadily with decrease of crystal thickness within the range of 0.1 to 10 μ; this is attributed to reduction of the mean distance of the exciton track and hence the probability of an exciton being trapped by the impurity. Excitation spectra measurements showed that tetracene was substitutionally included in the naphthalene lattice and that no regions of crystalline tetracene existed for mole concentrations below 5×10^{-4}.

No change in phase occurred as the systems were cooled to 4.2°K or upon warming to room temperature. The tetracene fluorescence showed pronounced splitting as the temperature was lowered to 4.2°K, and the polarization of these bands showed that the tetracene molecules occupy regular positions in the monoclinic naphthalene lattice. In measuring the variation of energy transfer with temperature, spectra were recorded as the specimens warmed from liquid helium temperature, and the total (integrated) fluorescence intensity and the intensity of various bands were measured from traces made on a Bristol recorder. The temperature dependence of the fluorescence from naphthalene alone, and of tetracene (in naphthalene) when the tetracene was excited directly, was also measured.

The total fluorescence from naphthalene alone showed an increase in intensity as the temperature was lowered from room temperature to 60–80°K, a steady decrease in intensity to approximately 7°K, and finally a sharp increase in intensity in the range 7–4.2°K. Measurements of energy transfer showed that samples of the same concentration prepared by different methods sometimes behaved slightly differently, though particular specimens showed reproducible characteristics.

In the temperature range 4.2 to 35°K, there were no discontinuities in the total fluorescence from naphthalene or tetracene. Variation of the concentration was shown to cause small variations in the temperature dependence of the transfer process, but it was not possible to attribute the quenching to a decrease of the mean distance of the exciton track with lowering of temperature. Further discussion and interpretation are given.

1,010. THE TEMPERATURE DEPENDENCE OF THE LUMINESCENCE FOR ANTHRACENE HOST CRYSTALS [ABSTRACT]

Lyons, L. E.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 20–24
National Research Council, Ottawa, Canada, 1962

The position of the free exciton (*b*) origin near 25,000 cm^{-1} in an anthracene crystal was not settled in 1960, nor was the magnitude of the factor group splitting between the *b* and *ac* origins. The *ac* origin has been placed by many workers at 25,486 cm^{-1}, but splittings of various magnitudes from 0 to 220 cm^{-1} had been reported. Then both Brodin and Lacey measured splittings up to 230 cm^{-1}. This was attributed to molecular octupole interactions, as was later shown to be reasonable. The free exciton *b* origin was placed at 25,150 cm^{-1}, using a splitting extrapolated to zero crystal thickness. This then marks the origin also of luminescence from the free exciton level ($K = 0$).

The luminescent (*b*) band of greatest energy at 4°K differs in position according to the sample. In anthracene (commercial grade) subjected to 120 passes in zone refining, a value of 25,050 cm^{-1} has been observed here, the greatest reported so far, although Wolf's value of 25,020 is very close.

The existence of further luminescence origins below 25,050 cm^{-1} is generally accepted. Most anthracene luminescence at 4°K which has been reported originates, in fact, at levels of energy less than 25,050.

In the region 24,800–25,030 cm^{-1}, crystals 10 μ thick showed no absorption in a repeatedly zone-refined sample. Bands are made to appear at 24,926 and 25,010 cm^{-1} by subliming twice in air; by subliming with a small amount of anthraquinone in the absence of air, bands appeared at 24,804 and 24,916 cm^{-1}. Less-pure anthracene showed bands at 24,906, 24,926, and 25,029 cm^{-1}.

A study was made of the temperature dependence of luminescence in anthracene and of energy transfer in anthracene containing tetracene. The determination of impurities in anthracene and the nature of luminescence centers, some of which are associated with impurities, are considered.

1,011. ABSORPTION AND FLUORESCENCE SPECTRA OF SINGLE ANTHRACENE-PHENANTHRENE CRYSTALS [ABSTRACT]

Ferguson, J.
In "Program and Abstracts: Organic Crystal Symposium October 10–12, 1962," p. 25
National Research Council, Ottawa, Canada, 1962

Measurements of the spectra of single crystals with polarized light reveal interesting information about the energy levels of the anthracene. With flakes grown by sublimation there is a continuous shift of the *a*-polarized absorption spectrum to low energy as the mole ratio of anthracene is increased, signifying a solid solution of the two components throughout the whole range of composition. Data are presented on a graph. The polarization ratio (*b/a*) of the absorption band at low mole ratio is very close to the oriented gas value (2.7:1). No quantitative data have been obtained for the fluorescence polarization ratio. The absorption and fluorescence bands are sharp at low mole ratios but broaden (especially the fluorescence bands) and shift as the mole ratio of anthracene is increased. The fluorescence spectrum is considerably broader than the absorption spectrum at mole ratios of about 0.1, but the polarization ratio is not constant (as is observed with pure anthracene crystals). At mole ratios of about 0.5, splitting of the absorption bands and pronounced broadening of the *b* component are observed. At the same time the fluorescence spectrum moves to lower energy. Further increase of the anthracene mole ratio results in increased broadening, splitting, and shift of the spectrum until that of pure anthracene is reached.

1,012. RAPID TRIPLET EXCITATION MIGRATION IN ORGANIC CRYSTALS [ABSTRACT]

Nieman, G. C., Robinson, G. W.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 26–28
National Research Council, Ottawa, Canada, 1962

Impurity quenching of the lowest triplet state of crystalline naphthalene has been found to be much more effective than quenching of the lowest singlet. Using the reasonable assumption that migration of excitation is responsible for quenching, this result implied that in π-electron organic crystals the degree of triplet excitation migration is much greater than that for the singlet. The long lifetime of the triplet state accounts for part of this effect. It is the purpose of this communication to point out that, in addition, the interaction matrix element associated with the triplet may very well be of the same order as that for the lowest singlet.

The use of three-component isotopic mixed crystals was thought to be a help in putting the study on a more quantitative basis, and a crystal composed of 99.2% C_6D_6, 0.4% C_6H_5D, and 0.4% C_6H_6 was used. The isotopic traps C_6H_5D and C_6H_6 have excitation energies 170 and 200 cm^{-1}, respectively, below that of C_6D_6. A "control" crystal containing 99.2% C_6D_6 plus 0.8% C_6H_5D was also studied. (The C_6H_5D itself contained ~1% C_6H_6 isotopic impurity.) Radiation is initially absorbed by the bulk crystal. Excitation energy is then transferred rapidly to both traps. At sufficiently low temperatures, emission occurs from the traps only. Singlet states of the traps can (1) fluoresce, (2) transfer excitation intermolecularly to singlet states of other traps, or (3) transfer excitation intramolecularly to triplet states. Triplet states of the traps formed by mechanism 3 above or from triplet states of the bulk crystal can phosphoresce, or can transfer excitation intermolecularly to other traps. Quenching back to the ground state may occur during any of the above steps. The point of this kind of experiment is, of course, to detect the presence of long range, trap-to-trap excitation migration as in mechanism 2 above. If there is no trap-to-trap transfer the ratio of emission intensity from the two kinds of traps should be roughly equal to their concentration ratio. Trap-to-trap transfer distorts this ratio in favor of the deepest trap. Results of experiment are presented and interpreted.

1,013. A STUDY OF THE DELOCALIZATION OF TRIPLET EXCITATION ENERGY IN MOLECULAR CRYSTALS AND MIXED CRYSTALS OF ORGANIC MOLECULES [ABSTRACT]

Hochstrasser, R. M.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 29–32
National Research Council, Ottawa, Canada, 1962

This paper describes an experimental investigation of the behavior of excited triplet states of molecular crystals and the influence of impurity molecules on the phosphorescence of the crystal, and of the nonradiative processes occurring after excitation.

To account for the total number of quanta absorbed by a crystal, it is necessary to study the course of excitation through other states of the lattice, notably the lower lying triplet states. For crystals containing impurities, the lowest triplet states of the impurity must also be included. To assess the importance of singlet–triplet and triplet–triplet nonradiative energy transfer in crystals, six distinct arrangements of crystal and impurity states can be foreseen: (1) $S_g > T_g > S_h > T_h$, e.g., for a saturated hydrocarbon in an aromatic crystal lattice; (2) $S_h > T_h > S_g > T_g$, e.g., for tetracene in naphthalene; (3) $S_g > S_h > T_g > T_h$, e.g., for benzene in naphthalene; (4) $S_g > S_h > T_h > T_g$, e.g., for naphthalene in triphenylene; (5) $S_h > S_g > T_g > T_h$, e.g., for triphenylene in naphthalene; and (6) $S_h > S_g > T_h > T_g$, e.g., for anthracene in naphthalene. The results of experiments on certain systems belonging to the above categories are described.

1,014. THE ELECTRONIC SPECTRUM OF 2,2'-PARACYCLOPHANE [ABSTRACT]

Ron, A., Schnepp, O.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," p. 38
National Research Council, Ottawa, Canada, 1962

The polarized absorption and fluorescence spectra of single crystals of 2,2′-paracyclophane at 20°K were recorded in the region 3300–3100 A. The spectra consist of narrow lines, 87 of which could be measured in absorption and nine in emission.

1,015. ELECTROLUMINESCENCE IN ORGANIC CRYSTALS [ABSTRACT]

Pope, M., Kallmann, H. P., Magnante, P.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 106–108
National Research Council, Ottawa, Canada, 1962

Electroluminescence has been observed in single-crystal anthracene, and in single-crystal anthracene with about 10^{-1} mole % tetracene as an impurity. The luminescence in the case of anthracene was the usual anthracene fluorescence; in the case of anthracene with tetracene impurity, it was that of tetracene.

The crystals were 10 to 20 μ thick and two electrode configurations were used, with their results differing markedly. In one, the electrodes were symmetrically disposed on both sides of the crystal and consisted of 0.1 *N* aqueous solutions of NaCl; the area of the electrode was 0.1 cm^2 (total crystal area was 0.5 cm^2). In the second configuration, silver paste electrodes were used, the area of one electrode being made very small compared with the opposite electrode, so as to provide a highly inhomogeneous electric field.

Using electrolyte electrodes, the luminescence appeared only when the voltage was applied as a square wave, and only during the time when the voltage was changing polarity. The intensity of emitted light was a function of the peak-to-peak voltage only. Thus, using biased square waves, the light intensity was the same for rising and falling voltages regardless of whether the voltage remained always positive or always negative. A sharp surge of current through the crystal occurred simultaneously with a given light emission. This surge of current was not the usual transient effect due to the crystal's capacitance, because of its extremely short duration. For a given voltage swing, more light was emitted if the period of changing voltage was decreased. The intensity of the light emitted per cycle was greater at lower frequencies; beyond 100 cps, with the photomultiplier equipment on hand, no luminescence could be observed. Two of the prerequisites for maximum electroluminescence per cycle in this electrode system seem to be a rapidly changing voltage and a relatively long duration for the applied field.

The applied field strength was about 10^6 v/cm. The intensity of luminescence increased approximately with the square of the applied voltage from 5×10^5 to 10^6 v/cm. This voltage dependence is similar to that reported by Bernanose, and by Namba and co-workers, who studied the electroluminescence of dyes dispersed in cellophane. The relative light intensity was measured with a photomultiplier and the reproducibility of results was about 25%.

1,016. ELECTROLUMINESCENCE OF ANTHRACENE [ABSTRACT]

Gurnee, E. F.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 109–116
National Research Council, Ottawa, Canada, 1962

It has been found that certain condensed ring systems exhibit electroluminescence in the presence of a small amount of a finely divided electronic conductor. For example, anthracene in the presence of about 1% of carbon black gives blue electroluminescence that is characteristic of anthracene emission bands. If a small amount of tetracene, approximately 0.1%, is added to this system, a green electroluminescence typical of tetracene emission bands is obtained.

In this paper are described some of the experimental results obtained in the study of the mechanism of this type of electroluminescence. Sections are presented on (1) preparation of phosphors and cells, (2) brightness as a function of voltage, (3) wave forms of light output, (4) electroluminescence emission spectra, and (5) explanation of the mechanism involved.

1,017. MAGNETIC PROPERTIES OF CRYSTALLINE ORGANIC RADICALS BY MAGNETIC RESONANCE STUDIES [ABSTRACT]

Anderson, M. E., Pake, G. E.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 156–157
National Research Council, Ottawa, Canada, 1962

On lowering *kT* to values comparable to the exchange interaction, a lattice which is exchange-linked in three dimensions is expected to exhibit a cooperative transition to either the ferromagnetic or the antiferromagnetic state, depending upon the sign of the coupling. It was thus anticipated that crystals of the organic radicals might show such transitions at temperatures within an order of magnitude of 10°K. The measured electron spin susceptibilities in these crystals, however, do not (except perhaps for Wurster's blue perchlorate) exhibit the abrupt transitions characteristic of such cooperative phenomena. Structural explanations from several different studies are reported. Magnetic resonance has been used in several ways to investigate such systems. The electron resonance intensity is proportional to the susceptibility of the crystal.

Another useful technique is the nuclear magnetic resonance of protons which have hyperfine interaction with the unpaired electrons of such molecules. The exchange interaction averages away most of the hyperfine structure, leaving a Knight shift of the proton resonance. The shift is proportional to the electron magnetization. A striking example presented here is that of 1,3-bisdiphenylene-2-phenyl-allyl (BDPA), for which the electron susceptibility has been studied by both electron resonance intensity and nuclear resonance shift. For this particular substance, the existence of singlet and triplet pairs may be indicated by the form of the susceptibility vs. temperature.

There remain unexplained experimental facts. Wurster's blue perchlorate, although its crystal structure is known to exhibit linear chains, has at 180°K a sharp break in the susceptibility that is reminescent of a classic antiferromagnetic transition in a three-dimensional exchange-coupled net. The ESR line width in BDPA shows an abrupt maximum at 1.9°K; W. O. Hamilton has found that the crystal's specific heat has an anomaly at that temperature. It is possible that weaker exchange interactions complete an exchange-coupled net of higher dimensionality than one, leading to a cooperative transition at 1.9°K.

1,018. EPR STUDIES OF SPIN CORRELATION IN SOME ION RADICAL SALTS [ABSTRACT]

Chesnut, D. B.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 158–159
National Research Council, Ottawa, Canada, 1962

In previous studies a number of the electrically conducting ion radical salts based on the strong electron acceptor tetracyanoquinodimethan (TCNQ) has been shown to exhibit a paramagnetism characteristic of entities residing in thermally accessible triplet states. The triplet state characterization has been made from the observation and analysis of the anisotropic fine structure splitting coupled with observed temperature dependences of the magnetic susceptibility and EPR signal intensities. Values of *J*—the energy separation of the triplet state above the singlet ground state—measured below room temperature from integrated signal intensities range from several hundredths to several tenths of an electron volt.

Single crystal investigations of the $(\Phi_3PCH_3)^+(TCNQ)(TCNQ^-)$, $(\Phi_3AsCH_3)^+(TCNQ)(TCNQ^-)$, and $(Cs^+)_2(TCNQ)(TCNQ^-)_2$ salts show that the observed paramagnetic resonance spectra may be characterized by an orthorhombic spin Hamiltonian

$$\mathcal{H} = \beta H \cdot g \cdot S + DS_z^2 + E\,(S_x^2 - S_y^2),$$

where the absolute magnitudes of D and E are 0.00616 and 0.00097 cm^{-1}, respectively, for the phosphonium and arsonium salts, and 0.00937 and 0.00152 cm^{-1} for the cesium salt. The g-factors and g-factor anisotropies are typical of those found in organic systems. Interpreted in terms of electronic dipole-dipole interactions, the relatively small magnitude of the zero-field splitting in these materials suggests a TCNQ supermolecular structure in the solid in which the triplet spin density is distributed over several TCNQ molecules, these doubly-charged species possessing a singlet ground state and a thermally accessible triplet state. Preliminary structural data from X-ray studies indicate that face-to-face packing of the TCNQ molecules is prevalent in these salts. From these various considerations, it is suggested that perhaps a more appropriate representation of these salts may be, e.g., $(\Phi_3PCH_3)_2^{=}(TCNQ)_4^{=}$ and $(Cs^+)_2(TCNQ)_3^{=}$.

Exchange narrowing of the triplet fine structure is observed, the measured exchange frequencies varying exponentially as a function of temperature with characteristic exchange activation energies. Detailed studies of the effects of spin exchange on the spectra of a number of ion-radical salts have been carried out where exchange parameters have been derived from all three limiting approximations relating to line width and line separation of the exchange-modified Block equations. While in general the exchange frequency, ν, can be expressed as

$$\nu = \nu_0 e^{-\Delta E/kT}$$

different values of ν_0 and ΔE (for a given material) are obtained depending upon the limiting approximation employed. The presumed existence of triplet excitons offers an explanation of the exchange behavior.

1,019. PARAMAGNETISM OF TRIPLET STATE ORGANIC MOLECULES IN CRYSTALS [ABSTRACT]

Hutchison, C. A., Jr.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 160–162
National Research Council, Ottawa, Canada, 1962

The paramagnetic resonance absorption of phosphorescent organic molecules was first observed in single crystals of an optically suitable organic compound containing a small concentration of the phosphor. Five such crystal systems have been investigated in detail: (1) naphthalene in durene, (2) deuteronaphthalene in durene, (3) phenanthrene in biphenyl, (4) naphthalene in biphenyl, and (5) phenanthrene in fluorene.

Studies of the fine structures and hyperfine structures of the magnetic spectra of these systems have shown that (1) the phosphorescent species are in electronic triplet states; (2) the chemical identity of the phosphorescent species may be determined; (3) the triplet degeneracy is removed in the absence of the magnetic field, the splittings being of order 0.1 cm^{-1}; (4) the zero-field splittings are mainly of intramolecular origin arising from magnetic dipole–dipole interactions; (5) the phosphor molecules are well oriented in the host crystal and the precise orientation may be determined; and (6) the symmetry character of the electronic triplet states may be determined. The spin-Hamiltonian summarizing the fine structure studies is presented, and some numerical results tabulated. Magnetic resonance absorptions in such single crystal solutions at zero external magnetic field have been investigated and their polarizations with respect to molecular axes have been determined.

Paramagnetic resonance spectra of single crystals of biphenyl containing naphthalene and phenanthrene simultaneously, as oriented solutes, have been examined. Transfer of energy in this crystal from optically excited phenanthrene triplet state molecules to naphthalene molecules with creation of triplet states in the latter has been shown to occur.

Precise measurements of spin-Hamiltonian parameters for the naphthalene-phenanthrene-biphenyl crystal lead to the conclusion that (1) complex formation between naphthalene and phenanthrene, or (2) some type of molecular association or juxtaposition of the two solute species in the crystal structure. did not occur to an observable extent.

Stable ground state triplet molecules in organic single crystals have also been investigated, in cooperation with Professor Closs, by magnetic resonance methods. A crystal of benzophenone containing a small concentration of biphenyldiazo-methane is considered. and a model of the triplet state molecule is suggested.

1,020. ELECTRON PARAMAGNETIC RESONANCE STUDIES OF TRIPLET STATES AND ENERGY TRANSFER [ABSTRACT]

Smaller, B., Remko, J. R.
In "Program and Abstracts: Organic Crystal Symposium, October 10–12, 1962," pp. 163–138
National Research Council, Ottawa, Canada, 1962

The application of electron paramagnetic techniques to the study of the triplet state in organic phosphors originated with the work of Hutchison and Mangum on naphthalene diluted in a durene crystal. From the results quantitative measurements were made of the correlation effects in the dipole–dipole interaction of the two unpaired electrons comprising the $S = 1$ state. The correct triplet state wave function can then be deduced in terms of the possible excitation functions consistent with the determined parameters. The utility of the EPR technique was greatly enhanced by van der Waals and de Groot's discovery that the resonance due to the "forbidden transition" $\Delta M = \pm 2$, can be detected with sensitivity comparable to that of the allowed $\Delta M = \pm 1$ transition. In a glassy matrix, the $\Delta M = \pm 2$ transitions are considerably less sensitive to angular variation and the resultant line widths are greatly reduced so that detection sensitivity is comparable to that of free radicals. The resonant magnetic field is determined by the values of D and E pertinent to the triplet state wave function for the specific molecule and identifies the molecular species. Thus, triplet state concentrations of combinations of organic phosphors dissolved in a common glassy matrix, as well as possible interactions between the excited species, can be studied and identified unambiguously. The zero-field splittings for a series of aromatic, substituted aromatic, and heterocyclic compound triplet states are tabulated along with the determined line widths. Line widths are determined, in the main, by nuclear magnetic broadening. This is evidenced by substituting the deuterated species for the series benzene, naphthalene, diphenyl, phenanthrene and anthracene. The ratio of line widths of the light-to-heavy species was correspondingly 1.7, 2.7, 2.8, 3.1, 3.3. The theoretically expected ratio of totally magnetically broadened lines is 3.25. Lifetime measurements of the triplet states of the above deuterated series were 17, 23, 12, 15, and 0.15 sec. respectively. In all cases, except possibly the last, the values are apparently the radiative lifetime. The application of the EPR technique to the study of energy transfer between triplet states of organic molecules has been especially rewarding. Relative triplet concentration of both energy donor and acceptor has been determined for a great many pairs of phosphors, and energy transfer verified, the prime requirement being that the triplet level of the donor lie above that for the acceptor. In order to insure that the acceptor triplet occupancy is due to transfer, it is also advisable to choose a system where the donor singlet level is below that of the acceptor. A monochromatic light source is used, with wavelength adjusted so that the acceptor singlet level cannot be excited. The system studied most extensively was that of phenanthrene(donor)–naphthalene(acceptor), selected because it represented a pure hydrocarbon system where strong complexing effects were assumed not to exist. Analysis of the data reveals that the sum of the triplet state concentrations of both acceptor and donor is constant, independent of acceptor concentration, while the ratio of acceptor to donor triplet states is linearly dependent on the acceptor concentration.

The studies have been extended from the indicated one-step transfer to processes involving a two-step reaction. The requirements on triplet level of the intermediate is that its triplet level lie between that of the donor and acceptor, while for unambiguity of results its singlet level is chosen so that its first excited singlet (like that of the acceptor) is too high for direct absorption by the incident light. The results for the diphenylamine(donor)–indole(intermediate)–fluorene (acceptor) system are presented. Relative triplet concentrations of donor and acceptor are shown when no intermediate is present, and compared with that of all three triplet concentrations when the intermediate is added. Several models proposed in an attempt at a correct theoretical interpretation of the energy transfer phenomenon are explained and compared.

1,021. THE TESLA-COIL METHOD FOR PRODUCING FREE RADICALS FROM SOLIDS

Bamford, C. H., Jenkins, A. D., Ward, J. C.
***Nature*, v. 186, no. 4726, pp. 712–713, May 28, 1960**

A radical concentration of approximately 10^{-3} mole/l could be obtained by applying the discharge from a Tesla coil to finely ground crystals of organic compounds contained in partially evacuated ESR specimen tubes. Glycine, diketopiperazine, acrylamide, itaconic acid, and acrylonitrile were examined, and all gave strong radical spectra. Prolonged excitation by the Tesla coil was applied to methacrylic acid at approximately −195°C, thereby producing radicals which initially reside mainly on the surface. Warming the specimen to 0°C for 5 min caused the radical concentration to decay to the limit of detectability ($\sim 10^{-6}$ mole/l); decay of the surface radicals at various temperatures was investigated.

1,022. PYRENE DIMERS

Berlman, I. B.

***Nature*, v. 191, no. 4788, pp. 594–595, August 5, 1961**

Results are reported of studies of changes in the fluorescence lifetime and in the emission spectrum of pyrene in paraxylene and in cyclohexane for various concentrations of pyrene. Decay times were measured using apparatus which produced a pulsed beam of electrons of 75-kev energy to excite the fluorescence, and a 1P28 photomultiplier and associated equipment for detecting and graphically recording the shape of the emitted light pulse. Each component in the fluorescence emission was studied by interposing either a 9863 Corning filter or a Wratten 2 Series VI filter to pass the violet and blue components, respectively. This equipment can measure decay times conveniently over a range of 2–200 nsec. Longer components in the decay could be observed but not accurately determined. Although the results provide supporting evidence for the assumption of transient dimers as postulated by Förster and Kasper, they are not sufficiently conclusive to eliminate other interpretations.

1,023. EVIDENCE FOR THE PHOTO-ASSOCIATION OF AROMATIC HYDROCARBONS IN FLUID MEDIA

Stevens, B.

***Nature*, v. 192, no. 4804, pp. 725–727, November 25, 1961**

Although photo-association appears to be of general occurrence unless sterically hindered, the intermolecular binding forces will depend on the electronic properties of the molecules involved and may be of less general origin. Emission, delayed fluorescence, self-quenching, and sensitized delayed fluorescence are tabulated for benzene, naphthalene, anthracene, phenanthrene, fluorene, carbazole, naphthacene, pyrene, 3,4-benzpyrene, perylene, 1,12-benzperylene, coronene, anthanthrene, and 9,10-diphenylanthracene. The last compound does not show evidence of excimer formation.

1,024. FLUORESCENCE SPECTRUM OF ANISOLE VAPOR

Prakash, S.

***Nature*, v. 193, no. 4812, p. 268, January 20, 1962**

The fluorescence spectrum of anisole in the vapor state has been developed following the technique of Bass and Sponer.

The spectrum extends from 2700 to 3100 A, and consists of about 60 bands degraded toward the red.

The strong band at 36,386 cm^{-1}, which has appeared due to self-absorption, is taken as the 0–0 band. This is in good agreement with the value 36,389 cm^{-1} measured in ultraviolet absorption. The vibrations which are excited in the ground state have the frequencies 265, 450, 522, 611, 788, 1,000, 1,029, 1,178, 1,250 and 1,310 cm^{-1}, which agree well with Raman data. The symmetries to which the frequencies belong are mentioned.

Bands due to combinations of the above frequencies have been observed. In addition, the difference frequencies 30, 56 and 120 cm^{-1} resulting from v–v transition have also been recorded.

1,025. EXCIMER FLUORESCENCE OF AROMATIC HYDROCARBONS IN SOLUTION

Birks, J. B., Christophorou, L. G.

***Nature*, v. 194, no. 4827, pp. 442–444, May 5, 1962**

The appearance of a broad structureless emission band at long wavelengths in the fluorescence spectrum of certain aromatic hydrocarbons in concentrated solution is attributed to the formation of excited dimers (excimers). Data on the monomer and excimer spectra of ten compounds (1:2-benzanthracene and its 2′-, 3′-, 5-, 6-, 8-methyl and 2′,6-dimethyl derivatives, pyrene, 1:2-benzpyrene and 3:4-benzpyrene) which exhibit this behavior are tabulated. Perylene and anthanthrene form fluorescent dimers which are also stable in the ground state. (*PA*, 1962, #11,376)

1,026. OBSERVATION OF TRAPPED ELECTRONS IN POLYMETHACRYLIC ACID

Ormerod, M. G., Stoodley, L. G.

***Nature*, v. 195, no. 4838, pp. 262–263, July 21, 1962**

ESR work on polymethacrylic acid and its esters suggests that the unpaired spins observed at 77°K after irradiation at that temperature are trapped electrons. To test this idea the effect of electron acceptors was investigated, the additives used being pyromellitic dianhydride (PMDA) and tetracyanoethylene (TCNE). The same number of spins was produced in all systems by similar irradiations, but the shape of the ESR spectrum was different. The spectrum from the sample containing TCNE was identical to the spectrum of TCNE radical ions produced by chemical reduction. The changes produced on warming to room temperature were also investigated. (*PA*, 1963, #2684)

1,027. SPECTRA OF AMINE–CHLORANIL COMPLEXES

Slifkin, M. A.

***Nature*, v. 195, no. 4842, pp. 693–694, August 18, 1962**

The absorption spectra of some aliphatic amine–chloranil mixtures and solutions were measured. The observed shift in the chloranil absorption band is attributed to the formation of 1:1 charge-transfer complexes of the n–π type. (*PA*, 1963, #1894)

1,028. VISCOSITY DEPENDENCE OF UNIMOLECULAR CONVERSION FROM THE TRIPLET STATE

Porter, G., Stief, L. J.

***Nature*, v. 195, no. 4845, pp. 991–992, September 8, 1962**

The rate constants of first-order triplet decay of 9,10-dibromoanthracene were determined from +150 to −196°C in three solvents of different viscosity. Three regions of behavior occur: (1) a low-viscosity region where the rate constant, at a given temperature, is independent of viscosity;

(2) a high-viscosity region where the rate constant is again nearly independent of viscosity; and (3) an intermediate region where the rate decreases rapidly with increasing viscosity from (1) to (2). (3) appears in different temperature ranges for the three solvents and lies close to the melting point. It is concluded that there are two distinct modes of unimolecular triplet decay which predominate in regions (1) and (2). The only molecular parameter known to change drastically in region (3) is the relaxation time of Brownian rotations, suggesting that the rate constant in region (1) may correspond to a radiationless transition in which coupling of molecular rotation and electronic motion is important. (*PA*, 1963, #3811)

1,029. RESONANCE INTERACTIONS OF FLUORESCENT ORGANIC MOLECULES IN SOLUTION

Birks, J. B., Christophorou, L. G.

***Nature*, v. 196, no. 4849, pp. 33–35, October, 1962**

Four types of concentration-dependent behavior in solutions of fluorescent aromatic compounds are distinguished, depending on whether or not they exhibit dimer emission and/or absorption. Twenty-five compounds forming excimers are listed. Experimental evidence is given for the resonance interaction of two different molecular species to form excited "mixed dimers," which may be either fluorescent (e.g., pyrene and 1-methyl pyrene) or nonfluorescent (e.g., pyrene and 3:4-benzphenanthrene). The possibility of stable "mixed dimers" (e.g., anthracene and 2-methyl anthracene) is also considered. (*PA*, 1963, #7215)

1,030. SECONDARY PROCESSES IN CHEMILUMINESCENT SOLUTIONS

Vasilev, R. F.

***Nature*, v. 196, no. 4855, pp. 668–669, November 17, 1962**

Excitation energy transfer and quenching of excited states are known to be of importance in many phenomena. Evidence is presented in this communication that processes of this kind may occur in chemiluminescent solutions.

Activation of chemiluminescence was obtained by adding luminescent materials to the reactants. Anthracene, its alkyl-, phenyl-, halogen-derivatives, oxazoles, and pyrazolines have been used as activators. Chemiluminescence spectra were recorded and the intensity was studied as a function of activator concentrations in the oxidation of benzene solutions of cyclohexane and ethylbenzene.

Activated chemiluminescence spectra were found to be identical to the fluorescence spectra of activators. This indicates that the singlet state of the activator is the excited one.

The enhancing action of activators becomes stronger with increasing concentration. Their efficiency builds up with halogen substitution in spite of the fact that substitution-induced changes lead to decreasing fluorescence yield.

An experimental kinetic curve of chemiluminescence intensity in methylethylketone oxidation at 60°C is presented. Activation data are tabulated for chemiluminescence accompanying cyclohexane oxidation, with halogen-substituted anthracene activators.

1,031. LUMINESCENCE IN PLASTICS

Oster, G., Geacintov, N., Khan, A. U.

***Nature*, v. 196, no. 4859, pp. 1089–1090, December 15, 1962**

Many aromatic hydrocarbons (naphthacene, phenanthrene, chrysene, dibenz [*a*, *h*] anthracene, fluoranthene) dissolved in many plastics (polycarbonate, polystyrene, polymethylmethacrylate, polyvinyl acetate, cellulose acetate, ethyl cellulose, methyl cellulose) exhibit phosphorescence at room temperature, as do dyes dissolved in polyvinyl alcohols. Oxygen quenches the phosphorescence, and diffusion of oxygen into a plastic specimen can be observed by the movement of the phosphorescent boundary. Other effects observed in the plastic solutions at room temperature include (1) metastable luminescent intermediates produced photochemically from 2-methyl anthraquinone in cellulose acetate, (2) photo-dimers of pyrene in polycarbonate, and (3) benzophenone-sensitized phosphorescence of naphthalene in polymethylmethacrylate. (*PA*, 1963, #7213)

1,032. EFFECT OF NAPHTHALENE ON THE QUENCHING OF LIQUID SCINTILLATION SOLUTIONS

Dobbs, H. E.

***Nature*, v. 197, no. 4869, p. 788, February 23, 1963**

The effect of adding naphthalene to liquid scintillation systems containing tritium was investigated. It was found that the effect depends entirely on the chemical nature of the quenching agent. With some substances the quenching effect is almost entirely removed; with others it is enhanced. Specifically, it was found that the addition of naphthalene to liquid scintillator containing benzoic acid results in a small increase in counting efficiency at low concentrations of benzoic acid and a decrease in efficiency at high concentrations. The addition of naphthalene to a benzoate-quenched solution, on the other hand, results in a considerable increase in counting efficiency at all quencher concentrations. Reasons for these results are discussed. (*PA*, 1963, #11,801)

1,033. STIMULATED SINGLET–TRIPLET TRANSITIONS IN ORGANIC PHOSPHORS

Wilkinson, F., Smith, E. B.

***Nature*, v. 199, no. 4894, pp. 691–692, August 17, 1963**

The phosphors investigated were naphthalene and 1-bromonaphthalene. A 640-joule flash was used. To prevent production of triplet phosphor by singlet–singlet excitation followed by intersystem crossing, the mechanism usually responsible for triplet states observed in flash experiments, filter solutions were placed in an outer jacket surrounding the reaction vessel. Spectra of such filter solutions and of solutions of naphthalene and 1-bromonaphthalene in liquid paraffin are presented as graphs, and transients detected in flash photolysis experiments using degassed liquid paraffin solution within a pyrex vessel are tabulated for the two compounds. The observations are interpreted and compared with the calculations.

1,034. **DIE FESTKÖRPERPHOSPHORESZENZ DES TRIPHENYLENS (PHOSPHORESCENCE OF SOLID TRIPHENYLENE)**
Zander, M.
***Naturwissenschaften*, v. 49, no. 1, pp. 7–8, January 1962**

The triphenylene spectrum is markedly temperature dependent, with the displacement far higher than that in solid glycerol solution. The intensity distribution shows a great shift during solidification.

1,035. **VERZÖGERTE FLUORESZENZ BEI AROMATISCHEN KOHLENWASSERSTOFFEN (DELAYED FLUORESCENCE OF AROMATIC HYDROCARBONS)**
Zander, M.
***Naturwissenschaften*, v. 50, no. 8, pp. 327–328, April 1963**

Phosphorescence spectra were determined for solid solutions containing 1 wt. % of chrysene, tetraphene, 1,2,5,6-dibenzanthracene, or coronene in phenanthrene. The temperature range in which the delayed fluorescence spectrum of the solid solutions can be observed varies with the hydrocarbon.

1,036. **DAMPING OF PHOSPHORESCENCE OF CEMENTED PHOSPHORS ACTIVATED BY TEREPHTHALIC ACID**
Dvorovenko, V. K.
***Nauchnye Zapiski, Odesskii Gosudarstvennyi Pedagogicheskii Institut imeni K. D. Ushinskoyo, Kafedry Matematiki, Fiziki i Estestvoznaniya*, v. 22, no. 1, pp. 47–52, 1958**
(See also *Referativnyi Zhurnal, Khimiya*, 1961, #2B210)

Cemented phosphors activated by terephthalic acid exhibit two different stages of damping of phosphorescence, not the simple, continuous, exponential curve. It is hypothesized that there may be two types of centers responsible for the phosphorescence of organic luminophors.

1,037. **DAMPING OF ORGANIC LUMINOPHORS**
Dvorovenko, V. K.
***Nauchnye Zapiski, Odesskii Gosudarstvennyi Pedagogicheskii Institut imeni K. D. Ushinskogo, Kafedry Matematiki, Fiziki i Estestvoznaniya*, v. 24, no. 1, pp. 47–40, 1959**
(See also *Referativnyi Zhurnal, Fizika*, 1961, #8V370)

As a result of the study of phosphorescence damping of cemented and organic oxide luminophors, damping curves are given for terephthalic acid. These closely approximate a hyperbolic function of the form $I = I_0\beta_\gamma/(t + \beta)_\gamma$ at $\beta = 1.5$ (γ and β for the same activator depend on the treatment).

1,038. **PHOTOLUMINESCENCE OF MIXED ORGANIC CRYSTALS**
Kuche[illegible]v, I. Ya.
***Naukovi Zapiski, Kiivs'kii Derzhavnii Universitet imeni T. G. Shevchenka*, v. 18, no. 3, pp. 51–62, 1959**

Mixed crystals of naphthalene with anthracene and anthracene with naphthacene were investigated for effects of crystal thickness, concentration of the optically inactive admixture, absorption coefficient of excited light, and the temperature on the energy transfer of electron excitation. It was found that a decrease in thickness, addition of optically inactive admixture, increase of absorption coefficient of the excited light, and a decrease of temperature reduce the efficiency of energy transfer from the compound toward the mixture. The results are discussed as exciton transfer of the excitation energy. 22 references

1,039. **RESEARCH ON SOLID STATE RADIATION-INDUCED PHENOMENA**
Kallman, H.
June 1961
New York University, Washington Square College, N. Y.
Quarterly Progress Report 5 for February–April 1961,
DA 36-039-sc-85126
AD-260,388
(Also available through U.S. Dept. of Commerce, Office of Technical Services, Washington, D. C.)

The gamma-ray-induced fluorescence of methyl and methoxy substituted *p*-oligophenylenes is studied. The methyl substitution does not greatly change the fluorescence intensity, but the methoxy substitution greatly enhances the fluorescence in some cases. Introduction of CCl_4 as a quencher gives results which differ somewhat from the usual behavior found with other solutes. The variation of intensity of fluorescence with temperature was measured for a number of organic solutions.

1,040. **RESEARCH ON SOLID STATE RADIATION-INDUCED PHENOMENA**
Kallman, H.
August 1961
New York University, Washington Square College, N. Y.
Quarterly Progress Report 6 for May 1–July 31, 1961,
DA 36-039-sc-85126
AD-264,879
(Also available through U.S. Dept. of Commerce, Office of Technical Services, Washington, D. C.)

The fluorescence decay times in solution of four substituted *p*-oligophenylenes are reported. The times are found to be shorter than those of other efficient scintillator solutes. Mixed crystals were prepared by the Bridgman method. Several clear or almost clear crystals with less than 0.5 wt. % initial dosage of guest substances were obtained for each combination. Distributions of concentrations in the mixed crystals are not homogeneous but increase gradually from the bottom to the top. The middle parts have almost homogeneous concentration but their values are much less than average concentrations. Emission spectra were measured on anthracene-in-naphthalene crystals of various concentrations.

1,041. RESEARCH ON SOLID STATE RADIATION-INDUCED PHENOMENA

Kallman, H.
November 1961
New York University, Washington Square College, N. Y.
Quarterly Progress Report 7 for August 1–October 31, 1961, DA 36-039-sc-85126
AD-269,907
(Also available through U.S. Dept. of Commerce, Office of Technical Services, Washington, D. C.)

1,042. RESEARCH ON SOLID STATE RADIATION-INDUCED PHENOMENA

Kallman, H.
February 1962
New York University, Washington Square College, N. Y.
Quarterly Progress Report 8 for November 1961–January 1962, DA 36-039-sc-85126
AD-295,029
(Also available through U.S. Dept. of Commerce, Office of Technical Services, Washington, D. C.)

Quenching studies afford a convenient method for discriminating between the possible processes of nonradiative energy transfer. The similarities of the concentration dependence of energy transfer from solvent to solute to that of solvent quenching within the solvent system, and of the concentration dependence of energy transfer in liquids to that in rigid systems, show the importance of energy transport by migration in both liquid and rigid systems. Further support for migration is found in the reduction of quenching rate obtained upon dilution with a nontransferring liquid. The connection of energy transfer and quenching by the energy transport process is demonstrated by the use of *o*-terphenyl as a quencher in liquid systems. It is found that this compound acts as both a quencher and an energy transferring agent.

1,043. EFFECT OF IRRADIATION ON LIQUID SCINTILLATORS

Anderson, W. R., Berlman, I. B.
***Nucleonics*, v. 20, no. 7, pp. 62, 64, 66, 67, July 1962**

p-Xylene was irradiated to 2×10^7 rad and PPO added to both irradiated and unirradiated samples. Separate measurements were made of the decreased transparency of the solvent and of the quenching of the scintillator and excited solvent by radiation-produced molecules. Comparison of the results with the overall loss of scintillation efficiency shows these two processes are the main and probably the only ones involved. (*PA*, 1962, #19,570)

1,044. LOW-TEMPERATURE THERMOLUMINESCENCE OF THE γ-IRRADIATED AMINO ACIDS AND PROTEINS

Carter, J. G.
1960
Oak Ridge National Laboratory, Tenn.
ORNL-2970

Four proteins and 23 L-amino acid preparations were irradiated at 77°K by Co^{60} γ-irradiation. The light intensity and temperatures were then recorded simultaneously as the samples were heated at 12°C per min. Glow curve peaks and intensity in μa are given for the preparations. The crystalline system to which an amino acid belongs seems to play only a minor role in determining the nature of the glow curves. Small traces of impurities exerted a relatively strong influence on the thermoluminescence from some amino acids.

1,045. ENERGY TRANSFERS BETWEEN CRYSTALS AND ADSORBED DYES. I. DESENSITIZATION

Nelson, R. C.
***Optical Society of America, Journal of the*, v. 48, no. 1, pp. 1–3, January 1958**

The electron affinities of several desensitizing dyes have been measured and found to lie in the neighborhood of 3.5 ev, and it seems unlikely that the dye can compete with sensitivity specks for electrons at equilibrium. The dyes produced a desensitization of photoconductivity in cadmium sulfide films, indicating that they can serve as surface electron traps. A mechanism of desensitization is suggested according to which the photoelectrons are loosely bound by one or several dye molecules seriatim, in consequence of which their times of arrival at the sensitivity speck are spread out over a long enough period so that the factors which contribute to the instability of the latent image become effective, and the sensitivity is thereby reduced.

1,046. ENERGY TRANSFERS BETWEEN CRYSTALS AND ADSORBED DYES. II. EFFECT OF CONCENTRATION ON EFFICIENCY OF SENSITIZATION

Nelson, R. C.
***Optical Society of America, Journal of the*, v. 48, no. 12, pp. 948–952, December 1958**

The effect of density of sensitizer molecules (malachite green, pinacyanole, erythrosin, and 3,3′-diethylthiacarbocyanine) on a CdS surface has been studied. The process of energy transfer is considered, and the type of adsorption (singly, broadside, or as a close-packed aggregate) is given cognizance.

1,047. COMMENT ON MELANKHOLIN'S ARTICLE ON ABSORPTION SPECTRA OF THIAZINE DYES

Meyer-Arendt, J. R.
***Optical Society of America, Journal of the*, v. 51, no. 5, p. 583, May 1961**

(For original article, see Entry #1,049.) Larger crystals may produce different spectra from those of very small ones which require high microscopic magnification. Discrepancies occurring in the latter case are ordinarily attributed to poor resolution and other phenomena which frequently limit biological microspectrophotometric measurements.

Melankholin deserves credit for having shown that deviations of this kind are not necessarily due to technical limitations of the image-producing system nor to differences between the liquid and the crystalline state, but that they may be caused solely by the varying orientation of the tiny crystals themselves. It should not be overlooked, however, that essentially similar findings on hexamethylbenzene crystals have been reported before by Scheibe and co-workers.

1,048. POLARIZATION OF MOLECULAR LUMINESCENCE IN PLASTIC MEDIA BY THE METHOD OF PHOTOSELECTION

El-Sayed, M. A.
***Optical Society of America, Journal of the,* v. 53, no. 7, pp. 797–800, July 1963**

In the method of photoselection for measuring molecular polarization, it is not necessary that the molecule be embedded in a crystal of known structure, but merely rigidly fixed in a random arrangement. In this paper the possibility of using a plastic as the host solvent is examined. This would replace the previously used mixtures of organic solvents that form glasses at 77°K, and which, because of experimental conditions, might give rise to great depolarization effects. In methyl methacrylate polymer (lucite), the phosphorescence of phenanthrene, coronene, and pyrazine is found to be polarized at room and liquid-nitrogen temperatures. The measured degree of polarization in the plastic is found to be in good agreement with the expected value. The effect on the degree of polarization of temperature, concentration, thickness, and shape of the plastic sample is discussed. The importance is pointed out of using this method for further polarization investigations to better understand the structure and spectroscopic properties of complex luminescent guest molecules, as well as the internal structure and motions of different host polymers.

1,049 ABSORPTION SPECTRA OF CRYSTALS OF SOME THIAZINE AND OXAZINE DYES

Melankholin, N. M.
***Optika i Spektroskopiya,* v. 7, no. 4, pp. 498–504, October 1959**
(Translated from the Russian in *Optics and Spectroscopy,* v. 7, no. 4, pp. 314–317, October 1959)

Absorption spectra of crystals of three dyes were studied: thionine blue, toluidine blue, and capri blue. Characteristic absorption curves were obtained, corresponding to vibrations parallel to the different axes of the optical indicatrix of the crystals studied. Certain peculiarities were established which appear in the absorption spectra and were found earlier in other dyes. Anomalous dispersion of the axes of the indicatrix was discovered in crystals of capri blue. An attempt was made to explain the observed shift of the absorption bands with a change in the wave normal.

1,050. THE MECHANISM OF TRANSITIONS OF EXCITED ORGANIC MOLECULES INTO METASTABLE STATES

Mokeeva, G. A., Sveshnikov, B. Ya.
***Optika i Spektroskopiya,* v. 10, no. 1, pp. 86–90, January 1961**
(Translated from the Russian in *Optics and Spectroscopy,* v. 10, no. 1, pp. 41–43, January 1961)

A study is reported of the effect of temperature on the duration of fluorescence and phosphorescence and on the relative phosphorescence yield of boron–glycerin phosphors activated with fluorescein, glacial sugar phosphors activated with trypaflavine, acridine orange, and esculine, as well as boron phosphors activated with phthalimide. In the first three phosphors, increase of temperature raised the phosphorescence yield and reduced the duration of fluorescence. Both these effects were explained by the dependence of the probability of transitions of excited molecules into metastable states on the vibrational energy of the molecules. (*PA*, 1961, #14,613)

1,051. POLARIZATION OF PHOSPHORESCENCE IN ORGANOPHOSPHORS

Pilipovich, V. A.
***Optika i Spektroskopiya,* v. 10, no. 2, pp. 209–213, February 1961**
(Translated from the Russian in *Optics and Spectroscopy,* v. 10, no. 2, pp. 104–107, February 1961)

The anisotropy of the afterglow and total luminescence of organophosphors is studied. A variation in the degree of polarization of β-phosphorescence in the emission spectrum was found for all the compounds investigated. The results are discussed from the viewpoint of the hypothesis of the complex structure of a metastable state. (*PA*, 1961, #17,916).

1,052. EXCITATION ENERGY TRANSFER IN RIGID SOLUTIONS OF ORGANIC SUBSTANCES

Rozman, I. M.
***Optika i Spektroskopiya,* v. 10, no. 3, pp. 354–361, March 1961**
(Translated from the Russian in *Optics and Spectroscopy,* v. 10, no. 3, pp. 178–182, March 1961)

Measurement of the efficiency of the transfer of electronic excitation energy from *p*-terphenyl to 1,3,5-triphenyl-Δ^2-pyrazoline in polystyrene and of the fluorescence yield of *p*-terphenyl as a function of the concentration of the energy acceptor is reported. For an acceptor concentration $\gtrsim 0.01$ mole/l, transfer by means of resonance interaction of the molecules plays the principal role. It is proposed that the deviation from the Förster-Galanin theory is associated with the migration of energy via the solvent. (*SSA*, #11,05)

1,053. INFLUENCE OF SOLVENT VISCOSITY ON THE FLUORESCENCE SPECTRA OF CERTAIN ORGANIC COMPOUNDS

Cherkasov, A. S., Dragneva, G. I.
***Optika i Spektroskopiya*, v. 10, no. 4, pp. 466–472,**
April 1961
(Translated from the Russian in *Optics and Spectroscopy*,
v. 10, no. 4, pp. 238–241, April 1961)

A study was made of the influence of the change in solvent viscosity with change in temperature on the position and shape of fluorescence spectra of solutions of 2-acetylanthracene and 3-aminophthalimide. There were sharp differences between the temperature dependences of the positions of the maxima in the fluorescence spectra and those of the static dielectric constant of the solvent. As the temperature of solutions of 2-acetylanthracene in butyl alcohols was lowered, a spectrum appeared with fine structure (characteristic for temperatures of −183 and −196°C) against the background of a continuous spectrum (characteristic for high temperatures). The experimental facts obtained are interpreted on the basis of the concept that, in the systems studied, the influence of the solvent on the spectra is fundamentally determined by the interaction between excited molecules of the fluorescing substance and solvent molecules oriented in a definite way relative to them during the lifetime of the excited state. (*PA*, 1962, #56)

1,054. DAVYDOV SPLITTING AND POLARIZATION RATIO IN THE REGION OF THE FIRST ELECTRONIC TRANSITION OF ANTHRACENE CRYSTAL

Brodin, M. S., Marisova, S V.
***Optika i Spektroskopiya*, v. 10, no. 4, pp. 473–476,**
April 1961
(Translated from the Russian in *Optics and Spectroscopy*,
v. 10, no. 4, pp. 242–243, April 1961)

The measured values are given of Davydov splitting Δ_ν and of the polarization ratio K for three fundamental bands of the first electronic–vibrational transition of anthracene crystal at $T = 20°K$. It is pointed out that an inaccuracy of orientation of the light vector incident on the crystal along the b-crystal axis has a strong influence on these quantities, resulting in a decrease in their values. This explains the fact that almost all published values of Δ_ν and K are much smaller than those obtained in the present work, in which these errors are eliminated. (*PA*, 1962, #694)

1,055 EFFECT OF *p*-TOLUIDENE AND POTASSIUM IODIDE ON THE FLUORESCENCE AND PHOTO-OXIDATION OF 9,10-DI-*n*-PROPYLANTHRACENE

Vember, T. M., Cherkasov, A. S.
***Optika i Spektroskopiya*, v. 10, no. 4, pp. 544–546,**
April 1961
(Translated from the Russian in *Optics and Spectroscopy*,
v. 10, no. 4, pp. 282–284, April 1961)

A study was made of the kinetics of fluorescence quenching and photooxidation quenching using compounds which quench the photooxidation process much more than the fluorescence. The results are analyzed in terms of processes involving singlet- and triplet-state quenching. (*PA*, 1962, #721)

1,056. POLARIZATION OF THE LUMINESCENCE FROM MOLECULAR CRYSTALS UNDER β-RAY EXCITATION

Gribkov, V. I., Zhevandrov, N. D., Khan-Magometova, Sh. D.
***Optika i Spektroskopiya*, v. 10, no. 4, pp. 549–550,**
April 1961
(Translated from the Russian in *Optics and Spectroscopy*,
v. 10, no. 4, pp. 285–286, April 1961)

Measurements were made of the dependence of the degree of polarization on the wavelength of the luminescence for a stilbene crystal and an anthracene crystal, under excitation with (1) 313-mμ wavelength light and (2) β-radiation. Differences in the two modes of excitation occur near the absorption edge, and these are discussed in terms of the free exciton theory. (*PA*, 1961, #20,025)

1,057. A STUDY OF THE PHOTOLUMINESCENCE AND SCINTILLATION PROPERTIES OF SOME 1,3,4-OXADIAZOLE DERIVATIVES IN POLYSTYRENE

Nagornaya, L. L., Bezuglyi, V. D., Grekov, A. P.
***Optika i Spektroskopiya*, v. 10, no. 4, pp. 555–556,**
April 1961
(Translated from the Russian in *Optics and Spectroscopy*,
v. 10, no. 4, pp. 289–291, April 1961)

Data are recorded on the absorption and luminescence spectra, the relative fluorescence quantum yield, and the relative scintillation efficiency of polystyrene solutions of 13 derivatives of 1,3,4-oxadiazole. An FEU-29 photomultiplier (maximum sensitivity ~4000 A) was used, and two solutions with higher practical scintillation efficiencies than polystyrene–terphenyl–POPOP solutions are reported. (*PA*, 1962, #1160)

1,058. THE LUMINESCENCE SPECTRA AND SCINTILLATION PROPERTIES OF PARA-MONOHALOGEN SUBSTITUTED TRANS-STILBENE

Malkes, L. Ya., Nagornaya, L. L., Timchenko, A. I.
***Optika i Spektroskopiya*, v. 10, no. 4, pp. 557–558,**
April 1961
(Translated from the Russian in *Optics and Spectroscopy*,
v. 10, no. 4, pp. 291–292, April 1961)

The luminescence and absorption spectra, and the relative scintillation efficiencies in toluene solution, were measured for 4-fluoro-, 4-chloro, 4-bromo-, and 4-iodo-stilbene. The scintillation efficiencies are similar to that of a stilbene solution (which is only 10% of a p-terphenyl solution), except for the iodo compound, which is reduced. (*PA*, 1962, #722)

1,059. THE INFLUENCE OF TEMPERATURE AND VISCOSITY ON THE POLARIZATION OF FLUORESCENCE IN PHTHALIMIDES

Surzhevskii, A. M.
***Optika i Spektroskopiya*, v. 10, no. 5, pp. 621–626, May 1961**
(Translated from the Russian in *Optics and Spectroscopy*, v. 10, no. 5, pp. 326–329, May 1961)

The influence of temperature and solvent on the polarization of the fluorescence of a series of derivatives of phthalimide is investigated. It is shown that the formula of Levshin–Perrin is also valid for this class of compounds. Using this formula, the effective volumes of the molecules in different solvents and mixtures have been calculated and compared with the molecular volumes in the solid state. The data obtained show that the volume of the molecules in the solution strongly depends on the solvent. (*PA*, 1962, #57)

1,060. ABSORPTION SPECTRA OF CRYSTALS OF ORDINARY AND DEUTERATED BENZENES AT 20°K

Broude, V. L., Onoprienko, M. I.
***Optika i Spektroskopiya*, v. 10, no. 5, pp. 634–639, May 1961**
(Translated from the Russian in *Optics and Spectroscopy*, v. 10, no. 5, pp. 333–336, May 1961)

A study was made of the absorption spectra of mixed monocrystals of isotopically substituted benzenes (benzene-D_6, benzene-D_5, benzene-D_4, benzene-D_3, and benzene-H_6) in polarized light at 20°K. It is shown that the splitting of the pure electronic transition into two sharply polarized bands, which is inherent in the spectra of crystals of ordinary benzene and hexadeuteriobenzene, is also retained in the spectra of mixtures of variously deuterated molecules. The magnitude of the observed splitting is proportional to the intensity of the corresponding transition. It is shown that the peculiarities found in the spectra of the mixed crystals give evidence of the formation of impurity exciton states in them. The observed anomalies in the intensity of the impurity exciton absorption bands may be interpreted from the standpoint of the "Rashba" effect (which describes the redistribution of intensity in impurity absorption bands located near the exciton zone of the solvent crystal). (*PA*, 1962, #695)

1,061. THE NATURE OF THE FIRST INTRINSIC ABSORPTION BANDS IN CRYSTALLINE NAPHTHALENE

Sheka, E. F.
***Optika i Spektroskopiya*, v. 10, no. 5, pp. 684–686, May 1961**
(Translated from the Russian in *Optics and Spectroscopy*, v. 10, no. 5, pp. 360–362, May 1961)

The absorption spectra of a binary crystalline mixture of naphthalene and octodeuterated naphthalene were measured in order to determine if the A_1 and B_1 bands can be attributed to splitting of the same molecular term. It was concluded that the two bands are components of the 0–0 transition. (*PA*, 1962, #6566)

1,062. DURATION OF THE PHOTO- AND RADIOLUMINESCENCE OF ANTHRACENE AND NAPHTHALENE CRYSTALS

Galanin, M. D., Chizhikova, Z. A.
***Optika i Spektroskopiya*, v. 11, no. 2, pp. 271–273, August 1961**
(Translated from the Russian in *Optics and Spectroscopy*, v. 11, no. 2, pp. 143–144, August 1961)

The radioluminescence decay time, τ_r, and the photoluminescence decay time, τ_f, were re-measured for zone-refined single crystals of anthracene and naphthalene. The photoluminescence was excited by a spark produced between platinum electrodes by the discharge of a 10-$\mu\mu$ F condenser charged to 1 kv, while the radioluminescence was stimulated by Co^{60} γ-rays. τ_r was found to be equal to τ_f if the decay times were calculated from the later portions of the trailing edges of the pulses, which showed a truly exponential decay. τ_f was also measured with a fluorometer and the resultant value was about half that obtained with the spark excitation. It is suggested that this difference arises because the fluorometer result is more sensitive to the initial part of the decay curve. This portion is nonexponential because of the effects of secondary fluorescence. (*PA*, 1962, #6628)

1,063. SOME CONCENTRATION EFFECTS IN PLASTIC SCINTILLATORS

Kukushkin, L. S., Nagornaya, L. L.
***Optika i Spektroskopiya*, v. 11, no. 3, pp. 385–389, September 1961**
(Translated from the Russian in *Optics and Spectroscopy*, v. 11, no. 3, pp. 206–208, September 1961)

Qualitative calculations are presented which make it possible to describe concentration effects on a number of the optical characteristics of plastic scintillators. The behavior of the luminescence spectra of plastic scintillators based on polystyrene with different concentrations of luminescing additives is studied. It is shown that the experimental data are in good agreement with the point of view presented. (*PA*, 1962, #6638)

1,064. LUMINESCENCE OF *p*-TERPHENYL IN A MIXTURE OF TOLUENE AND CARBON TETRACHLORIDE

Kilin, S. F., Kovyrzina, K. A., Rozman, I. M.
***Optika i Spektroskopiya*, v. 11, no. 3, pp. 390–396, September 1961**
(Translated from the Russian in *Optics and Spectroscopy*, v. 11, no. 3, pp. 209–212, September 1961)

The dependence of the yield and duration of the photo- and high-energy luminescence of *p*-terphenyl in toluene was investigated as a function of the concentration of the quencher (carbon tetrachloride). The constants of quenching, as well as the efficiency of energy transfer, were determined for different methods of excitation. Comparison with the diffusion theory of quenching shows that the values of the constants for the quenching of toluene and for the energy transfer can be obtained only on the assumption of a large radius of the sphere of action ($R \geq 20$ Å). (*PA*, 1962, #7224)

1,065. LUMINESCENCE OF IONIC FORMS OF URANIN IN LIQUID AND SOLID SOLUTIONS

Adamov, V. S., Kantardzhyan, L. T.
***Optika i Spektroskopiya*, v. 11, no. 3, pp. 419–422, September 1961**
(Translated from the Russian in *Optics and Spectroscopy*, v. 11, no. 3, pp. 226–227, September 1961)

A study of the luminescence spectra of liquid solutions of uranin shows association between the relative preponderance of three bands in the visible region and the pH of the solutions. The bands are attributed to singly and doubly charged anions and the cation. From a similar study of uranin in hard sugar candies and borate beads as a function of the pH of the preparing solution, it is concluded that in the former any of the three ionic forms can give rise to luminescence, while in the latter the cation alone is responsible. (*PA*, 1962, #9284)

1,066. THE LUMINESCENCE OF SIMPLE DERIVATIVES OF BENZENE. I. THE AROMATIC AMINES

Ermolaev, V. L.
***Optika i Spektroskopiya*, v. 11, no. 4, pp. 492–497, October 1961**
(Translated from the Russian in *Optics and Spectroscopy*, v. 11, no. 4, pp. 266–269, October 1961)

The fluorescence and phosphorescence spectra of aniline, dimethylaniline, diethylaniline, diphenylamine, triphenylamine, indole, carbazole, 9,10-dihydroacridine, and fluorene were measured in solid solution at 77°K. The ratios of the quantum yields of fluorescence and phosphorescence and the phosphorescence decay times of the substances were determined under identical conditions. The influence of structural factors on the luminescent properties of the compounds studied is discussed. Arguments are examined for and against the interpretation of the long-wavelength absorption and fluorescence bands of the anilines as electron transition spectra. (*PA*, 1962, #6629)

1,067. PHOSPHORESCENCE OF ORGANIC MOLECULES WITH TWO METASTABLE LEVELS

Khalupovskii, M. D.
***Optika i Spektroskopiya*, v. 11, no. 5, pp. 617–621, November 1961**
(Translated from the Russian in *Optics and Spectroscopy*, v. 11, no. 5–6, pp. 332–335, November–December 1961)

Phosphorescence spectra of organic phosphors were investigated at various temperatures in different stages of decay. The experimental data are explained by postulating the possibility of two metastable levels in the organic molecule. (*PA*, 1962, #10,627)

1,068. INFLUENCE OF EXCITED LIGHT BIREFRINGENCE ON THE LUMINESCENCE POLARIZATION IN MOLECULAR CRYSTALS

Zhevandrov, N. D., Gribkov, V. I., Khan-Magometova, Sh. D.
***Optika i Spectroskopiya*, v. 11, no. 5, pp. 629–635, November 1961**
(Translated from the Russian in *Optics and Spectroscopy*, v. 11, no. 5–6, pp. 338–341, November–December 1961)

It is shown that in molecular crystals the polarization of luminescence does not depend on the polarization of the exciting light. This independence always exists, even when such complicating factors as birefringence, dichroism, and optical activity are eliminated or accounted for. This phenomenon can be explained by the migration of the excitation energy in the crystals.

1,069. OPTICAL INVESTIGATIONS OF CERTAIN 1,2-SUBSTITUTED-DIARYLS OF ETHYLENE IN POLYSTYRENE

Nagornaya, L. L., Malkes, L. Ya., Shubina, L. V.
***Optika i Spektroskopiya*, v. 12, no. 1, pp. 117–121, January 1962**
(Translated from the Russian in *Optics and Spectroscopy*, v. 12, no. 1, pp. 58–59, January 1962)

The literature contains virtually no data on the properties and applications of thermally stable luminescing materials derived from 1,2-substituted-diaryls of ethylene. However, previous studies indicate that it should be possible to find promising compounds within this class of materials.

The following materials were chosen for investigation: 1,2-diphenylethylene-PPE (m.p. 125°C); 1-phenyl-2-(4-biphenylyl)ethylene-PBE (m.p. 224°C); 1-phenyl-2-(β-naphthyl)ethylene-$P_\beta NE$ (m.p. 146°C); 1,2-di-(4-biphenylene)-ethylene-BBE (m.p. 295°C); 1-(4-biphenylyl)-2-(α-naphthyl)ethylene-$B_\alpha NE$ (m.p. 144°C); 1-(4-biphenylyl)-2-(β-naphthyl)ethylene-$B_\beta NE$ (m.p. 262°C); 1,2-di-(α-naphthyl)-ethylene-$D_\alpha NE$ (m.p. 161°C); 1,2-di-(β-naphthyl)ethylene-$D_\beta NE$ (m.p. 234°C), and 1-(α-naphthyl)-2-(β-naphthyl)-ethylene-${}_\alpha N_\beta NE$ (m.p. 191°C). All of the compounds except $P_\beta NE$ were synthesized by thermal dissociation of the corresponding azines. $P_\beta NE$ was obtained by the Grignard method from β-naphthaldehyde and benzyl chloride. The materials were purified by multiple recrystallization from various solvents (benzene, dichloroethane, dioxane, methanol, and petroleum ether), with subsequent purification on activated aluminum oxide. Fluorescence spectra and quantum yields were measured with a monochromator consisting of an SF-4 spectrophotometer with a special photoelectric attachment. The relative luminescence yield with respect to a standard plastic containing 1-phenyl-2-(4-biphenylyl)ethylene was determined by the total absorption method. Photoluminescence and scintillation characteristics of 1,2-diaryl derivatives of ethylene in polystyrene are tabulated, as are light yields of plastic scintillators. Luminescence spectra of 1,2-substituted-diaryls of ethylene in polystyrene are graphed.

1,070. QUENCHING RADIOLUMINESCENCE BY BROMIDES IN DIOXANE SOLUTIONS OF TERPHENYL

Gusynin, V. I., Talroze, V. L.
***Optika i Spektroskopiya*, v. 12, no. 1, pp. 136–137,**
January 1962
(Translated from the Russian in *Optics and Spectroscopy*,
v. 12, no. 1, p. 71, January 1962)

The experimental method and quenching properties of some alcohols were described earlier by the authors (Entry #692). The determined dependence of the luminescence quenching upon the concentration of the bromides indicates that the process takes places predominantly due to energy transfer from the molecules of the solvent to the bromide molecules. The quenching by bromides was found to be by an order of magnitude more effective than by alcohols. (*PA*, 1962, #14,750)

1,071. EXCITON LUMINESCENCE OF NAPHTHALENE-H_8–NAPHTHALENE-D_8 MIXED CRYSTALS

Sheka, E. F.
***Optika i Spektroskopiya*, v. 12, no. 1, pp. 137–140.**
January 1962
(Translated from the Russian in *Optics and Spectroscopy*,
v. 12, no. 1, p. 72, January 1962)

The low-temperature (20 and 77°K) luminescence of these crystals was studied. As a result of these investigations, it has been established that the low-temperature luminescence of mixed crystals of isotopic compounds is connected with transitions from the lowest excited states which appear as impurity-exciton states; its concentration dependence can be understood from the transition scheme shown.

1,072. THE EFFECT OF TEMPERATURE ON THE KINETICS OF THE SENSITIZED LUMINESCENCE OF SOME IMPURITIES IN NAPHTHALENE CRYSTALS

Kovalev, V. P.
***Optika i Spektroskopiya*, v. 12, no. 1, pp. 143–144,**
January 1962
(Translated from the Russian in *Optics and Spectroscopy*,
v. 12, no. 1, p. 76, January 1962)

Measurements are reported of the dependence of the average fluorescence time of the following impurities on sample temperature: anthranilic acid, diphenylhexatriene, and diphenylbutadiene. It is pointed out that a localized exciton in a given case does not differ from an excited naphthalene molecule located near an impurity molecule, and that it is natural to assume that the last stage of energy transfer is of a resonance nature.

1,073. SYMMETRY OF THE THIRD EXCITED STATE OF NAPHTHALENE

Derkacheva, L. D.
***Optika i Spektroskopiya*, v. 12, no. 2, pp. 329–330,**
February 1962
(Translated from the Russian in *Optics and Spectroscopy*,
v. 12, no. 2, pp. 178–179, February 1962)

The comparison of absorption spectra of naphthalene and eight of its dihydroxy derivatives showed that the third excited state of naphthalene possesses B_{1u} symmetry. The transition from the totally symmetric ground-state to the state of this symmetry must have longitudinal polarization in agreement with theoretical calculations. The dihydroxy derivatives can be split into two groups. In the first group 1,8-, 1,5-, 2,6-, and 2,7-dihydroxynaphthalenes had only one peak whereas 1,4-, 1,7-, 1,2-, and 2,3- derivatives had two maxima in the 190–260 mμ region. (*PA*, 1962, #29,855)

1,074. PHOTOCHROMISM AND ELECTRON PARAMAGNETIC RESONANCE OF α-(*o*, *p*-DINITROBENZYL)PYRIDINE

Kuindzhi, B. M., Igonin, L. A., Gribova, Z. P., Shabadash, A. N.
***Optika i Spekstroskopiya*, v. 12, no. 2, pp. 220–223,**
February 1962
(Translated from the Russian in *Optics and Spectroscopy*,
v. 12, no. 2, pp. 118–120, February 1962)

Electron paramagnetic resonance spectra have been obtained for the radicals appearing in α-(*o*,*p*-dinitrobenzyl)-pyridine under the action of ultraviolet radiation. It is shown that the reversible change in color and the appearance of paramagnetism in α-(*o*,*p*-dinitrobenzyl)pyridine are brought about by tautomeric radical changes taking place in it under the action of the ultraviolet radiation.

1,075. ON THE LUMINESCENCE OF CERTAIN SOLVENTS

Kovyrzina, K. A., Rozman, I. M.
***Optika i Spektroskopiya*, v. 12, no. 2, pp. 248–253,**
February 1962
(Translated from the Russian in *Optics and Spectroscopy*,
v. 12, no. 2, pp. 133–136, February 1962)

The intensity of luminescence of certain solvents excited by ionizing radiation which does not produce Vavilov–Cherenkov radiation was measured. The lifetimes of the excited states of heptane, dioxane, and acetone are estimated from the efficiency of energy transfer. It is shown that the fraction of activated (excited and ionized) solvent molecules which attain the "fluorescent" state depends essentially on the nature of the solvent. On the basis of the experimental data, it is suggested that in scintillating solutions specific processes occurring during excitation by particles can produce a quenching of the acceptor molecules. (*PA*, 1962, #15,609)

1,076. UNIVERSAL MOLECULAR INTERACTIONS AND THEIR EFFECT ON THE POSITION OF ELECTRONIC SPECTRA OF MOLECULES IN TWO-COMPONENT SOLUTIONS. II. PHTHALIMIDE DERIVATIVES (IN LIQUID SOLUTIONS)

Bakhshiev, N. G.
***Optika i Spektroskopiya*, v. 12, no. 3, pp. 350–358, March 1962**
(Translated from the Russian in *Optics and Spectroscopy*, v. 12, no. 3, pp. 193–197, March 1962)

(For Part I, see Entry #621.) A comparison is made between a previously developed theory (describing the influence of universal molecular interactions on the position of electronic spectra of molecules in liquid two-component solutions) and experimental data for a group of phthalimide derivatives. It is shown that the theory is in good quantitative agreement with the experiments, thus allowing certain conclusions to be drawn concerning (1) the nature of the forces in molecular interactions in solution, and (2) the properties and structures of the molecules investigated.

1,077. UNIVERSAL MOLECULAR INTERACTIONS AND THEIR EFFECT ON THE POSITION OF ELECTRONIC SPECTRA OF MOLECULES IN TWO-COMPONENT SOLUTIONS. III. DERIVATIVES OF NAPHTHALENE, STILBENE, DIPHENYL, ANILINE, FLUORENE, AND PYRIDINE (IN LIQUID SOLUTIONS)

Bakhshiev, N. G.
***Optika i Spektroskopiya*, v. 12, no. 3, pp. 473–478, March 1962**
(Translated from the Russian in *Optics and Spectroscopy*, v. 12, no. 4, pp. 261–263, April 1962)

The previously developed theory, describing the influence of universal molecular interactions on the position of electronic molecular spectra in liquid two-component solutions, is compared with experimental data found in the literature on the spectra of a large group of aromatic compounds (derivatives of naphthalene, stilbene, diphenyl, fluorene, aniline, and others) in a wide range of solvents.

It is shown that the theory is in satisfactory quantitative agreement with experiment. On the basis of the data obtained, a series of conclusions is presented concerning the properties of the investigated molecules.

1,078. THE RELATIONSHIP BETWEEN THE ELECTRONIC ABSORPTION AND LUMINESCENCE SPECTRA OF COMPLEX MOLECULES

Mazurenko, Yu. T., Neporent, B. S.
***Optika i Spektroskopiya*, v. 12, no. 5, pp. 571–575, May 1962**
(Translated from the Russian in *Optics and Spectroscopy*, v. 12, no. 5, pp. 317–319, May 1962)

A universal relationship between absorption and luminescence spectra over a wide spectral range is shown to be valid over a range of 10^0- to 10^8-fold in relative spectral intensity. It is shown that for complex molecules, the necessary condition in the derivation of a universal relationship is satisfied; i.e., thermal equilibrium is attained rapidly among the vibrational states. The effect of statistical weights of molecular vibrational states is taken into consideration. Experimental work is reported on solutions of organic dyes and phthalimide derivatives in various solvents, at room temperature and, in one case, at 350 and 400°K.

1,079. THE FLUORESCENCE AND ABSORPTION SPECTRA OF STILBENE IN OCTANE AT LOW TEMPERATURES

Levshin, V. L., Mamedov, Kh. I.
***Optika i Spektroskopiya*, v. 12, no. 5, pp. 593–598, May 1962**
(Translated from the Russian in *Optics and Spectroscopy*, v. 12, no. 5, pp. 329–332, May 1962)

The fluorescence and absorption spectra of stilbene were studied in *n*-octane at liquid nitrogen temperature. The broad fluorescence bands observed in frozen alcoholic solutions of stilbene break up in *n*-octane into a large number of very narrow bands. On the basis of an analysis of the electron-vibrational fluorescence and absorption spectra of stilbene, series formulae are given covering all observed luminescence lines with fair accuracy. A scheme is proposed for the location of energy levels in stilbene. (PA 1962, #23,609)

1,080. THE INFLUENCE OF SOLVENT CRYSTALLIZATION ON THE LUMINESCENCE OF DYES

Morozov, Yu. V., Naberukhin, Yu. I., Gurskii, G. V.
***Optika i Spektroskopiya*, v. 12, no. 5, pp. 599–605, May 1962**
(Translated from the Russian in *Optics and Spectroscopy*, v. 12, no. 5, pp. 332–336, May 1962)

In the freezing of aqueous solutions of many fluorescing dyes the following phenomena are observed: At a temperature somewhat below 0°C, luminescence in the frozen portion of the solution practically vanishes; for a further temperature decrease, beginning approximately at −30°C, there appears a new luminescence band shifted to the long wavelength side. Adding different substances in comparatively small quantities to the solution before freezing influences these phenomena substantially. Thus, on adding to the solution 1 to 2% (by volume) of alcohol the "yellow" fluorescence band does not vanish on freezing of the solution. On the other hand, on addition of 1 to 2% of glucose the phenomenon occurs qualitatively the same as in pure water, but the "red" band is intensified. Szent-Györgyi has noticed numerous and unusually interesting analogies between the biological activity of many substances and their influence on the fluorescence of frozen aqueous solutions of dyes. Szent-Györgyi has explained these phenomena by saying that on the crystallization of water the restriction on singlet–triplet transitions is raised and their probability becomes much greater than the probability of fluorescence, so that practically all of the excited molecules are found in the triplet state in which, at comparatively high temperatures, they experience thermal quenching (internal conversion). On a temperature decrease this quenching is lowered and there arises the "red" luminescence band which Szent-Györgyi considers as "phosphorescence," i.e., radiation from the triplet level. From this point of view the influence of different adducts consists of reestablishment of the restriction on the transition $S^* \rightarrow T$ (in the case of alcohol) or an increase of the probability of the transitions $T \rightarrow G$ (in the case of glucose).

However, it has been shown that the proposed Szent-Györgyi interpretation of the described phenomena is not valid. The basic experimental facts arguing against it are the following:

1. The observed effects depend to a large extent on the dye concentration in solution. They are observed only in solutions of comparatively high concentration (10^{-4} mole/l). For dye concentrations (rhodamine B) of 10^{-5} mole/l in water the radiation does not disappear on freezing, and in the spectrum of the radiation at low temperatures both bands—the "yellow" and the "red"—appear strongly. At concentrations of 10^{-6} mole/l the intensities of both bands are equal. This dependence on concentration in solutions is still more sharply noted for glucose addition.

2. Measurements on the phase fluorometer have shown that the "yellow" band in the solid as well as in the liquid state is characterized by a lifetime of the excited state of the radiating molecules $\tau = 4.5 \times 10^{-9}$ sec, and the "red" band by the value $\tau = 2.7 \times 10^{-8}$ sec. These data indicate that in both cases there is emitted radiation from a singlet excited level but the centers responsible for the luminescence in the two cases are different.

3. Finally, the relative output of phosphorescence does not exceed 2% in rhodamine B and approximately 3% in acridine orange.

4. These and a few other facts allow explanation of the phenomenon observed on freezing of aqueous dyes by the proposal that on water crystallization there occurs a breakdown of the solution homogeneity and a trapping of the dissolved molecules in a few regions where their concentration is significantly higher than the average. Here there are formed associations of luminescing molecules which also act as centers responsible for the appearance of the "red" luminescence band.

In the present work a series of complementary results are presented confirming the explanation given and investigating the process of forming the associations during crystallization of water and of a few other solvents.

The method of investigation is described. This method permitted investigation of the temperature shift of the luminescence intensity and measurement of the phosphorescence spectra as well as the spectrum of the total radiation for any temperature within the interval indicated.

The phenomena described were observed in a large number of different fluorescing substances. The investigation was restricted to the organic dyes, rhodamine B, and acridine orange.

1,081. EFFECT OF IMPURITIES ON THE VALIDITY OF A UNIVERSAL RELATIONSHIP BETWEEN THE ABSORPTION AND LUMINESCENCE SPECTRA OF COMPLEX MOLECULES

Kravtsov, L. A., Rubinov, A. N.
***Optika i Spektroskopiya*, v. 12, no. 5, pp. 636–638, May 1962**
(Translated from the Russian in *Optics and Spectroscopy*, v. 12, no. 5. pp. 355–356, May 1962)

A theoretical relation between luminescence intensity and absorption coefficient as a function of frequency and temperature, deduced by Stepanov, was confirmed in several publications. Modified relations applying in the presence of an absorbing impurity are quoted here without proof. Measurements with 3-aminophthalimide, and chlorophyll as an impurity, confirm these relations. (*PA*, 1962, #22,944)

1,082. THE PHOTOLUMINESCENCE AND ABSORPTION OF ACRIDONE IN SOLUTION

Kilimov, A. P., Voloshina, V. V.
***Optika i Spektroskopiya*, v. 12, no. 5, pp. 647–649, May 1962**
(Translated from the Russian in *Optics and Spectroscopy*, v. 12, no. 5, pp. 362–363, May 1962)

The absorption and luminescence spectra of the molecular and cationic forms of acridone were measured as a function of concentration in *n*-dioxane and in ethanol. The results indicate that there is no association of the material in either the molecular or cationic forms, even in solutions near saturation. (*PA*, 1963, #141)

1,083. DEPENDENCE OF THE LUMINESCENCE YIELD OF MIXED SINGLE CRYSTALS ON IMPURITY CONCENTRATION

Naboikin, Yu. V., Dobrokhotova, V. K., Uglanova, V. V.
***Optika i Spektroskopiya*, v. 12, no. 5, pp. 649–651, May 1962**
(Translated from the Russian in *Optics and Spectroscopy*, v. 12, no. 5, pp. 364–365, May 1962)

The γ-ray-excited scintillation efficiency of single crystals of naphthalene containing (1) phenylbiphenylethylene and (2) $\beta\beta'$-dinaphthylethylene was measured as a function of impurity concentration. (1) and (2) dissolve in naphthalene with distribution coefficients of 10^{-2} and > 1, respectively. Analysis of the scintillation data shows the probability of excitation energy transfer to (1) and (2) to be 6×10^{13} and 1.5×10^{13} sec^{-1}, respectively. This indicates that less soluble impurities cause more serious local deformations in the lattice, and that the probability of trapping the excitation energy at such impurity centers is increased accordingly. (*PA*, 1963, #963)

1,084. STUDY OF MOLECULAR TRIPLET STATES BY LUMINESCENCE AND EPR

Shigorin, D. N., Volkova, N. V., Piskunov, A. K., Gurevich, A. I.
***Optika i Spektroskopiya*, v. 12, no. 5, pp. 657–659, May 1962**
(Translated from the Russian in *Optics and Spectroscopy*, v. 12, no. 5, pp. 369–370, May 1962)

Fluorescence spectra of N-ethylacridone were observed in powder form and in solution in ethanol, HCl, and H_2SO_4 at 290 and 77°K. Frozen solutions at 77°K in hexane, hexane/dioxane, and ether/hexane give luminescence spectra with fine structure. The fluorescence spectrum (3900–4500 Å) is much weaker than the phosphorescence spectrum (4500–6500Å), which has a decay time of about 10 sec. The phosphorescent triplet state was also studied by electron paramagnetic resonance by observation of the $\Delta M = \pm 2$ transitions. (*PA*, 1963, #962)

1,085. THE LUMINESCENCE OF INDIGO SOLUTIONS AT 77°K

Shigorin, D. N., Nurmukhametov, R. N., Kozlov, Yu. I.
***Optika i Spektroskopiya*, v. 12, no. 5, pp. 659–661, May 1962**
(Translated from the Russian in *Optics and Spectroscopy*, v. 12, no. 5, pp. 371–372, May 1962)

The structural emission and absorption spectra of indigo are described, as well as the conditions under which these spectra were observed. It is known that indigo does not dissolve in *n*-hydrocarbons and, moreover, it does not yield true solutions because of the strong association of its molecules through intermolecular hydrogen bonds. It has been found that it is possible to break down these associations by dissolving the indigo in dioxane. The molecules of dioxane implant themselves between indigo molecules (breaking the hydrogen bonds $> N - H \ldots O = C <$ and forming new hydrogen bonds $> N - H \ldots O <$) and isolate these molecules from each other. After this, the associated solution of indigo and dioxane is diluted with hexane. When a solution of this kind is irradiated with ultraviolet light at 77°K, a red fluorescence is observed. The brightest light output is observed when the dioxane solution ($C = 10^{-4}$ mole/l) is diluted to a dioxane: hexane ratio of 1:15. Results are presented and explained.

The structural fluorescence spectra of 5,5′,7,7′-tetrabromo, 5,5′,7,7′-tetrachloro, and 5,5′-dichloroindigo were also obtained at 77°K in solutions of dioxane + hexane. The spectra of these compounds differed very little in either structure or band diffusion from the emission spectrum of indigo itself. The effect of the substituents on the intensity of the fundamental band was the most noticeable.

On the basis of the distinct similarity of the quasi-line spectra of indigo and its halide derivatives to the thioindigo spectra, a conclusion can be drawn regarding the common nature of the electronic transitions in indigoid dyes. In these compounds the $C_2 = C'_2$ group is the chromophor primarily responsible for the electron excitation of the molecule ($\pi \rightarrow \pi^*$ transition), and the valence vibrational frequency of this group appears characteristically in the quasi-line absorption and emission spectra.

1,086. THE DURATION OF THE PHOTO- AND RADIOLUMINESCENCE OF ORGANIC COMPOUNDS

Kilin, S. F.
***Optika i Spektroskopiya*, v. 12, no. 6, pp. 733–737, June 1962**
(Translated from the Russian in *Optics and Spectroscopy*, v. 12, no. 6, pp. 414–416, June 1962)

The duration of the photo- and radioluminescence of plastic scintillators, organic crystals, and powders was measured by a phase method. It was found that $\tau_s \leq \tau_f$. Measurement of the depth of modulation of the luminescent light output showed that there is a slow component in the quenching of radioluminescence in organic powder luminophors. It can become as large as one third of the total light output.

1,087. EFFECT OF THE MEDIUM ON THE PROPERTIES OF THE ELECTRONIC SPECTRA OF COMPLEX MOLECULES DURING THE GRADUAL TRANSITION FROM VAPORS TO SOLUTIONS

Neporent, B. S., Bakhshiev, N. G., Lavrov, V. A., Korotkov, S. M.
***Optika i Spektroskopiya*, v. 13, no. 1, pp. 32–42, July 1962**
(Translated from the Russian in *Optics and Spectroscopy*, v. 13, no. 1, pp. 18–23, July 1962)

The position and width of the absorption and fluorescence spectra of 3-methylaminophthalimide, and the intensity of absorption and the fluorescence yield, were studied, the concentration of the foreign substance (ethyl ether) varying from 0 to 58×10^{20} mol./cm^3, this substance passing from gaseous into liquid state with subsequent cooling of the solution down to 20°C. All aforementioned characteristics of 3-methylaminophthalimide change monotonically with the concentration of ether, displaying no sudden variation at the phase transition. These changes are in agreement with the theory based on the idea of internal field. The temperature dependence of the transition probabilities with and without radiation was determined. It was found that the temperature quenching of fluorescence is of an intramolecular nature. The stabilization effect was used to determine the mean quantity of vibrational energy which is transmitted to the excited molecule on collision with the molecule of ether, and to determine the value of the coefficient accommodation. (*PA*, 1963, #1703)

1,088. MIGRATION OF ENERGY BETWEEN THE IMPURITY MOLECULES IN MOLECULAR CRYSTALS

Zhevandrov, N. D., Gribkov, V. I., Khan-Magometova, Sh. D.
***Optika i Spektroskopiya*, v. 13, no. 1, pp. 96–99, July 1962**
(Translated from the Russian in *Optics and Spectroscopy*, v. 13, no. 1, pp. 52–55, July 1962)

Making use of the fact that the polarization of the fluorescence of a molecular crystal is independent of the polarization of the exciting light, it was demonstrated that a migration of energy over a distance of up to 25 lattice constants takes place between the interstitial naphthacene molecules in the anthracene lattice. The same method was used to demonstrate the migration of energy in the crystals of stilbene, anthracene, and anthracene with naphthacene at −196°C. (*PA*, 1963, #2691)

1,089. ELECTRON PARAMAGNETIC RESONANCE AND ABSORPTION SPECTRA IN THE VISIBLE REGION IN ALCOHOLIC AND GLYCEROL SOLUTIONS OF Ti^{3+}

Garifyanov, N. S., Danilova, A. V., Shagidullin, R. R.
***Optika i Spektroskopiya*, v. 13, no. 2, pp. 212–215,**
August 1962
(Translated from the Russian in *Optics and Spectroscopy*,
v. 13, no. 2, pp. 116–117, August 1962)

The EPR method ($\nu = 9320$ Mc, $T = 295\text{–}77°K$) was used to determine the content of the green modification of $TiCl_3 \cdot H_2O$ in solutions in glycerol, methanol, ethanol, and isopropanol. The investigation of the optical spectra in the visible region bears out the existence of the green modification in the violet solutions of Ti^{3+}. (*PA*, 1963, #1712)

1,090. EFFECT OF TEMPERATURE ON THE KINETICS OF α-PHOSPHORESCENCE OF ORGANIC SUBSTANCES

Aristov, A. V., Sveshnikov, B. Ya.
***Optika i Spektroskopiya*, v. 13, no. 2, pp. 222–228,**
August 1962
(Translated from the Russian in *Optics and Spectroscopy*,
v. 13, no. 2, pp. 121–125, August 1962)

A study was made of the effect of temperature on the spectra, yield, and duration of phosphorescence and fluorescence in organic phosphors activated with fluorescein (I), trypaflavine (II), and auramine (III). At the same time the temperature dependence was studied of the number of photons emitted in the form of phosphorescence during an extremely short time following the excitation, the duration of which was short compared with the period of phosphorescence. It was found that no temperature decay occurs in I and II, whereas in III there is a considerable decay on the fluorescence level, but only a small one on the phosphorescence level. It was also found for I and II that the probabilities of transitions from the fluorescent into phosphorescent state coincide with those of the inverse transitions. (*PA*, 1963, #3063)

1,091. TEMPERATURE QUENCHING OF THE β-PHOSPHORESCENCE OF ORGANIC PHOSPHORS

Aristov, A. V., Sveshnikov, B. Ya.
***Optika i Spektroskopiya*, v. 13, no. 3, pp. 383–385,**
September 1962
(Translated from the Russian in *Optics and Spectroscopy*,
v. 13, no. 3, pp. 212–213, September 1962)

The effect of temperature on the duration, phosphorescence yield, and phosphorescence efficiency during short-time excitation of phosphors activated by esculin and phthalimide is investigated. It is shown that in both phosphors there exists a temperature quenching of the phosphorescence with a very small activation energy and small probability of a radiationless transition to the normal state from the phosphorescent state for molecules which have obtained the activation energy necessary for this transition. Certain considerations are expressed regarding the nature of the quenching of the phosphorescence. (*PA*, 1963, #10,999)

1,092. EFFECTS OF REABSORPTION ON THE LUMINESCENCE DECAY LAW OF ANTHRACENE CRYSTAL. LUMINESCENCE IN PLASTICS

Galanin, M. D., Konobeev, Yu. V., Chizhikova, Z. A.
***Optika i Spektroskopiya*, v. 13, no. 3, pp. 386–389,**
September 1962
(Translated from the Russian in *Optics and Spectroscopy*,
v. 13, no. 3, pp. 214–216, September 1962)

The luminescence decay law of anthracene crystal under γ- and photoexcitation is measured by the method of reflecting pulses in shorted lines. It is shown that the decay law is nonexponential. A decay law that takes into consideration effects of reabsorption and secondary luminescence is derived on a theoretical basis. The deviations from the exponents observed experimentally agree qualitatively with those anticipated from theory. (*PA*, 1963, #8626)

1,093. A STUDY OF THE PHOTOLUMINESCENCE AND SCINTILLATION PROPERTIES OF SOME 1,3-OXAZOLE DERIVATIVES IN POLYSTYRENE

Nagornaya, L. L., Bezuglyi, V. D., Demchenko, N. P.
***Optika i Spektroskopiya*, v. 13, no. 4, pp. 518–521,**
October 1962
(Translated from the Russian in *Optics and Spectroscopy*,
v. 13, no. 4, pp. 288–290, October 1962)

Photoluminescence and scintillation characteristics which have not been described in the literature were investigated for 2-(4-biphenylyl)-5-(2-naphthyl)-oxazole-1,3; 2-(4-biphenylyl)-5-(1-naphthyl)-oxazole-1,3; and 1,2-biphenyloxazole derivatives of ethylene and ethane. It was established that the most efficient plastic scintillators are those which use 2-(4-biphenylyl)-5-(2-naphthyl)-oxazole-1,3 as the luminophor. The effectiveness of scintillators of this kind is ~105% compared to a standard polystyrene calibrating block containing 2% *p*-terphenyl and 0.06% POPOP.

1,094. NATURE OF THE LUMINESCENCE SPECTRA OF CRYSTALLINE BENZENE AT LOW TEMPERATURES

Shpak, M. T., Solovev, A. V., Sheremet, N. I.
***Optika i Spektroskopiya*, v. 13, no. 5, pp. 694–700,**
November 1962
(Translated from the Russian in *Optics and Spectroscopy*,
v. 13, no. 5, pp. 393–396, November 1962)

In the luminescence spectra of crystalline benzene, regions which matched the initial regions of the intrinsic absorption of the crystal in resonance were observed and investigated. It was shown that at low temperatures this luminescence can be explained by transitions from exciton levels of the primary excited state to levels of the ground state of the crystal. (*PA*, 1963, #11,003)

1,095. LUMINESCENCE IN CASTOR OIL UNDER THE ACTION OF AN ALTERNATING VOLTAGE

Eidelberg, M. I.
***Optika i Spektroskopiya*, v. 14, no. 2, pp. 299–300, February 1963**
(Translated from the Russian in *Optics and Spectroscopy*, v. 14, no. 2, pp. 155–156, February 1963)

During investigations of the electroluminescence of zinc sulfide phosphors under the influence of an alternating voltage applied to plane-parallel electrodes, it was noticed that, at sufficiently high field intensities (of the order 10^4 to 10^5 v/cm), a weak luminescence in the form of white spots could be observed when the cell contained castor oil of a certain type.

The usual type of electroluminescent condenser was used in this investigation; the distance between the plates of this condenser was 0.04 mm. To supply the voltage, an audiogenerator 3G-10 with a step-up transformer was employed. To perform the optical measurements, a photomultiplier FEU-19M with a mirror galvanometer was used. The castor oil was purified by filtration in a heated state through a paper filter. A report is given of the phenomena observed when the alternating voltage applied to the electrodes of the cell filled with castor oil is gradually raised. An explanation is offered for the mechanism of the observed luminescence.

1,096. LUMINESCENCE OF ANTHRACENE CRYSTALS OBTAINED BY SUBLIMATION IN AN OXYGEN ATMOSPHERE UNDER IRRADIATION

Zima, V. L., Faidysh, A. N.
***Optika i Spektroskopiya*, v. 14, no. 3, pp. 371–377, March 1963**
(Translated from the Russian in *Optics and Spectroscopy*, v. 14, no. 3, pp. 198–201, March 1963)

A report of investigation of the luminescence spectra of anthracene crystals obtained by sublimation in an oxygen atmosphere under irradiation is presented. An addition (O) luminescence spectrum, in which the polarization ratio is significantly larger than for the usual spectrum of pure anthracene crystals, was observed in these crystals. These experiments provide a basis for the assumption that the O spectrum is due to radiation of anthracene molecules located close to molecules which have been photo-oxidized. The radiation of O centers basically occurs because of the transfer of electronic excitation energy from the crystal to these centers.

1,097. FLUORESCENCE OF SOLUTIONS OF CERTAIN SUBSTITUTED POLYENES

Nikitina, A. N., Ter-Sarkisyan, G. S., Mikhailov, B. M., Minchenkova, L. E.
***Optika i Spektroskopiya*, v. 14, no. 5, pp. 655–663, May 1963**
(Translated from the Russian in *Optics and Spectroscopy*, v. 14, no. 5, pp. 347–350, May 1963)

The fluorescence and absorption spectra of thirteen substituted polyenes in various solvents have been studied. The spectra, quantum yields, and duration of fluorescence have been measured. It has been shown for some substituted hexatrienes that on changing from such solvents as heptane to aromatic solvents (benzene, toluene), an increase of quantum yield is accompanied by a decrease in the duration of fluorescence. It is conjectured that such a change in yield and duration of fluorescence of these hexatrienes is explained by an interaction of their excited molecules with the molecules of the aromatic solvents.

1,093. ON THE RELATION BETWEEN THE ABSORPTION AND DISPERSION OF LIGHT IN CONCENTRATED FLUORESCENT SOLUTIONS OF DYES

Alperovich, L. I.
***Optika i Spektroskopiya*, v. 14, no. 6, pp. 756–759, June 1963**
(Translated from the Russian in *Optics and Spectroscopy*, v. 14, no. 6, pp. 400–402, June 1963)

The Kramers-Kronig dispersion relations have been shown, within limits of experimental error, to be applicable inside the absorption bands of concentrated fluorescent solutions of dyes, in which electronic excitation energy migration processes occur, and also inside the absorption band of *i*-polymers of pseudo-isocyanin, which are usually attributed to nonlocalized excitons. Measurements are reported.

1,099. NEW DATA ON THE DEPENDENCE OF THE DEGREE OF POLARIZATION ON THE WAVELENGTH OF FLUORESCENCE

Gurinovich, G. P., Sarzhevskii, A. M., Sevchenko, A. N.
***Optika i Spektroskopiya*, v. 14, no. 6, pp. 809–812, June 1963**
(Translated from the Russian in *Optics and Spectroscopy*, v. 14, no. 6, pp. 428–430, June 1963)

In earlier publications the authors have shown that the degree of polarization of complex molecules depends both on the frequency of absorption ν_{abs} and on the frequency of emission ν_{emis}, and for molecules possessing mirror-symmetrical spectra, these dependencies are also symmetrical relative to the frequency of a purely electronic transition. These results were criticized in a recent paper by Klochkov and Neporent.

In order to verify the previous data, some of the measurements were repeated and additional experiments were performed on the dependence of degree of polarization on emission frequency for certain phthalimides in glycerin at room temperature and in alcohols at a reduced temperature. Some new samples of 3-monomethylaminophthalimide in plexiglass were obtained, and a careful examination of the dependence of the fluorescence spectra on λ_{exc} showed that, on excitation by the wavelengths 436, 405, and 365 mμ, the emission spectra are in good agreement. The variation in the degree of polarization for the emission spectrum is 6.5% for this substance in a range of 6000 cm^{-1}, which agrees well with previous data. The dependence of P on ν_{emis} is linear and no discontinuities are observed. Measurements repeated after a time lapse showed that the spectra start to depend on λ_{exc}.

This fact indicates that phthalimide in plexiglass undergoes some changes.

A careful study of the dependence of P on ν_{emis} in glycerin was next undertaken, since the criticizing authors found no such dependence in this solvent. An investigation of the emission spectra as a function of λ_{exc} showed that a small dependence of the fluorescence spectrum on the wavelength of excitation light is observed in glycerin at room temperature. On excitation by 365 mμ the short-wavelength end of the spectrum is somewhat elevated. The noncoincidence of the spectra is a consequence of the addition of the "blue" luminescence of glycerin which is readily excited by ultraviolet. Experiments in other solvents, using the phthalimides, are reported and discussed.

Besides the phthalimide derivatives, the change in the degree of polarization along the fluorescence spectrum of 2-acetylanthracene in glycerin at 20°C and in isobutyl alcohol at −120°C was studied.

Results corroborate the previous viewpoint about the existence of a dependence of the degree of polarization on the emission frequency of complex molecules. Corroborating evidence is cited by Laffitte; Zanker, et al.; Kubarev; and Zimmerman, et al.

1,100. NATURE OF THE LUMINESCENCE OF CRYSTALLINE ANTHRACENE AT LOW TEMPERATURES

Shpak, M. T., Sheremet, N. I.
***Optika i Spektroskopiya*, v. 14, no. 6, pp. 816–818, June 1963**
(Translated from the Russian in *Optics and Spectroscopy*, v. 14, no. 6, pp. 433–435, June 1963)

Results are presented of a study of the luminescence spectra of zone-refined crystalline anthracene (40 passes) in polarized light at 20.4, 77, and 290°K (using the spectrographs ISP-22 and DFS-13). A single crystal of anthracene in the form of a small platelet grown by the sublimation method was held loosely between crossed Glan–Thomson prisms. The luminescence was excited with the light of a DPSh-250 mercury lamp filtered through a Wood filter. A prism placed before the spectrograph slit served as the analyzer. Experimental results are interpreted.

1,101. ELECTRONIC SPECTRA OF 2,6-DIMETHYLNAPHTHALENE IN SOLUTIONS

Kharitonova, O. P.
***Optika i Spektroskopiya*, v. 15, no. 1, pp. 21–26, July 1963**
(Translated from the Russian in *Optics and Spectroscopy*, v. 15, no. 1, pp. 9–11, July 1963)

The absorption and luminescence spectra of solutions of 2,6-dimethylnaphthalene in ethyl alcohol and n-hexane have been studied at low temperatures on medium and high dispersion spectrographs. Two absorption regions have been found, and their oscillator strengths determined. A vibrational analysis has been performed, and the frequencies of the normal oscillations of molecules of 2,6-dimethylnaphthalene have been determined in the ground and excited states.

1,102. TEMPERATURE DEPENDENCE OF THE INTENSITY AND SHAPE OF THE ABSORPTION AND FLUORESCENCE SPECTRA OF ANTHRACENE DERIVATIVE VAPORS

Klochkov, V. P., Makushenko, A. M.
***Optika i Spektroskopiya*, v. 15, no. 1, pp. 52–60, July 1963**
(Translated from the Russian in *Optics and Spectroscopy*, v. 15, no. 1, pp. 25–29, July 1963)

The temperature dependence of the shape and intensity of the absorption and fluorescence spectra of 9-methyl, 9,10-dimethyl and 9-diacetylaminoanthracenes was investigated. An increase in fluorescence quantum yield with temperature rise was detected in the first two compounds. This explains the increased probability of radiating transitions in the case of radiation from high vibrational levels of the excited state when there is a weak temperature dependence of radiationless transition probability. The problem of the origin of the shift of the absorption and fluorescence spectra to the long-wave side with temperature increase is considered.

1,103. EMISSION AND ABSORPTION SPECTRA OF PHTHALOCYANINE IN FROZEN CRYSTALLINE SOLUTIONS

Personov, R. I.
***Optika i Spektroskopiya*, v. 15, no. 1, pp. 61–71, July 1963**
(Translated from the Russian in *Optics and Spectroscopy*, v. 15, no. 1, pp. 30–35, July 1963)

The fluorescence and absorption spectra of free phthalocyanine in three normal paraffins (octane, nonane, and decane) were investigated at 77°K. Under the indicated conditions a large number of narrow lines, rather than the usual diffuse bands, was observed in the spectra. A vibrational analysis of the observed spectra was made. Two regions in the absorption spectra which refer to different electronic transitions were isolated. The question of the interpretation of the phthalocyanine absorption spectrum is discussed.

1,104. THE EFFECT OF SUBSTITUENT RADICALS ON THE ABSORPTION SPECTRA OF MONOALKYLBENZENE CRYSTALS

Klimusheva, G. V., Bragin, O. V., Mikhailova, E. A., Safonova, I. L.
***Optika i Spektroskopiya*, v. 15, no. 1, pp. 72–78, July 1963**
(Translated from the Russian in *Optics and Spectroscopy*, v. 15, no. 1, pp. 35–38, July 1963)

The results of an investigation of the absorption spectra of monoalkylbenzene crystals at 20°K in the 2700-Å region corresponding to the first electron transition are presented. A comparison of these spectra, using the data on vapor spectra, has shown that the different effect of alkyl groups on the electron cloud of the benzene ring, as estimated by the position of the spectra and their fine structure, can be explained by the hyperconjugation effect. The degree of conjugation of substituent radicals and the benzene ring was evaluated by means of a spectral method.

1,105. TEMPERATURE DEPENDENCE OF THE FLUORESCENCE YIELD OF COMPLEX MOLECULES IN THE VAPOR PHASE AND THE ACTIVATION ENERGY OF RADIATIONLESS TRANSITIONS

Tolkachev, V. A., Borisevich, N. A.
Optika i Spektroskopiya, Akademiya Nauk SSSR, Otdelenie Fiziko-Matematicheskikh Nauk, Sbornik Statei,
v. 1, pp. 16–21, 1963

The work was done on three derivatives of phthalimide and 1-aminoanthraquinone. In the second absorption band, the velocity of decrease of the yield with temperature does not depend on the frequency of exciting radiation and the temperature extinction is weaker. Activation energy is determined of the radiationless transitions. In 3-aminophthalimide, activation energy does not depend on the characteristic temperature of vibration of the molecules; in 3,6-tetramethyldiamino- and 3-dimethylamino-6-aminophthalimides, it increases with increasing characteristic temperature of vibration.

1,106. RELATIONS BETWEEN THE ABSOLUTE YIELDS OF LUMINESCENCE AND SPECTRAL CHARACTERISTICS OF CERTAIN XANTHENE DYES

Zelinskii, V. V., Kolobkov, V. P., Saganenko, A. A.
Optika i Spektroskopiya, Akademiya Nauk SSSR, Otdelenie Fiziko-Matematicheskikh Nauk, Sbornik Statei,
v. 1, pp. 28–36, 1963

Absolute quantum yields of luminescence and spectra of absorption and emission were measured in a series of derivatives of fluorescein (in the form of salts) in solid alcohol solutions at −196°C. The basic process of radiationless deactivation of excited states of the investigated compounds is most probably the direct conversion from the excited to the ground state. Variations in position of electronic spectra, with accompanying variation in fluorescence yield, occur during transition from one substance to another.

1,107. SPECTROSCOPY OF FROZEN CRYSTALLINE SOLUTIONS OF DIPHENYL POLYENES AND POLYPHENYLS. I. BIPHENYL, TRIPHENYL, AND QUADRIPHENYL

Gobov, G. V., Bolotnikova, T. N.
Optika i Spektroskopiya, Akademiya Nauk SSSR, Otdelenie Fiziko-Matematicheskikh Nauk, Sbornik Statei,
v. 1, pp. 36–43, 1963

A comparative study was made of the luminescence and absorption spectra of biphenyl, triphenyl, and quadriphenyl. Luminescence spectra are successively displaced toward the red in these three compounds. In biphenyl the most intense spectral lines form a system with the initial line at 32,725 cm^{-1}. There are nine absorption bands in all. The luminescence spectra of triphenyl consist of five groups of bands separated by 1600 cm^{-1} intervals. The initial line is situated at 30,715 cm^{-1}. The discrete absorption spectrum of triphenyl could not be obtained. The initial line in the fluorescence spectra of quadriphenyl is at 28,080 cm^{-1}. The frequencies 1000, 1250, and 1600 cm^{-1} are common to the vibration-electronic spectra of the three compounds.

1,108. TEMPERATURE EFFECT ON THE FLUORESCENCE SPECTRA OF *n*-PARAFFIN SOLUTIONS OF SOME DERIVATIVES OF PYRENE

Khesina, A. Ya.
Optika i Spektroskopiya, Akademiya Nauk SSSR, Otdelenie Fiziko-Matematicheskikh Nauk, Sbornik Statei,
v. 1, pp. 43–51, 1963

The method of experiment is described. Temperature dependence of fluorescence spectra of the frozen solutions was investigated from 77°K to the melting point of the solvent; the phenomena occurring at the transition at the melting point were also investigated. Results are reported.

1,109. TEMPERATURE DEPENDENCE OF THE QUANTUM YIELD OF FLUORESCENCE IN SOLUTIONS

Klochkov, V. P., Korotkov, S. M.
Optika i Spektroskopiya, Akademiya Nauk SSSR, Otdelenie Fiziko-Matematicheskikh Nauk, Sbornik Statei,
v. 1, pp. 51–57, 1963

Fluorescence of PrOH solutions of anthracene, 1,4-diphenylbutadiene, and 9,10-diphenylanthracene was investigated from 77 to 293°K. The effects of temperature and solvent on the quantum yield are reported. The energy of activation is determined for the transition of molecules from the excited singlet state into the triplet state.

1,110. ABSORPTION AND LUMINESCENCE SPECTRA OF THIONAPHTHENE IN THE NEAR ULTRAVIOLET

Kharitonova, O. P.
Optika i Spektroskopiya, Akademiya Nauk SSSR, Otdelenie Fiziko-Matematicheskikh Nauk, Sbornik Statei,
v. 1, pp. 77–83, 1963

Crystals and solutions of thionaphthene were investigated at 77 and 20°K. Intense absorption consisting of broad bands was observed in the crystal. Dibenzyl, *n*-hexane, and EtOH were used as solvents. Observed spectral bands of the crystals and of the various solutions are given and interpreted.

1,111. LUMINESCENCE OF NAPHTHALENE CRYSTALS AT 4, 20, AND 77°K

Broude, V. L., Sheka, E. F., Shpak, M. T., Shpakovskaya, L. G.
Optika i Spektroskopiya, Akademiya Nauk SSSR, Otdelenie Fiziko-Matematicheskikh Nauk, Sbornik Statei,
v. 1, pp. 98–102, 1963

The intrinsic exciton luminescence, due to electron-vibrational transitions and characterized by a strong temperature dependence of the half widths, is noted and contrasted with exciton luminescence due to impurities and characterized by weak temperature dependence.

1,112. EFFECT OF THE ADDITION OF THIONAPHTHENE ON THE LUMINESCENT PROPERTIES OF CRYSTALLINE NAPHTHALENE

Shpak, M. T., Sheremet, N. I.
Optika i Spektroskopiya, Akademiya Nauk SSSR, Otdelenie Fiziko-Matematicheskikh Nauk, Sbornik Statei,
v. 1, pp. 110–119, 1963

The absorption and luminescence spectra of naphthalene crystals containing thionaphthene in the lattice were studied at 20.4°K. The concentration of thionaphthene was determined by activation analysis. The spectra were compared with those of the pure substances. A small shift of the bands to longer wavelengths was noted with thionaphthene additions to pure naphthalene. Intensity depended on additive concentration.

1,113. LUMINESCENCE AND EXCITATION ENERGY TRANSFER IN ANTHRACENE CRYSTALS WITH THE ADDITION OF NAPHTHACENE

Korsunskii, V. M., Faidish, O. M.
Optika i Spektroskopiya, Akademiya Nauk SSSR, Otdelenie Fiziko-Matematicheskikh Nauk Sbornik Statei,
v. 1, pp. 119–127, 1963

Spectra of anthracene crystals with up to 7.8 × 10^{-5} moles/mole naphthacene were investigated from 90 to 300°K. From these data diffusion shift of excitons and the probability of energy transfer were calculated. The dipole–dipole resonance theory is shown to be a good approximation for energy transfers in organic crystals.

1,114. THE FLUORESCENCE SPECTRUM AND FRANCK-CONDON PRINCIPLE IN SOLUTIONS OF AROMATIC COMPOUNDS

Lippert, E., Lueder, W., Boos, H.
In 'Advances in Molecular Spectroscopy. Proceedings of the IVth International Meeting on Molecular Spectroscopy, Bologna, Italy, 1959," Volume 1, pp. 443–457
Mangini, A., Editor
Pergamon Press, Ltd., London, England, and
The Macmillan Co., New York, N. Y., 1962

Two fluorescence bands (${}^1L_a \rightarrow A$ and ${}^1L_b \rightarrow A$) are emitted by p-dimethylaminobenzonitrile and p-diethylaminobenzonitrile in polar solvents. The dependence of the Stokes' red shift of the former band (${}^1L_a \rightarrow A$) on the orientation polarization of the solvent leads to a value of 23 Debyes for the dipole moment of the former compound in the ${}^1L_a$ state.

1,115. SIGNIFICANCE OF THE TRIPLET STATE OF SENSITIZING DYES IN OPTICAL SENSITIZATION

West, W.
In "Scientific Photography, Proceedings of International Colloquium, Liège, [September 14–19] 1959," pp. 557–568
Sauvenier, H., Editor
Pergamon Press, Ltd., London, England, and
The Macmillan Co., New York, N. Y., 1962

The phosphorescence maximum at −196°C of the following cyanine dyes in EtOH solution are examined for triplet level position: 3,3′-diethylthiacyanine; 3,3′,8-triethylthiacyanine; 3,3′-triethyl-4,5,4′,5′-dibenzothiacyanine; 3,3′-diethylthiacarbocyanine, 3,3′,9-triethyl-5,5′-dichlorothiacarbocyanine; 1,1′-methylene-2,2′-cyanine; 1,1′-ethylene-2,2′-cyanine; 1,1′-diethyl-2,2′-cyanine; 1,1′,3,3′-tetramethyl-2,2′ cyanine; and 2-methyl-6-dimethylaminobenzothiazole. The excited states and related properties are discussed.

1,116. EXCITON DIFFUSION IN NAPHTHALENE CRYSTALS

Kazzaz, A. A., Zahlan, A. B.
***Physical Review,* v. 124, no. 1, pp. 90–95, October 1, 1961**

Exciton capture by anthracene in naphthalene crystals is studied as a function of impurity concentration (4 × 10^{-8} to 4.8 × 10^{-3}), temperature, annealing, and wavelength of exciting radiation. It is shown that surface, incoherent, and possibly coherent free excitons participate in these excitonic processes. A method for annealing molecular crystals is described. Some observations on the temperature dependence of these processes are reported.

1,117. STIMULATED LIGHT EMISSION BY OPTICAL PUMPING AND BY ENERGY TRANSFER IN ORGANIC MOLECULES

Morantz, D. J., White, B. G., Wright, A. J. C.
***Physical Review Letters,* v. 8, no. 1, pp. 23–25, January 1, 1962**

Stimulated light emission by optical pumping and by energy transfer in organic molecules is discussed. Stimulated emission in organic systems depends on the spin-forbidden triplet → singlet transition. Stimulated emission has been observed at 77°K in a system consisting of benzophenone, in a rigid glass matrix between parallel reflecting plates, which was pumped by an intense flash of light. The advantages of organic glass matrices (e.g., the wide range of possible frequencies) as optical maser materials are indicated. An investigation of stimulated light emission by means of energy transfer in a system consisting of a rigid glass containing approximately 0.02% of benzophenone and of naphthalene is discussed. (SSA, #14,222)

1,118. STIMULATED RAMAN SCATTERING FROM ORGANIC LIQUIDS

Eckhardt, G., Hellwarth, R. W., McClung, F. J., Schwarz, S. E., Weiner, D., Woodbury, E. J.
***Physical Review Letters,* v. 9, no. 11, pp. 455–457, December 1, 1962**

The existence of stimulated emission near 7670 Å accompanying normal emission from a ruby laser operating in the pulsed reflector mode has now been found to originate in the nitrobenzene of the Q-spoiling Kerr shutter. The same mechanism can be employed to produce other laser lines from nitrobenzene and also from benzene, toluene, 1-bromonaphthalene, pyridine, cyclohexane, and deuterated benzene C_6D_6. Experimental details are reported; in each instance, laser emission was observed at one of the most intense Raman lines. Carbon tetrachloride and sulphuric acid failed to produce laser action. It appears that (1) only ring compounds with five or more C-H (or C-D) bonds have produced strong induced emission, and (2) no such liquid compound has failed to operate as a laser to date.

1,119. DOUBLE PHOTON EXCITATION IN ORGANIC CRYSTALS

Peticolas, W. L., Goldsborough, J. P., Rieckhoff, K. E.
***Physical Review Letters*, v. 10, no. 2, pp. 43–45, January 15, 1963**

Two-photon excitation by ruby laser radiation in polycyclic aromatic molecular crystals was detected through observation of the fluorescence radiation in the 4000–5000 Å region. For a 2×10^{-4} sec excitation flash flux of maximum value 3×10^{23} quanta cm^{-2} sec^{-1} in the active region, the total number of fluorescence photons emitted was estimated as 5×10^7, 10^8, and 10^9, for pyrene, anthracene, and 3,4-benzpyrene, respectively. No double excitation fluorescence was observed from phenanthrene. (*PA*, 1963, #11,002)

1,120. TRIPLET EXCITONS AND DELAYED FLUORESCENCE IN ANTHRACENE CRYSTALS

Kepler, R. G., Caris, J. C., Avakian, P., Abramson, E.
***Physical Review Letters*, v. 10, no. 9, pp. 400–402, May 1, 1963**

Laser-induced fluorescence in powdered anthracene and several other organic materials was recently reported. The fluorescence was attributed to double photon excitation from the singlet ground state to the first excited singlet state. While studying this fluorescence in anthracene single crystals, delayed fluorescence was detected after the laser pulse ended. The rate of decay of this fluorescence and other experimental observations are explained by assuming that the singlet state giving rise to the fluorescence is produced not by a double photon process as concluded by Peticolas, Goldsborough, and Rieckhoff, but via bimolecular annihilation of triplet excitons generated directly by the ruby laser light. The lifetime and the bimolecular interaction rate constant of the triplet excitons were found to be 10 msec and 10^{-11} cm^3 sec^{-1}, respectively.

Melt-grown anthracene single crystals produced from zone-refined Eastman starting material were illuminated at room temperature by approximately 0.02 *J* per laser pulse focused into a volume of 10^{-}[illegible] cm^3. Incident laser radiation was passed through a Corning 2-58 filter, while the fluorescence was observed with a photomultiplier through a Corning 5-56 filter. A 2-μsec time constant was introduced to integrate over individual laser spikes. The measured fluorescent signal contained a negligible amount of scattered laser light. To measure the weak delayed fluorescence, it was necessary to blank out the oscilloscope amplifier during the intense portion of the fluorescent pulse to prevent its saturation.

By correcting the fluorescent flux density incident on the photomultiplier for detector solid angle, and by assuming isotropic emission, it is inferred that about 10^{11} fluorescent quanta were emitted per laser pulse of about 10^{17} quanta. The fluorescence spectrum, measured with a monochromator and photomultiplier, was identical to the normal anthracene fluorescence spectrum in the presence of self-absorption.

Oscilloscope traces are presented showing the time dependence of (1) the laser emission and (2) the blue anthracene fluorescence around the time of laser shutoff. Both traces were initiated 1.3 msec after the beginning of the laser pulse, and both time scales are 100 μsec/large division.

Time dependence of the delayed fluorescence is plotted. One graph shows that around the time of laser shutoff the fluorescent flux varies inversely with the square root of time, while another shows that at later times the fluorescence decays exponentially. Results are discussed.

1,121. PHOTOFLUORESCENCE DECAY TIMES OF ORGANIC PHOSPHORS

Hamilton, T. D. S.
***Physical Society, Proceedings of the*, London, v. 78, pt. 5(i), pp. 743–752, November 1, 1961**

An accurate and convenient method for measuring photofluorescence decay times in the nanosecond region is described. Results are given for a number of organic compounds and reasons for differences with previous results are discussed. For anthracene, a value of 24.2 nsec has been measured for a 1-cm-cube crystal. Some previous results for quantum efficiencies are corrected on the basis of these measurements, and apparent inconsistencies are examined with regard to the mean free path of excitons in very thin crystals. (*SSA*, #13,285)

1,122. ELECTRICAL PROPERTIES OF ORGANIC INSULATING LIQUIDS CONTAINING FLUORESCENT SOLUTES

Darveniza, M., Tropper, H.
***Physical Society, Proceedings of the*, London, v. 78, pt. 5(ii), pp. 854–868, November 15, 1961**

A new phenomenon is reported which is concerned with the excitation of fluorescent solutes in organic liquid dielectrics when high electric fields are applied. The characteristics of the emitted light were studied and related to the pre-breakdown conduction current and the electric strength. Dielectric liquids showing this effect were synthesized by dissolving known concentrations of fluorescent materials in simple organic liquids. These confirmed the experimental results obtained with more complex transformer oil. Experiments are described which show that even highly degassed liquids exhibit a pressure dependence of electric strength if brought into a state of supersaturation by applying tension to the liquid. (*PA*, 1962, #59)

1,123. POLARIZATION OF OPTICAL SPECTRA OF 1-12 BENZ-PERYLENE ($C_{22}H_{12}$)

Ganguly, S. C., Mukherjee, B. C.
***Physical Society, Proceedings of the*, London, v. 79, pt. 1, pp. 220–221, January 1962**

Measurements were made on two absorption systems of thin crystals at room temperature. The first system consists of one band with a peak at 4602 Å and a polarization ratio (I_b/I_a) of 1.04, while the second system contains two of the four bands seen in the solution spectrum with peaks at 3895 and 4120 Å and polarization ratios of 1.71 and 1.88, respectively. It is concluded that the second absorption system is due to an electronic transition directed along the short axis of the molecule, and it is suggested that the first system is due to a long-axis polarized transition, which is considerably depolarized by the induced polarization from the more intense second system. (*PA*, 1962, #6572)

1,124. THE SCINTILLATION PHENOMENON IN ANTHRACENE. I. RADIATION DAMAGE

Clarke, H. B., Northrop, D. C., Simpson, O.
***Physical Society, Proceedings of the*, London, v. 79, pt. 2, pp. 366–372, February 1962**

The effects of radiation damage on the scintillation efficiency of anthracene crystals are shown to be comparatively small. They cannot account for the low efficiency observed for particles of high specific ionization, even where the integrated effects of prolonged irradiation are very marked. Some evidence is found for a reduction in scintillation efficiency in impure anthracene, where emission occurs only from impurity centers, but this is a cooperative effect between excited states and is not connected with permanent radiation damage. (*PA*, 1962, #6636)

1,125. THE SCINTILLATION PHENOMENON IN ANTHRACENE. II. SCINTILLATION PULSE SHAPE

Gibbons, P. E., Northrop, D. C., Simpson, O.
***Physical Society, Proceedings of the*, London, v. 79, pt. 2, pp. 373–382, February 1962**

Detailed examination of the scintillation pulse shape in anthracene leads to the hypothesis that the slow components (~ 1 μsec decay time) are due to short-range interactions between pairs of excitons. These components are observed in the fluorescence decay due to pulsed ultraviolet excitation when the intensity is increased to produce an exciton density approaching that near the track of an ionizing particle. A number of deductions concerning the scintillation pulse shape in impure anthracene are borne out by experiment. (*PA*, 1962, #6637)

1,126. THE FLUORESCENCE AND SCINTILLATION DECAY TIMES OF CRYSTALLINE ANTHRACENE

Birks, J. B.
***Physical Society, Proceedings of the*, London, v. 79, pt. 3, pp. 494–496, March 1962**

The experimental data are analyzed and conclusions are drawn. The molecular decay time τ_0 of a thin anthracene crystal lamina at room temperature is 19 nsec. The thick crystal values are increased by self-absorption to 31.6 nsec (volume excitation, e.g., by γ-rays), 24.1 nsec (surface excitation, e.g., by ultraviolet or α-rays, and emission observed by transmission) and 19.4 nsec (surface excitation, and observation by reflection). Surface oxidation or reduction in crystal thickness yields lower values. For microcrystals of dimension comparable with the exciton mean free path (~ 0.1 μ), the decay time is reduced below τ_0 due to premature conversion of excitons into photons at the crystal surface. (*PA*, 1962, #8582)

1,127. THE PHOTOLUMINESCENCE DECAY OF ORGANIC CRYSTALS

Birks, J. B., King, T. A., Munro, I. H.
***Physical Society, Proceedings of the*, London, v. 80, pt. 2, pp. 355–361, August 1962**

The photoluminescence decay of single (1 cm^3) organic crystals was observed over the time interval 0–250 nsec, using a pulsed light source, fast photomultiplier, and pulse-sampling oscilloscope. The initial decay is exponential with decay time τ_0: for anthracene (fresh surface), 25.8 nsec; naphthalene, 82 nsec; *p*-terphenyl, 6.2 nsec; and *trans*-stilbene, 6.0 nsec. The decay of anthracene with an aged surface approximates to two successive exponentials with $\tau_1 \sim 16$ nsec, $\tau_2 \sim 32$ nsec. The decays of *trans*-stilbene, anthracene (fresh surface), and *p*-terphenyl are exponential over 100 (~ 17 decay periods), 250, and 100 nsec, respectively. (*PA*, 1962, #18,869)

1,128. DELAYED FLUORESCENCE FROM MICROCRYSTALLINE AROMATIC HYDROCARBONS

Stevens, B., Hutton, E.
***Physical Society, Proceedings of the*, London, v. 81, pt. 5, pp. 893–897, May 1963**

A small ($<1\%$) component of delayed fluorescence was observed from the sublimates of pyrene, 3,4-benzpyrene, 3,4-benztetraphene, chrysene, and coronene excited by ultraviolet light *in vacuo* at room temperature. The spectrum of this component is similar to that of the total luminescence emitted at room temperature, but it persists for some milliseconds after excitation cutoff. The failure to observe the delayed fluorescence in the presence of air and the increase in intensity of the delayed component with the state of subdivision of the solid particles indicates that the emission originates at the crystal surface. The decay of the fluorescence in the millisecond region is virtually exponential for 3,4-benzpyrene and 3,4-benztetraphene, but is nonexponential for the other compounds.

1,129. THE BEHAVIOURS OF FREE RADICALS TRAPPED IN γ-IRRADIATED POLYETHYLENE

Kashiwabara, H., Shinohara, K.
***Physical Society of Japan, Journal of the*, v. 15, no. 6, p. 1129, June 1960**

Samples of high-density Marlex 50 and low-density Sumikathene were irradiated in vacuum at room temperature and examined by ESR. The two gave similar spectra; from these the yield of free radicals as a function of radiation dosage, and the number of radicals remaining after heating as a function of temperature were determined. It is suggested that free radicals are trapped in the crystalline regions of the samples, and that they disappear on heating because of the melting of the crystalline regions. (*PA*, 1961, #14,344)

1,130. EMISSION SPECTRA FROM GLOW DISCHARGE THROUGH VAPORS OF AROMATIC HYDROCARBONS AND *n*-HEXANE

Nishi, M., Hamamura, S., Araki, H.
***Physical Society of Japan, Journal of the*, v. 15, no. 8, p. 1536, August 1960**

Many aromatics show four regions of emission, designated "A," "B," "C" and "D." "A" is due to π-electron transitions in the benzene ring, and "D" to benzyl radicals. Because of the variation of intensity with pressure and with nature of the aromatic, Schuler's assignments of the "B" and "C" continua to C_6H_5CH and C_6H_5C radicals are doubted. (*PA*, 1961, #14,044)

1,131. THE ENERGY SPECTRA OF SECONDARY ELECTRONS IN VARIOUS MATERIALS IRRADIATED BY GAMMA RAYS FROM ^{60}Co AND ^{137}Cs

Oda, N., Suzuki, H.
***Physical Society of Japan, Journal of the*, v. 15, no. 12, pp. 2365–2366, December 1960**

Measurements were made with a scintillation spectrometer, and target materials of polyethylene, Al, Cu, and Pb were used. Energy spectra data are given over the energy range 0–1.4 Mev for Co^{60} and 0–0.7 Mev for Cs^{137}. (*PA*, 1961, #13,120)

1,132. ELECTRON SPIN RESONANCE IN IRRADIATED POLYTETRAFLUOROETHYLENE: TEMPERATURE DEPENDENCE OF THE SPECTRA

Tamura, N.
***Physical Society of Japan, Journal of the*, v. 16, no. 11, pp. 2338–2339, November 1961**

The temperature dependences of the spectral shape are examined and some data are given. ESR spectra of irradiated polytetrafluoroethylene at 300 and 77°K are graphed. The relation between the spectral changes and the properties and structures of the polymers is discussed.

1,133. ELECTRON SPIN RESONANCE STUDIES OF IRRADIATED HIGH POLYMERS: POLYETHYLENE

Kashiwabara, H.
***Physical Society of Japan, Journal of the*, v. 16, no. 12, pp. 2494–2503, December 1961**

The molecular structure and behavior of the free radicals produced in irradiated polyethylene were investigated by means of electron spin resonance. ESR spectra of high polymers are, in general, so complicated that the identification of the hyperfine structure of the spectral patterns observed is difficult. Reasonable interpretations could, however, be made for polyethylene. Variations of spectral shape and spectral intensities at various temperatures were discussed in connection with the identification of the free radicals produced and some of the irradiation effects in polyethylene. (*PA*, 1962, #3779)

1,134. PHOSPHORESCENCE OF NAPHTHALENE-DOPED CRYSTALS OF DURENE

Hayakawa, S., Nakamura, T.
***Physical Society of Japan, Journal of the*, v. 18, no. 4, pp. 531–535, April 1963**

Fluorescence and phosphorescence have been observed in a naphthalene-doped crystal of durene. Measured fluorescence spectra under various conditions show transfer of excitation energy from durene to naphthalene molecules and a buildup of a new green band by irradiation of shorter ultraviolet light. Phosphorescence spectra and decays show that phosphorescence is due to a transition from a triplet state to a ground state in a naphthalene molecule. Two decay times have been observed: a larger one belonging to an ordinary triplet state, and a smaller one belonging to a triplet state coupled with a newly introduced center emitting a green band. An energy level scheme in the crystal is presumed.

1,135. INFLUENCE OF DISORDER ON THE LIFETIME OF POSITRONS IN ANTHRACENE

Cottini, C., Fabri, G., Gatti, E., Germagnoli, E.
***Physics and Chemistry of Solids*, v. 17, no. 1/2, pp. 65–68, December 1960**

The decay features of positrons in anthracene were investigated using both single- and polycrystals at temperatures between −196 and 295°C. In solid specimens the annihilation lifetime was 3.7×10^{-10} sec independent of temperature, but a very notable effect was found near the melting point (218°C), a complex decay appearing at about 210°C. Neutron-irradiated specimens showed a complex decay even at room temperature. (*PA*, 1961, #17,524)

1,136. THERMOLUMINESCENCE STUDIES OF THE γ-RAY IRRADIATED FERROELECTRICS ROCHELLE SALT AND GUANIDINE ALUMINUM SULFATE HEXAHYDRATE

Gilliland, J., Jr., Yockey, H. P.
***Physics and Chemistry of Solids*, v. 23, pp. 367–374, April 1962**

Samples of rochelle salt and guanidine aluminum sulfate hexahydrate were irradiated with various doses of Co^{60}

gamma rays up to 3.5×10^6 r at liquid nitrogen temperature, after which they were warmed at a constant rate and observed with a 1P28 photomultiplier tube. The reagent grade rochelle salt powder was found to produce a glow peak at about −61°C, corresponding to a trap depth of about 0.42 ev, which was removed completely by two recrystallizations from water solution. Rochelle salt single crystals also yield no detectable thermoluminescence, indicating a maximum trap concentration significantly less than 10^6/g.

Guanidine aluminum sulfate hexahydrate showed three glow peaks at −146, −119 and about −5°C, corresponding to trap depths of 0.25, 0.31 and 0.54 ev, respectively. The major peak at −146°C becomes more prominent as the dose is increased to 3.5×10^6 r. At low doses (10,000 r) the −119°C peak is largest, but becomes completely concealed by the lower temperature peak at 3.5×10^6 r. The low and very broad peak at −5°C is most easily seen at intermediate doses of 10^5 and 10^6 r, becoming undetectable at lower doses and becoming poorly resolved at higher doses. Trap concentration for an exposure of 3.5×10^6 r is estimated to be 7×10^9/g.

1,137. OPTICAL MASER ACTION IN EUROPIUM BENZOYLACETONATE

Lempicki, A., Samelson, H.
***Physics Letters*, v. 4, no. 2, pp. 133–135, March 15, 1963**

The observation is reported of optical maser action in a metallo-organic complex contained in solution. The new feature of this system is that the emitting ion is excited by an energy transfer process rather than by direct absorption of pump radiation. Results of the experiment are presented and discussed. Stimulated emission spikes are evident and the threshold of EuB_3 is about twice that of ruby.

1,138. CHARACTERISTICS OF SCINTILLATING SUBSTANCES. II

Fort, A.
***Pokroky Matematiky, Fysiky a Astronomie*, v. 3, pp. 161–173, 1958**

The decay of luminescence is studied by observations of three processes: fluorescence decay, which is temperature independent; phosphorescence, which is temperature dependent; and bimolecular decay, which depends on the density of excitation. For the first process, anode pulses of a photomultiplier are observed on an oscilloscope. For the second, the scintillation material is irradiated by periodic X-rays or UV light, the resulting periodic luminescence observed, and the intensity and phase shift measured. For the third, the photomultiplier pulse is superimposed on its own delayed and inverted signal. The measured properties of organic plastic, liquid inorganic, and alkali halide scintillators are given. Results are discussed and analytical expressions are set up.

1,139. PLASTIC SCINTILLATORS CONTAINING 1,2-DI-(1-NAPHTHYL)-ETHYLENE

Nagornaya, L. L., Kilimov, A. P.
***Pribory i Tekhnika Eksperimenta*, v. 1959, no. 4, pp. 63–65, July–August 1959**
(Translated from the Russian in *Instruments and Experimental Techniques*, v. 1959, no. 4, pp. 577–580, July–August 1959)

The luminescence and scintillation properties of 1,2-di-(1-naphthyl)-ethylene solutions in polystyrene were studied. By the method of high-temperature polymerization, plastic scintillators were obtained that contained 1,2-di-(1-naphthyl)-ethylene serving as the basic luminescence admixture or as a spectrum shifter. By γ-excitation, these scintillators produced a luminescence yield reaching, respectively, 125–130% and 140–145% of the luminescence yield of a 2% solution of *p*-terphenyl in polystyrene.

1,140. MEASUREMENT OF PLASTIC SCINTILLATOR LIGHT YIELDS

Zaitseva, A. D., Panov, Yu. N.
***Pribory i Tekhnika Eksperimenta*, v. 1961, no. 1, pp. 64–67, January–February 1961**
(Translated from the Russian in *Instruments and Experimental Techniques*, v. 1961, no. 1, pp. 63–66, September 1961)

The dependence of the values of relative scintillation light yields on specimen dimensions and the excitation source shape has been determined. The existence of this dependence is determined by the different degrees of natural radiation absorption in different specimens.

1,141. ON THE DECAY TIME OF PLASTIC SCINTILLATORS

Baroni, E. E., Kilin, S. F., Kovyrzina, K. A., Rozman, I. M., Shoniya, V. M.
***Pribory i Tekhnika Eksperimenta*, v. 1961, no. 3, pp. 72–74, May–June 1961**
(Translated from the Russian in *Instruments and Experimental Techniques*, v. 1961, no. 3, pp. 486–489, December 1961)

An account is given of measurements of the scintillation decay time and the relative light output of a number of plastic scintillators based on polystyrene and polyvinyl toluene. It is shown that some of these crystals are faster than stilbene.

1,142. NEW SCINTILLATING ORGANIC SINGLE CRYSTALS

Naboikin, Yu. V., Dobrokhotova, V. K., Uglanova, V. V., Zadorozhnyi, B. A., Malkes, L. Ya.
***Pribory i Tekhnika Eksperimenta*, v. 1962, no. 1, pp. 57–59, January–February 1962**
(Translated from the Russian in *Instruments and Experimental Techniques*, v. 1962, no. 1, pp. 56–58, September 1962)

Data on scintillation effectiveness of mixed single crystals are summarized. Luminescence yields from naphthalene with

1,2-di-β-naphthylethylene and 4-phenylstilbene, and with 1,2-di-β-naphthylethylene and 1-β-naphthyl-2-(4-biphenylyl)-ethylene, are reported.

1,143. MAGNETIC AND ELECTROMAGNETIC PROPERTIES OF MACROMOLECULES

Blyumenfeld, L. A.
***Priroda*, v. 50, no. 2, pp. 55–59, February 1961**

The paramagnetic electron resonance absorption of high-polymer ribonucleic acid (RNA) and deoxyribonucleic acid (DNA) and of complexes with serum albumin and with egg albumin is measured at a wavelength of 3.2 cm, and the effects of pH and temperature are investigated. These substances resemble antiferromagnetics rather than free radicals, and the phenomenon is called "pseudoferromagnetism"; it is a structural effect. A theoretical model is developed. The dielectric constant of DNA can exceed 100,000.

1,144. DECAY TIMES OF HIGH-ENERGY INDUCED LUMINESCENCE

Burton, M., Ghosh, A., Yguerabide, J.
***Radiation Research*, Supplement 2, pp. 462–470, 1960**
(Proceedings of Bioenergetics Symposium, Brookhaven National Laboratory, Upton, N. Y., October 12–16, 1959, sponsored by the U. S. Atomic Energy Commission)

1,145. PATHWAYS OF ENERGY TRANSFER IN BIOLUMINESCENCE

Seliger, H. H., McElroy, W. D.
***Radiation Research*, Supplement 2, pp. 528–538, 1960**
(Proceedings of Bioenergetics Symposium, Brookhaven National Laboratory, Upton, N. Y., October 12–16, 1959, sponsored by the U. S. Atomic Energy Commission)

Chemical interactions are considered, and physical investigations of quantum yield and spectral emission are reported.

1,146. PARAMAGNETIC RESONANCE OF PHOSPHORESCENT ORGANIC MOLECULES

Hutchison, C. A., Jr.
***Record of Chemical Progress*, Kresge-Hooker Scientific Library, v. 24, no. 2, pp. 105–128, 1963**

1,147. PARAMAGNETIC RELAXATION OF FREE RADICALS IN IRRADIATED POLYETHYLENE

Yoshida, H., Hayashi, K., Okamura, S.
***Reports on Progress in Polymer Physics in Japan*, v. 6, pp. 253–256, 1963 (in English)**
(Available through Kobayasi Institute of Physical Research, Kokubunji, Tokyo, Japan)

In order to clarify the physical situation of free radicals trapped in irradiated polyethylene, microwave power saturation phenomena of ESR on the radicals are measured and paramagnetic relaxation mechanisms of the radicals are discussed. The saturation phenomena on each radical are examined under various measuring temperatures and various radical concentrations.

The ESR measurements are carried out at 9400 Mc, and the saturation phenomena are observed by the dual-attenuator method. Some observed saturation curves are shown.

1,148. EFFECTS OF CRYSTALLINITIES ON THE ESR SPECTRUM OF IRRADIATED POLYETHYLENE

Tamura, N., Shinohara, K.
***Reports on Progress in Polymer Physics in Japan*, v. 6, pp. 261–264, 1963 (in English)**
(Available through Kobayasi Institute of Physical Research, Kokubunji, Tokyo, Japan)

The samples used were different kinds of polyethylene and were prepared in the form of powder or pellets. Different crystallinities of the sample were obtained by different thermal treatments. Irradiation was carried out at 77°K *in vacuo* with electrons from a Van de Graaff accelerator or γ-rays from Co^{60}.

ESR spectra obtained for various samples irradiated to 40 Mrad with electrons are shown.

1,149. ELECTRON SPIN RESONANCE STUDIES OF IRRADIATED POLYVINYLFLUORIDE AND POLYVINYLIDENEFLUORIDE

Tamura, N., Shinohara, K.
***Reports on Progress in Polymer Physics in Japan*, v. 6, pp. 265–268, 1963 (in English)**
(Available through Kobayasi Institute of Physical Research, Kokubunji, Tokyo, Japan)

There is much interest in the ESR spectra of polymers intermediate in degree of fluorination between polyethylene and polytetrafluoroethylene; namely, polyvinylfluoride (PVF), polyvinylidenefluoride (PVdF), and polytrifluoroethylene. Studies on PVF and PVdF are described.

The samples used were in the form of powders which were molded into cylinder form. Irradiation was carried out *in vacuo* at 77°K with electrons from a Van de Graaff accelerator, or at room temperature with γ-rays of Co^{60}.

1,150. ESR STUDIES OF RADIATION GRAFT-COPOLYMERIZATION OF POLYETHYLENE AND STYRENE. I. BEHAVIORS OF GRAFTING AND FREE RADICALS AFTER IRRADIATION

Tamura, N., Tachibana, H., Takamatsu, T., Shinohara, K.
***Reports on Progress in Polymer Physics in Japan*, v. 6, pp. 269–272, 1963 (in English)**
(Available through Kobayasi Institute of Physical Research, Kokubunji, Tokyo, Japan)

In many irradiated polymers the presence of trapped radicals has been detected by ESR method. The radicals may initiate graft-copolymerization. This phenomenon is investigated by observing the behaviors of radicals both after irradiation and during grafting. In this report studies are given for the grafting of styrene onto polyethylene.

The sample of polyethylene was irradiated with electrons from a Van de Graaff accelerator *in vacuo* at room temperature, and was then brought into contact with styrene vapor which can diffuse into the polymer and thus reach the trapped radical sites.

1,151. TEMPERATURE DEPENDENCE OF SCINTILLATION PULSES IN ANTHRACENE AND CsI(Tl)

Homma, S., Takemoto, S.
***Review of Scientific Instruments*, v. 32, no. 9, pp. 1055–1056, September 1961**

Scintillation pulses were investigated for anthracene over the temperature range −269 to 20°C and for CsI(Tl) over the range −130 to 20°C, using polonium α-particles as a source of excitation. It was found that: (1) The pulse height of anthracene varies linearly with temperature over the range investigated; the temperature coefficient was found to be −0.61 ± 0.04% change in pulse height/°C. (2) The temperature coefficient of CsI(Tl) is a nonlinear function of temperature, the pulse height between −50 and 20°C being constant. It was also found that the resolution of the α-particle peak increased as the temperature decreased. The results obtained are compared with those of other workers. (*PA*, 1961, #17,918)

1,152. RELATIONS BETWEEN PERTURBATION EFFECTS ON THE AROMATIC STATE AND THE ULTRAVIOLET ABSORPTION SPECTRA OF ALKYLBENZENES

Titeica, R., Vintu, V., Trutia, A., Popescu, M.
***Revue de Physique, Academie de la Republique Populaire Roumaine*, v. 6, no. 2, pp. 225–244, 1961 (in French)**

A large number of alkylbenzenes have been studied and values obtained for the oscillator strengths. The results provide evidence for the authors' contention that these compounds can be differentiated spectroscopically in an easier fashion by using oscillator strengths rather than the more commonly used maximum extinction coefficients. (*PA*, 1962, #8107)

1,153. LUMINESCENCE OF SENSITIZING DYES. INFLUENCE OF THE DYE STRUCTURE ON ITS LUMINESCENCE

Kiciak, K.
***Roczniki Chemii*, v. 37, no. 2, pp. 225–247, 1963**

1,154. IDENTIFICATION OF FREE RADICALS BY USING THE METHOD OF ELECTRON PARAMAGNETIC RESONANCE

Blyumenfeld, L. A.
***Rol Perekisei i Kisloroda v Nachalnykh Stadiyakh Radiobiologicheskogo Effekta, Akademiya Nauk SSSR, Institut Biologicheskoi Fiziki*, pp. 97–98, 1960**

Radicals of the type $R - O - O^{\cdot}$ show an electron paramagnetic resonance spectrum in the form of asymmetric singlets of width some tens of oersted, depending on anisotropy of the *g* factor. Additional experiments are necessary.

1,155. RADIATIONLESS CONVERSION FROM THE TRIPLET STATE

Hoffman, M. Z., Porter, G.
***Royal Society of London, Proceedings of the, Series A — Mathematical and Physical Sciences*, v. 268, no. 1332, pp. 46–56, June 19, 1962**

The first-order decay of triplet states of naphthalene, anthracene, phenanthrene, and their halogenated derivatives was studied in cyclohexane and viscous paraffin solutions. The decay results partly from a bimolecular quenching process and partly from a true first-order radiationless conversion to the ground state. The rate of the quenching process is a function of the solvent, and, in anthracene derivatives, of the extent to which the solutions have been irradiated. The rates of radiationless conversion can only be measured when they exceed the rates of quenching processes. This is the case for all the anthracene derivatives in viscous paraffin, for the bromoanthracenes in cyclohexane, and probably for bromophenanthrene in viscous paraffins. Bromination of anthracene is ten times more effective in enhancing conversion than chlorination at the same position, and halogenation at the 9,10 positions has four times the effect of halogenation at other positions. In the one case where it could be tested (dibromoanthracene), the rate of radiationless conversion was unchanged by a 170-fold increase of solvent viscosity.

1,156. A COMPARISON OF THE EFFECTS OF ULTRAVIOLET AND GAMMA RADIATION IN POLYMETHYLMETHACRYLATE

Charlesby, A., Thomas, D. K.
***Royal Society of London, Proceedings of the, Series A — Mathematical and Physical Sciences*, v. 269, no. 1336, pp. 104–124, August 21, 1962**

The exposure of polymethylmethacrylate (PMM) and many other macromolecules to high-energy γ- or electron radiation produces a degradation of the molecular chains. This may result from either ionization or excitation. Ultraviolet light results in excitation only. This paper compares the effects of these forms of radiation. The degradation of PMM was studied in thick or thin films, and in solutions in benzene. It is found that at room temperature degradation (random main chain fracture) occurs with ultraviolet radiation, whereas at higher temperatures the reaction is one of chain depolymerization. The energy absorbed per main chain fracture is about 550 ev with ultraviolet radiation, so that less than 1% of the quanta absorbed is effective; this compares with about 65 ev of γ-energy absorbed per fracture. Apart from this difference in efficiency, the two reactions are very similar. In both cases the number of fractures is proportional to dose and the radicals formed (as seen by ESR) are identical in character. Somewhat similar changes also appear in the optical spectrum, although these may be modified by surface oxygen. These results show no significant contribution from any ionization produced by high-energy radiation. (*PA*, 1962, #18,503)

1,157. DELAYED FLUORESCENCE FROM SOLUTIONS OF ANTHRACENE AND PHENANTHRENE

Parker, C. A., Hatchard, C. G.
***Royal Society of London, Proceedings of the, Series A — Mathematical and Physical Sciences*, v. 269, no. 1339,**
pp. 574–584, October 9, 1962

Delayed fluorescence was observed in solutions of anthracene or phenanthrene alone, and sensitized delayed fluorescence from anthracene was observed in solutions of phenanthrene containing traces of anthracene. The intensities of both the delayed fluorescence and the sensitized delayed fluorescence were found to be proportional to the square of the rate of absorption of exciting light. The results can be explained in terms of a mechanism in which triplet–triplet quenching produces a molecular species carrying the energy from two triplet molecules. The proposed process could apply to other photochemical systems and may have a bearing on the mechanism of photosynthesis. (*PA*, 1963, #142)

1,158. THE THERMOLUMINESCENCE OF IRRADIATED POLYETHYLENE AND OTHER POLYMERS

Charlesby, A., Partridge, R. H.
***Royal Society of London, Proceedings of the, Series A — Mathematical and Physical Sciences*, v. 271, no. 1345,**
pp. 170–187, January 15, 1963

The thermoluminescence glow curves of various polymers were observed in the temperature range 77°K to ice point after Co^{60} γ-irradiation, and a number of them are reproduced. A detailed study of polyethylene thermoluminescence was made. The glow curve of this material in the absence of oxygen comprises three glow peaks, the α, β, γ peaks, whose luminescence intensities are proportional to irradiation dose for doses below 50 krad. The α, β, γ peaks all decay exponentially at constant temperature, and a study of the kinetics involved shows that all these peaks have the same activation energy at the lowest temperatures. At higher temperatures the β and γ peaks each show two different transition points, one in the visible region and one in the ultraviolet, which appear to be related to two of the known structural transitions of polyethylene. The glow curves of a variety of different polyethylenes were recorded. By comparison of these, it was found that the relative heights of the α, β, γ peaks are dependent on the degree of crystallinity of the materials, but the normal chemical impurities present in commercial polyethylenes have no effect on their glow curves. (*PA*, 1963, #4994)

1,159. THE EFFECT OF OXYGEN ON THE THERMOLUMINESCENCE OF IRRADIATED POLYETHYLENE

Charlesby, A., Partridge, R. H.
***Royal Society of London, Proceedings of the, Series A — Mathematical and Physical Sciences*, v. 271, no. 1345,**
pp. 188–206, January 15, 1963

The main thermoluminescence glow curve, the α, β, γ glow curve, of polyethylene irradiated by γ-rays at 77°K was found to be greatly affected by molecular oxygen absorbed in the material before irradiation. The oxygen removes the β and γ peaks almost entirely at low irradiation doses and adds another peak, the ε peak, at a lower temperature than these to form an α, ε glow curve. Kinetic studies showed that the ε peak has a higher probability constant at low temperatures than any of the α, β, γ peaks, but that it shares the same common activation energy. Since the ε luminescence cannot be observed at 77°K, it seems that some change, perhaps a structural change, must occur during warming from 77°K before it can begin to appear. The oxygen effect can be removed by pumping or by a pre-irradiation followed by preheating. The latter method is shown to remove the oxygen by conversion into peroxide radicals, produced when the oxygen combines with alkyl radicals formed during the pre-irradiation. The ε peak was found to occur only in the presence of oxygen molecules, but not with oxygen in the form of peroxides. Peroxide radical formation was observed by the electron spin resonance (ESR) method. ESR measurements also showed that thermoluminescence in polymers was not a direct product of free radical reactions. Various possible thermoluminescence mechanisms are discussed, and it is shown that the polyethylene thermoluminescence phenomena can be explained on the basis of a model involving the trapping of electrons followed by their recombination with different types of luminescence centers. (*PA*, 1963, #4995)

1,160. EXCIMER FLUORESCENCE. I. SOLUTION SPECTRA OF 1:2-BENZANTHRACENE DERIVATIVES

Birks, J. B., Christophorou, L. G.
***Royal Society of London, Proceedings of the, Series A — Mathematical and Physical Sciences*, v. 274, no. 1359,**
pp. 552–564, August 13, 1963

Observations have been made of the concentration dependence of the fluorescence spectra of solutions of 1:2-benzanthracene and 15 of its hydrocarbon derivatives. All of the compounds, except the 9,10-dimethyl derivative, exhibit dimer emission at higher concentrations. The lower excited states, ${}^1L_b$ and ${}^1L_a$, satisfy Förster's conditions for fluorescent dimer formation. The factors determining the relative quantum yield of excimer fluorescence are discussed. The different types of crystal fluorescence spectra shown by the compounds are explained in terms of excimer formation in the crystal lattice.

1,161. EXCIMER FLUORESCENCE. II. LIFETIME STUDIES OF PYRENE SOLUTIONS

Birks, J. B., Dyson, D. J., Munro, I. H.
***Royal Society of London, Proceedings of the, Series A — Mathematical and Physical Sciences*, v. 275, no. 1363,**
pp. 575–588, October 29, 1963

Measurements have been made of the concentration dependence of the rise and decay time characteristics of the monomer and excimer fluorescence of deoxygenated solutions of pyrene in cyclohexane from 293–340°K. Two independent methods were employed, one using a pulsed light source and a pulse-sampling oscilloscope, and the other a modulated light source and a phase and modulation fluorometer. In conjunction with observations of the monomer and excimer fluorescence quantum efficiencies, the results have been analyzed to determine the six rate parameters which describe the behavior of the system. Values of 6.8×10^{-7} and 0.9×10^{-7} sec are obtained for the radiative lifetimes of the monomer and excimer, respectively. Excimer formation is shown to be a diffusion-controlled collision process in which every collision between excited and unexcited molecules is effective. From the difference in the activation energies for excimer dissociation and formation, the excimer binding energy is found to be 0.34 ev.

1,162. APPARENT CONCENTRATION QUENCHING OF MORPHINE FLUORESCENCE

Brandt, R., Olsen, M. J., Cheronis, N. D.
***Science*, v. 139, no. 3559, pp. 1063–1064, March 15, 1963**

Fundamental fluorescence equations were examined. Deviations from the theoretical were observed by varying the light path length to determine effects on "apparent" fluorescence. It was found that the decrease in emission of morphine solutions with the increase in concentration was caused by absorption effects that prevented excitation of the whole system.

1,163. FINE STRUCTURE OF THE ABSORPTION AND FLUORESCENCE SPECTRA OF SOME PIGMENTS AT 77°K

Litvin, F. F., Personov, R. I.
***Soviet Physics—Doklady*, v. 6, no. 2, pp. 134–136,**
August 1961
(Translation of Entry #758, AI/LS 341)

1,164. DELAYED FLUORESCENCE FROM NAPHTHALENE SOLUTIONS

Parker, C. A.
***Spectrochimica Acta*, v. 19, no. 6, pp. 989–994, June 1963**
(in English)

The delayed emission spectra from solutions of naphthalene at low temperature show the presence of the dimer band which was previously observed by Döller and Förster in the normal fluorescence spectra of concentrated solutions. The relative intensities of the monomer and dimer bands in both the normal and delayed emission spectra of naphthalene solutions at low temperature are qualitatively similar to those observed with pyrene solutions at room temperature. They have been interpreted by a similar mechanism involving triplet–triplet quenching. Approximate values for the triplet formation efficiency of naphthalene have been derived

1,165. FLUORESCENCE SPECTRA OF ORGANIC COMPOUNDS IN SOLUTION. I. ON THE POSITIONS OF THE 0,0-BANDS OF THE FLUORESCENCE SPECTRA

Nakamizu, M., Kanda, Y.
***Spectrochimica Acta*, v. 19, no. 7, pp. 1235–1248, July 1963**
(in English)

Fluorescence spectra of various condensed ring compounds have been studied in various solvents at room temperature. The positions and intensities of the 0,0 bands of the fluorescence spectra were seen to depend on the concentration of the solutions. Especially, the 0,0 bands for anthracene phenanthrene, and two isomers of benzoquinoline agreed well with those of the absorption spectra when sample solutions were highly diluted On the other hand, no agreement was found for the 0,0 bands of the fluorescence and absorption spectra of long molecules, such as *trans*-stilbene, *trans,trans*-diphenyloctatetraene, biphenyl and *p*-terphenyl, even at a very low concentration.

1,166. PHOSPHORESCENCE SPECTRUM OF BENZOIC ACID, METHYL BENZOATE, AND BENZAMIDE AT 90°K

Kanda, Y., Shimada, R., Takenoshita, Y.
***Spectrochimica Acta*, v. 19, no. 7, pp. 1249–1260, July 1963**
(in English)

The phosphorescence spectrum of benzoic acid has been observed in rigid media of ethanol, petroleum ether, cyclohexane, carbon tetrachloride, and benzene at 90°K. Benzoic acid is known to form a hydrogen bond complex with ethanol and a dimer compound in nonpolar solvents. However, the spectra of these various solutions were found to be essentially identical and were very similar to the spectra of methyl benzoate which is regarded as a monomer in polar and nonpolar solvents. The spectra of both compounds appeared extremely sharp in benzene matrix. No frequency due to a carboxylic group was found, and the phosphorescence transitions of the compounds were concluded to be of π–π^* type. The vibrational analyses were made with the infrared data. The out-of-plane vibrations appeared strong. These points are quite anomalous. The fact seems to suggest that benzoic acid and methyl benzoate may be deformed in the solidified solutions. In the spectrum of benzamide, no such anomalous structure has been observed in benzene and in ethanol, although it has a molecular structure very similar to that of benzoic acid.

1,167. SPECTRAL DISPLACEMENT OF FLUORESCENCE OF ANTHRACENE SOLUTIONS AND OF 9,10-DIBROMANTHRACENE IN VARIOUS SOLVENTS

Mihul, C., Pop, V., Haba, M.
***Studii şi Cercetări Ştiinţifice, Fizică şi Ştiinţe Technice*,**
v. 11, no. 2, pp. 175–181, 1960 (in Roumanian)

1,168. A NEW CHEMILUMINESCENT SYSTEM
Chandross, E. A.
***Tetrahedron Letters*, v. 1963, no. 12, pp. 761–765, 1963**

A weakly chemiluminescent reaction involving oxalyl chloride and hydrogen peroxide can be carried out either in a homogeneous solution such as dioxane or in two-phase mixtures such as pentane or benzene with water. The vapors induce fluorescence in indicators, e.g., anthracene, suggesting a possible metastable excited state. Addition of a dioxane solution of $(COCl)_2$ to a dioxane solution of 30% H_2O_2 containing anthracene or a similar compound produces a bright chemiluminescence.

1,169. RADIOLUMINESCENCE OUTPUT OF ORGANIC SUBSTANCES
Chizhikova, Z. A.
***Trudy Fizicheskogo Instituta imeni P. N. Lebedeva, Akademiya Nauk SSSR*, v. 15, pp. 178–229, 1961**

A review is given on radioluminescence, including methods used to measure photoluminescence output of organic crystals, powders, and solutions. Luminescence of organic materials, excited with γ-rays and α-particles, was studied. Outputs in photo- and γ-excitations are compared.

1,170. ACCOUNTING FOR THE REABSORPTION OF IMPURITY LUMINESCENCE IN NAPHTHALENE-ANTHRACENE CRYSTALS
Vishnevs'kii, V. N.
***Ukrains'kii Fizichnii Zhurnal*, v. 3, no. 3, pp. 313–323, 1958**

The profile of the shortest waveband in the luminescence spectrum of the anthracene impurity is established for all anthracene impurity concentrations lying within the range of the solubility of the latter in naphthalene. This makes it possible to correct previous values for the quantum output of the anthracene components of the luminescence. It is shown that, because of the overlapping and absorption of luminescence spectra, about 15–20% of the initial energy emitted by the anthracene impurity molecules is reabsorbed. Introducing this correction into the values of the absolute quantum output of the impurity luminescence, it is possible to improve the accuracy of the earlier appraisal of a number of parameters characterizing the phenomenon of excitation-energy migration in molecular crystals. (*PA*, 1961, #14,646)

1,171. ABSORPTION AND LUMINESCENCE OF IMPURITIES IN ORGANIC COMPOUND CRYSTALS AT 20°K. I. SPECTRA OF SOLUTIONS OF NAPHTHACENE IN DIBENZYL AND DIPHENYL CRYSTALS
Prȳkhot'ko, A. F., Soloviov, A. V.
***Ukrains'kii Fizichnii Zhurnal*, v. 4, no. 1, pp. 92–107, 1959**

Inter alia, the dependence of the spectra on the concentration of the impurity (from 0.01 to 1–2% by weight) for crystals varying in thickness from 1 to 100 μ was investigated. An electron-vibrational analysis of the spectra was carried out. A possible cause of the complex structure is discussed. (*PA*, 1961, #11,374)

1,172. ABSORPTION AND LUMINESCENCE OF IMPURITIES IN ORGANIC COMPOUND CRYSTALS AT 20°K. II. SPECTRA OF NAPHTHACENE SOLUTIONS IN CRYSTALS OF CERTAIN UNCONDENSED AROMATIC HYDROCARBONS
Prȳkhot'ko, A. F., Soloviov, A. V.
***Ukrains'kii Fizichnii Zhurnal*, v. 4, no. 2, pp. 229–238, 1959**

Naphthacene impurities in tolan, stilbene, and *p*-ditolyl crystals were investigated. Polarization of certain bands, particularly pronounced at high concentrations of naphthacene, was observed in the impurity absorption spectra in the given crystals. (*PA*, 1961, #11,375)

1,173. ABSORPTION AND LUMINESCENCE OF IMPURITIES IN ORGANIC COMPOUND CRYSTALS AT 20°K. III. NAPHTHACENE SPECTRA IN CRYSTALS OF CERTAIN PARAPOLYPHENYLS
Soloviov, A. V.
***Ukrains'kii Fizichnii Zhurnal*, v. 4, no. 5, pp. 615–628, 1959**

Electronic absorption and luminescence spectra were obtained for naphthacene impurities in *p*-terphenyl and *p*-quaterphenyl crystals. A comparison was made of electron-oscillatory frequencies in spectra of naphthacene dissolved in a number of organic crystals. The author discusses the question of whether or not the frequencies of the solvents are affected by changes set up in the electron states of the impurity molecule. It is shown that a slight deformation of the naphthacene molecule skeleton by the surrounding solvent crystal molecules is sufficient to explain the observed changes in the electron-oscillatory frequencies. It is noted that the greater the shift of the impurity spectrum toward the long-waves region, as compared with the spectrum of its vapors, the more indistinct the bands in the impurity spectrum. (*PA*, 1961, #14,648)

1,174. ABSORPTION AND LUMINESCENCE OF IMPURITIES IN CRYSTALS OF ORGANIC COMPOUNDS AT 20°K. IV. SPECTRA OF ANTHRACENE IN CRYSTALS OF CERTAIN POLYPHENYLS
Soloviov, A. V.
***Ukrains'kii Fizichnii Zhurnal*, v. 6, no. 1, pp. 56–65, 1961**

Electron energy spectra were obtained for anthracene impurities in diphenyl, *p*-terphenyl, *p*-quaterphenyl, and dibenzyl crystals. By comparing the anthracene spectra in these solvents, the properties inherent in the impurity molecule may be distinguished from those due to the effect of the solvent. The spectra of anthracene and naphthacene impurities in the same solvents are compared. (*PA*, 1962, #6567)

1,175. ABSORPTION AND LUMINESCENCE OF IMPURITIES IN CRYSTALS OF ORGANIC COMPOUNDS AT 20°K. V. SPECTRA OF NAPHTHACENE IN CERTAIN MIXED CRYSTALS OF VARIABLE COMPOSITION
Soloviov, A. V.
Ukrains'kii Fizichnii Zhurnal, v. 6, no. 1, pp. 66–76, 1961

The electronic energy spectra of naphthacene were investigated in crystals of a variable composition of dibenzyl–stilbene, dibenzyl–tolane, and stilbene–tolane. The concentrations of the components constituting the mixed crystals varied from 0 to 100%. The naphthacene concentration was invariable (of the order of 0.01–0.05%). The naphthacene spectra in these mixed crystals were compared with those in dibenzyl, tolane, and stilbene crystals. With low concentrations of one of the substances constituting the mixed crystal, the changes in the naphthacene spectrum are accounted for by the influence of the changes in the crystal lattice of the solvent. With high concentrations the changes in the naphthacene spectrum may be associated with the effect of the molecules of this substance on the naphthacene molecules. The appearance in mixed crystals of absorption bands of naphthacene which are displaced in respect to the absorption bands of naphthacene in crystals of one of the components constituting the mixed crystals is due to the transition of the crystal structure of the mixed crystals, corresponding to one of the components, into the crystal structure of the other component (phase transition). The multiplet structure of the bands in the naphthacene impurity spectra may appear, change or vanish with variations in the composition of the mixed crystals. This may indicate that the naphthacene molecules form in the solvent crystals various centers, the origin of which is due to the crystal structure of the solvent. (*PA*, 1962, #6568)

1,176. ABSORPTION AND LUMINESCENCE OF IMPURITIES IN CRYSTALS OF ORGANIC COMPOUNDS AT 20°K. VI. EFFECT OF THE CRYSTALLINE SOLVENT ON THE FREQUENCY OF THE ELECTRON TRANSITION OF THE IMPURITIES
Soloviov, A. V.
Ukrains'kii Fizichnii Zhurnal, v. 7, no. 5, pp. 492–504, 1962

1,177. ABSORPTION AND LUMINESCENCE OF IMPURITIES IN CRYSTALS OF ORGANIC COMPOUNDS AT 20°K. VII. EFFECT OF THE VARIABLE COMPOSITION OF MIXED CRYSTALS ON THE FREQUENCY OF THE ELECTRON TRANSITION OF THE IMPURITIES IN THEM
Soloviov, A. V.
Ukrains'kii Fizichnii Zhurnal, v. 7, no. 5, pp. 505–511, 1962

Clarification is given of the causes of the displacement of the electron transition in impurity spectra of naphthacene in a mixed dibenzyl-stilbene crystal on varying the concentration of the components of this crystal. An attempt is made to explain the complex structure of the impurity spectra in organic crystals in general. (*PA*, 1962, #23,568)

1,178. THE NEAR ULTRAVIOLET ABSORPTION SPECTRA OF TOLAN
Kharytoneva, O. P.
Ukrains'kii Fizichnii Zhurnal, v. 4, no. 6, pp. 729–733, 1959

The absorption spectrum of tolan vapors and solutions was investigated at 77°K. The luminescence spectrum of a tolan solution in ethyl alcohol was studied at −170°C. The oscillator strengths in spectra of vapors and solutions were determined for electronic transitions of tolan vapors, and solutions in ethyl alcohol at 77°K were compared with the *a*-component of the tolan monocrystals at 20°K. For this purpose the spectrum of the solution was displaced in the ultraviolet by 1680 cm^{-1} and the spectrum of the crystal by 2520 cm^{-1}. (*PA*, 1961, #14,056)

1,179. ABSORPTION AND LUMINESCENCE OF ANTHRACENE IMPURITIES IN 9,10-DIHYDROANTHRACENE CRYSTALS AT 20°K
Vatul'ov, V. N.
Ukrains'kii Fizichnii Zhurnal, v. 5, no. 1, pp. 40–58, 1960

Absorption and luminescence spectra of anthracene impurities were obtained in 9,10-dihydroanthracene crystals at 20°K, and an electronic vibrational analysis was made. The changes in the spectra with change in the impurity concentration were studied. The author discusses the origin of weak satellites of the electronic transition band. Blue satellites in the absorption spectrum, and lines mirror-symmetrical to them in the luminescence spectra, are connected with lattice vibrations. Several series are distinguished in the spectra, intensity rising with concentration; these may be assumed to be due to different impurity centers—deformed and variously incorporated anthracene molecules, pairs of molecules, etc. Among these lines is the strongly polarized line in the absorption spectrum. (*PA*, 1961, #20,020)

1,180. STUDY OF THE NATURE OF THE SELF-ABSORPTION BAND OF A NAPHTHALENE CRYSTAL IN THE TEMPERATURE RANGE 20–290°K
Soskin, M. S.
Ukrains'kii Fizichnii Zhurnal, v. 5, no. 5, pp. 707–710, 1960

1,181. SPECTRAL DISTRIBUTION OF THE DEPENDENCE OF THE TRANSPARENCY OF ANTHRACENE SINGLE CRYSTALS ON THEIR THICKNESS

Brodin, M. S., Marisova, S. V.
***Ukrains'kii Fizichnii Zhurnal*, v. 6, no. 6, pp. 745–750, 1961**

Investigation was made for a number of wavelengths taken from the region of absorption of the first electronic-vibrational transition. The results indicate that the effect of spatial dispersion, which leads to the appearance of supplementary anomalous waves, is most pronounced in the region of the exciton band corresponding to a purely electronic transition.

1,182. SOME PECULIARITIES OF THE ABSORPTION SPECTRA AND LUMINESCENCE OF ANTHRACENE IMPURITIES IN CRYSTALS OF ITS HYDRATED DERIVATIVES

Vatul'ov, V. M.
***Ukrains'kii Fizichnii Zhurnal*, v. 6, no. 6, pp. 750–755, 1961**

On interpreting the spectra of anthracene impurities in crystals of its hydrated derivatives (Entry #1,179), it was assumed that the molecules of the impurity form impurity centers of several kinds. The question of the structure of these centers and the causes of their appearance remained obscure. In the present paper the author presents new data which throw light on this problem, although the complete solution has not yet been found. A recently conducted study of the absorption spectra of hydrated derivatives of anthracene yielded indications as to the orientation of the anthracene impurity molecules in a dehydroanthracene crystal. The peculiarities of the polarization of the bands in the absorption spectrum of this crystal can be accounted for by the fact that the molecules of the impurity are oriented along the length of the solvent molecules. In the case of anthracene impurity in an octahydroanthracene crystal, it was possible to ascertain the cause of the appearance of two kinds of spatially separated centers responsible for series (I) and (II). During crystallization of octahydroanthracene, the first observation is the formation of the high-temperature modification, which passes into the low-temperature modification on lowering the temperature. The phase transition meets with difficulty in a crystal clamped between the windows of a quartz cuvette. Series (I) is due to impurity molecules located in the regions of high-temperature modification; series (II), to molecules located in the regions where rearrangement of the crystal has occurred and which are, apparently, distributed throughout the bulk of the crystal. (*PA*, 1962, #18,835)

1,183. CONCENTRATION EXTINCTION OF PHOSPHORESCENCE

Kislyak, G. M.
***Ukrains'kii Fizichnii Zhurnal*, v. 6, no. 6, pp. 774–776, 1961**

Data are presented on concentration phosphorescence extinction during the excitation of phosphors by light from the long-wave anti-Stokes region of the spectrum. At liquid-O temperature the extinction is explained as resonance migration of energy from the excited to the unexcited molecule.

1,184. INFLUENCE OF THE pH MEDIUM UPON THE ABSORPTION AND LUMINESCENCE SPECTRA OF FLUORESCEIN

Panenko, V. V.
***Ukrains'kii Fizichnii Zhurnal*, v. 6, no. 6, pp. 797–800, 1961**

The influence of pH in liquid and solidifying solutions upon these spectra is analyzed. In liquid solutions the influence of the acids consists in changing the pH medium, which affects the dissociation of the dyestuff. The alteration of the luminescence spectra at the time of transition into the solid phase is regarded as the result of the interaction between the positive ions and of the nature of this interaction, and shows that the pH diminishes in the solidifying process of the melted acid. (*PA*, 1962, #19,565)

1,185. INFLUENCE OF THE TEMPERATURE UPON THE PHOSPHORESCENCE OF ORGANIC DYES

Pankeyeva, A. Yu.
***Ukrains'kii Fizichnii Zhurnal*, v. 6, no. 6, pp. 800–803, 1961**

The temperature extinction of the phosphorescence of fluorescein and tripaflavin solutions at low temperatures was investigated in various solvents: formic and acetic acids and ethyl alcohol. The temperature dependences of the phosphorescence intensity and the lifetime of a molecule in the metastable condition were found. It is shown that elevation of temperature increases the number of non-emitting transitions, at which the energy of the discharged metastable level electron turns into heat, i.e., temperature extinction of phosphorescence occurs. (*PA*, 1962, #18,875)

1,186. INVESTIGATION OF THE FORM OF THE INHERENT ABSORPTION BANDS OF THE NAPHTHALENE CRYSTALS. II.

Soskin, M. S.
***Ukrains'kii Fizichnii Zhurnal*, v. 6, no. 6, pp. 806–812, 1961**

(For Part I, see Entry #1,180). The true form and other characteristics of the bands were investigated at 20–290°K, and partially at 4°K, with "free" bracing of the samples and bracing on the optical contact with the substrate. A comparison with the theory was made for the various bands to determine the type of excitons and the nature of their connection with the lattice. The basic properties of the form of the bands are well described by exciton theory. A number of interesting phenomena are discovered which are not described by the theory. (*PA*, 1962, #18,837)

1,187. PHOSPHORESCENCE SPECTRA OF PHENANTHRENE SOLUTIONS

Teplyakov, P. A.
***Ukrains'kii Fizichnii Zhurnal*, v. 6, no. 6, pp. 812–816, 1961**

The author investigated the phosphorescence spectra of phenanthrene in heptane, hexane, and ethyl alcohol at the temperature of liquid oxygen, and in hexane at the temperature of liquid nitrogen. The spectra were taken on a glass spectrograph and the spectrograms analyzed by means of a microphotometer. The spectra are of a quasilinear nature. The solvents affect the number but not the position of the band maxima. The vibrational structure of the phosphorescence spectra of phenanthrene in hexane was established by the known frequencies of Raman dispersion. A definite regularity is observed in the location of the various lines. First, all the frequency differences agree well with the frequencies of the Raman dispersion of phenanthrene. Secondly, a constant difference of frequencies (1608 cm^{-1}) is noted between the most intense lines (first, seventh, fourteenth, twentieth). Thirdly, the interval between neighboring intense lines (between the first and second, the second and third, the seventh and tenth) is characterized by a constant vibrational frequency of 406 cm^{-1}. At the temperature of liquid oxygen, no doublets are observed in the phosphorescence spectra of phenanthrene solutions. At the temperature of liquid nitrogen, seven doublets were formed as the result of splitting. The wavelengths of the components of the doublets of the phosphorescence spectra of phenanthrene in hexane do not agree with the maxima of the phosphorescence spectra obtained at the temperature of liquid oxygen. (*PA*, 1962, #18,876)

1,188. CERTAIN PROPERTIES OF THE EXCITON ABSORPTION SPECTRUM OF A SODIUM URANYL ACETATE SINGLE CRYSTAL

Brodin, M. S., Dovhȳi, Ya. O.
***Ukrains'kii Fizichnii Zhurnal*, v. 7, no. 1, pp. 31–36, 1962**

Absorption spectra were obtained in circularly polarized light at temperatures of 20 and 4°K. At 20°K nine narrow bands were obtained, characterized to a considerable extent by circular dichroism. Most of them divided into two or three components at 4°K. In the case of one of these bands with a frequency of $\nu_m = 21{,}135$ cm^{-1}, it was shown that its intensity and form depend on the crystal thickness. (*PA*, 1962, #18,849)

1,189. ABSORPTION AND LUMINESCENCE [SPECTRA] OF ANTHRACENE IMPURITIES IN OCTAHYDRO-ANTHRACENE CRYSTALS AT 20°K

Vatul'ov, V. M.
***Ukrains'kii Fizichnii Zhurnal*, v. 7, no. 1, pp. 37–45, 1962**

An electron-vibrational analysis of the spectra was made. The changes in the spectra depending on the changes in the concentration of the impurity and the growth conditions of the crystal were investigated. The results confirm the earlier conclusions as to the origin of the initial multiplet in the spectrum. The lines coinciding by resonance in the absorption and luminescence spectra belong to various spatially distinct centers. Each resonance peak is surrounded by mirror-symmetrical satellites due to vibrations of the solvent lattice. At present, several other spectra of impurities in crystals are known in which mirror symmetry of the structure of initial multiplets is observed. (*PA*, 1962, #18,838)

1,190. ISOTOPIC EFFECT IN NAPHTHALENE CRYSTAL SPECTRA

Sheka, E. F.
***Ukrains'kii Fizichnii Zhurnal*, v. 7, no. 2, pp. 174–179, 1962**

The author investigated the electron absorption spectra of mixed crystals of naphthalene and deutero-substituted naphthalene at 20°K. It was established experimentally that the investigation of the spectra of isotopic compounds can ascertain the origin of sharply polarized bands of the inherent absorption of crystals, solving the question of their belonging to a definite Davydov multiplet. It is possible to determine the edges of the exciton zones, and to establish their position with respect to the point $k = 0$. The principles for determining the sign and value of the effective mass of the exciton are discussed. (*PA*, 1962, #18,821)

1,191. PECULIARITIES OF ABSORPTION AND LUMINESCENCE SPECTRA OF CERTAIN ALKYL DERIVATIVES OF ANTHRACENE AT LOW TEMPERATURES

Vatul'ov, V. M.
***Ukrains'kii Fizichnii Zhurnal*, v. 7, no. 3, pp. 305–314, 1962**

The author investigated the absorption and luminescence spectra of frozen solutions in hexane and of crystals of 9,10-dimethylanthracene, 9,10-diethylanthracene, 9,10-di-*n*-propylanthracene, and 9,10-diisobutylanthracene at 20°K. The absorption spectra of the crystals of all these compounds, except for diisobutylanthracene, are similar to the absorption spectrum of anthracene and differ from it by the width and polarization of the bands. Obtaining line spectra in frozen crystalline solutions established a slight difference between certain frequencies of intramolecular oscillations of anthracene and its derivatives. The luminescence spectrum of the diethylanthracene crystal consists of narrow lines, the appearance of which is linked with the presence of crystal structure defects. The absorption spectra of the crystals of the other three compounds remain wide-band even at the temperature of liquid hydrogen. The luminescence spectrum of the dimethylanthracene crystal is also, evidently, due to an unknown impurity or other defects of the crystal lattice. (*PA*, 1962, #18,823)

1,192. SOME CHARACTERISTICS OF THE OPTICAL PROPERTIES OF DOPED 9,10-DIHYDROANTHRACENE–ANTHRACENE CRYSTALS

Dovbyi, Ye. O.
***Ukrains'kii Fizichnii Zhurnal*, v. 7, no. 3, pp. 315–321, 1962**

The results are given of measurements of absorption and dispersion at 20°K. A comparison of absorption and dispersion was made. The Kramers–Kronig relations were checked. They hold for slight impurity concentrations. With increased impurity concentration, slight but systematic divergences, linked with the probable interactions among the impurity molecules, are noted. On the basis of these data, the author discusses the role of the locality principle in optical dispersion relations. (*PA*, 1962, #18,824)

1,193. INVESTIGATION OF THE FORM OF THE ABSORPTION BANDS OF TOLANE SINGLE CRYSTALS

Brodin, M. S.
***Ukrains'kii Fizichnii Zhurnal*, v. 7, no. 4, pp. 417–421, 1962**

On the basis of an analysis of the results obtained, the conclusion is drawn that the tolane crystal is an intermediate case and not one of the two extreme cases—a small effective mass of the exciton with weak exciton–phonon coupling, or a large effective mass with strong exciton–phonon coupling.

1,194. SPECTRAL INVESTIGATION OF CHEMICAL TRANSFORMATIONS IN CRYSTALLINE TRIPHENYLMETHANE

Shpak, M. T., Soloviov, A. V., Sheremet, N. I., Dmytrenko, Y. P.
***Ukrains'kii Fizichnii Zhurnal*, v. 7, no. 4, pp. 422–429, 1962**

Irradiation with light and β-rays of crystalline triphenylmethane cooled to low temperatures was found to result in the formation of several types of unstable luminescence centers, which vanish when irradiated samples are kept in an oxygen atmosphere at room temperature and may be preserved for several months in the absence of oxygen. Unstable luminescence centers are also formed in triphenylmethane when the latter is subjected to thorough mechanical grinding. An investigation of the luminescence spectra of the unstable luminescence centers in irradiated triphenylmethane showed that one type of center consists of triphenylmethyl radicals. The nature of the other centers has not yet been established. (*PA*, 1962, #21,277)

1,195. DISPERSION AND REFLECTION OF LIGHT IN [FREE] NAPHTHALENE SINGLE CRYSTALS AT 20°K

Soskin, M. S.
***Ukrains'kii Fizichnii Zhurnal*, v. 7, no. 6, pp. 635–642, 1962**

An investigation was made at normal incidence. The experimental setup and the methods of calculation are described. The data of the dispersion and the reflection curves show that within the limits of error the Kramers–Kronig dispersion relations hold for the sharply polarized absorption bands $B_1(\nu = 31{,}623$ cm^{-1}) and $B_2(\nu = 32{,}260$ cm^{-1}). The oscillator forces of various absorption bands of the first electronic transition are determined. (*PA*, 1962, #23,541)

1,196. PHOSPHORESCENCE OF BOROPHTHALIC PHOSPHORS

Kislyak, G. M. Lisenko, G. M.
***Ukrains'kii Fizichnii Zhurnal*, v. 7, no. 12, pp. 1309–1313, 1962**

The temperature dependence of the phosphorescence of phthalic acid in boric acid was studied at 160 to −183°C. The acids were mixed in various proportions and fused at 180–190°C. When borophthalic phosphors were prepared from purified boric acid, the temperature dependence of their phosphorescence followed the exponential phosphorescence extinction law. A deviation was observed for specimens prepared from nonpurified boric acid. The temperature dependence curves of the intensity and the duration of the phosphorescence showed that both decreased with temperature between −120 and +160°C. The activation energy between 160 and 60°C was calculated to be 0.150 ev. Between −183 and 0°C, the phosphorescence intensity remained practically unchanged. The energy of the extinction of the phosphorescence intensity at 100–150°C was 0.80 ev and at 60–100°C it was 1.40 ev. Results supported a previously proposed three-level mechanism of phosphorescence of borophthalic phosphors (α-phosphorescence at high temperature [60–160°C], α- and β-phosphorescence at intermediate temperature [between 60 and −20°C], and β-phosphorescence at low temperature [below −20°C]).

1,197. CONCENTRATION AND TEMPERATURE DEPENDENCE OF PHOTOLUMINESCENCE OF ANTHRACENE VAPOR

Vishnevs'kii, V. N., Pidzirailo, M. S.
***Ukrains'kii Fizichnii Zhurnal*, v. 8, no. 5, pp. 587–590, 1963**

Experimental data taken with the integral photometer method show that in the vapor pressure range of 0.2–1260 mm there is a considerable concentration dependence of the luminescence quenching, and a temperature dependence of the luminescence quenching was observed at 150–310°C. Migration distance of excitation energy was calculated to be 42 A.

1,198. LUMINESCENCE OF CRYSTALLINE OCTADEUTERIONAPHTHALENE DOPED WITH THIONAPHTHENE

Shpak, M. T., Sheremet, N. I.

Ukrains'kii Fizichnii Zhurnal, v. 8, no. 6, pp. 669–676, 1963

The luminescence and absorption spectra of crystalline octadeuterionaphthalene, doped with thionaphthene, were investigated at temperatures 20.4 and 77°K. The doping leads to the formation of local impurity centers of two types which produce luminescence spectra similar to those of pure octadeuterionaphthalene. A band at 31,560 cm^{-1} occurs with introduction of from 1 to 5% of thionaphthene, and the intensity of this band depends upon the percentage.

1,199. PHOSPHORESCENCE SPECTRA OF PHENANTHRENE IN HEPTANE AND IN MAGNESIUM OXIDE

Teplyakov, P. A., Grosul, V. P.
***Ukrains'kii Fizichnii Zhurnal*, v. 8, no. 6, pp. 864–869, 1963**

Phosphorescence was determined for phenanthrene in heptane (77°K) and in MgO (77 and 290°K). Temperature variations for the latter are reported. The phosphorescence of phenanthrene in heptane shows two metastable levels, and characteristic vibration frequencies are obtained.

1,200. ABSORPTION AND LUMINESCENCE [SPECTRA] OF CRYSTALLINE SOLUTIONS OF STILBENE IN TOLAN AT 20°K

Fugol', I. Ya.
***Ukrains' kii Fizichnii Zhurnal Dodatok*, v. 3, no. 2, pp. 40–48, 1958**

Curves were obtained for the impurity absorption $\kappa(\nu)$ and intensity distribution in the luminescence spectrum. It was found that the stilbene molecules are arranged in the tolan crystal in the same way as in their own lattice. The impurity absorption spectra are compared with the absorption spectrum of a pure stilbene crystal. The variation of the impurity absorption and of the luminescence was studied. In the crystalline petals obtained by sublimation, the same changes were noted in the frequency and intensity of the ines as those observed in spectra of crystals obtained on crystallization under pressure. Changes in the luminescence spectrum were observed in the same crystal on repeated heating and cooling. (*PA*, 1961, #11,376)

,201. ABSORPTION OF POLARIZED LIGHT BY PYRENE AND CHRYSENE MONOCRYSTALS

Yeremenko, V. V.
***Ukrains'kii Fizichnii Zhurnal Dodatok*, v. 3, no. 2, pp. 49–55, 1958**

Absorption spectra of these monocrystals, cooled at 20°K, vere photographed in polarized light. The first electronic transition apparently possesses $A_{1g} \rightarrow B_{1u}$ symmetry in pyrene, nd $A_g \rightarrow B_u$ symmetry in chrysene. (*PA*, 1961, #11,384)

1,202. FLUORESCENCE DECAY OF ANTHRACENE IN THE REGION 0.1–10 μsec

Wasson, M. M.
December 1962
United Kingdom Atomic Energy Authority, Harwell, Berks, England
AERE-M 1153

The scintillation decay of an anthracene crystal excited by α-particles, protons, and electrons was measured over the time interval from 0.1 to 10 μsec. The decay was independent of the exciting particle and of the form $I = I_0 \ (1 + t/t_0)^{-1.3}$ where I_0 is the initial intensity of the slow component, t is time and t_0 is a constant. (*PA*, 1963, #11,005)

1,203. STUDY OF ENERGY TRANSFER BY QUENCHING EXPERIMENTS

Brown, F. H., Furst, M., Kallmann, H.
In "Proceedings of the University of New Mexico Conference on Organic Scintillation Detectors, August 15–17, 1960," pp. 37–58
U.S. Atomic Energy Commission, Office of Technical Information, Oak Ridge, Tenn.
(Available in TID-7612, U.S. Dept. of Commerce, Office of Technical Services, Washington, D. C.)

The processes by which excitation energy produced in a bulk material can reach a fluorescent solute are discussed, and quenching experiments were made to determine the relative importance of the processes. The experiments were carried out on solutions of 9,10-diphenylanthracene, fluoranthene, *m*-terphenyl, pyrene, and α-naphthylphenyloxazole in various solvents, using carbon tetrachloride and hexachloroxylene as quenchers. Experiments were also conducted on the quenching of solute fluorescence in polyvinyl naphthalene solid by hexachloroxylene and diphenylmercury. The results indicate that, in solutions, quenching decreases with solvent dilution, and in solids, specific orientation between quencher and excited molecule may be necessary. (*NSA*, 1961, #29,404)

1,204. ON THE INFLUENCE OF BROWNIAN MOTION ON THE TRANSFER OF ENERGY IN SOLUTIONS

Weinreb, A.
In "Proceedings of the University of New Mexico Conference on Organic Scintillation Detectors, August 15–17, 1960," pp. 59–76
U.S. Atomic Energy Commission, Office of Technical Information, Oak Ridge, Tenn.
(Available in TID-7612, U.S. Dept. of Commerce, Office of Technical Services, Washington, D. C.)

The effects of Brownian motion on the process of energy transfer from an excited solvent to an accepting solute were studied by means of experiments on solutions in paraffin oil, using anthracene as the acceptor, and naphthalene, toluene, and anisole as donors. The results are in qualitative agreement with Förster's theory. (*NSA*, 1961 #29,405)

1,205. **SUBSTITUTED *p*-OLIGOPHENYLENES. PART II. SUBSTITUTED *p*-OLIGOPHENYLENES AS LIQUID SCINTILLATION SOLUTES**
Hermann, G., Eichhoff, H. J., Nay, U.
In "Proceedings of the University of New Mexico Conference on Organic Scintillation Detectors, August 15–17, 1960," pp. 92–98
U.S Atomic Energy Commission, Office of Technical Information, Oak Ridge, Tenn.
(Available in TID-7612, U.S. Dept. of Commerce, Office of Technical Services, Washington, D. C.)

(For Part I, see Entry #1,286.) The scintillation properties of substituted *p*-oligophenylenes were investigated in toluene solvent, and data are given. (*NSA*, 1961, #29,407)

1,206. **A COMPARATIVE SCINTILLATION STUDY OF SOME SELECTED BIS-BENZOXAZOLE SOLUTES. BENZOXAZOLES III**
Nyilas, E., Pinter, J. L.
In "Proceedings of the University of New Mexico Conference on Organic Scintillation Detectors, August 15–17, 1960," pp. 99–120
U.S. Atomic Energy Commission, Office of Technical Information, Oak Ridge, Tenn.
(Available in TID-7612, U.S. Dept. of Commerce, Office of Technical Services, Washington, D. C.)

Some tentative proof is presented of an hypothesis concerning the energy absorption and emission mechanism of conjugated bis-benzoxazole solutes. Two series of bis-benzoxazoles were prepared and tested as primary and/or secondary scintillators. A few of the compounds yielded favorable light outputs, and in certain cases the scintillation performance can be directly correlated with corresponding molecular structures. (*NSA*, 1961, #29,408)

1,207. **SOLID AND LIQUID SOLUTION SCINTILLATORS CONTAINING MONOISOPROPYLBIPHENYL**
Funt, B. L.
In "Proceedings of the University of New Mexico Conference on Organic Scintillation Detectors, August 15–17, 1960," pp. 141–160
U.S. Atomic Energy Commission, Office of Technical Information, Oak Ridge, Tenn.
(Available in TID-7612, U.S. Dept. of Commerce, Office of Technical Services, Washington, D. C.)

Studies were conducted on the scintillation properties of monoisopropylbiphenyl (MIPB) in plastic and liquid scintillators. MIPB was found to be an efficient chain transfer agent in vinyl toluene polymerization. The quenching constants of MIPB as solvent were found to be lower than those for toluene. (*NSA*, 1961, #29,410)

1,208. **THE DEPENDENCE OF PULSE HEIGHT ON THE MOLECULAR STRUCTURE OF THE SOLVENT AND FLUOR IN ORGANIC SCINTILLATORS**
Loshaek, S., Sandler, S. R.
In "Proceedings of the University of New Mexico Conference on Organic Scintillation Detectors, August 15–17, 1960," pp. 177–195
U.S. Atomic Energy Commission, Office of Technical Information, Oak Ridge, Tenn.
(Available in TID-7612, U.S. Dept. of Commerce, Office of Technical Services, Washington, D. C.)

Studies were conducted to determine the relationship of scintillation efficiency to the Hammett σ value of the fluor for plastic, liquid, and crystalline scintillators. Results are presented for substituted forms of styrene polymers, polyvinyltoluenes, 2,5-diphenyl-1,3-oxazoles, 2,5-diphenyl-1,3,4-oxadiazoles, and benzene crystals in the form of pulse height vs. σ curves. The implications of the results are discussed, and a scintillation mechanism is proposed. (*NSA*, 1961, #29,412)

1,209. **FLUORESCENCE AND PHOSPHORESCENCE SPECTRA OF β-METHYLNAPHTHALENE IN NORMAL AND ISOPARAFFIN SOLUTIONS AT 77°K**
Levshin, V. L., Mamedov, Kh. I.
***Vestnik Moskovskogo Universiteta, Seriya III, Fiziki, Astronomii*, v. 18, no. 2, pp. 30–36, 1963**

The fine structure of the fluorescence spectra was determined at 77°K for 2-methylnaphthalene in *n*-paraffins of six carbons and above, and in 2,2,4-trimethylpentane. Information concerning the structure of *β*-methylnaphthalene was obtained from the phosphorescence spectra in *n*-hexane.

1,210. **ELECTRONIC SPECTRA OF ORGANIC MOLECULES IN A DIFFUSION MEDIUM**
Gladchenko, L. F., Pikulik, L. G.
***Vestsi Akademii Navuk Belaruskai SSR, Seryya Fizika-Tekhnichnykh Navuk*, v. 1963, no. 1, p. 52, 1963**

1,211. **LENGTH OF DIFFUSION DISPLACEMENT OF EXCITONS IN ANTHRACENE CRYSTALS**
Faidysh, A. N.
***Visnik Kiivs'kogo Universitetu*, no. 3, *Seriya Fizika ta Khimiya*, no. 1, pp. 53–57, 1960**
(See also *Referativnyi Zhurnal, Khimiya*, 1962, #1B260)

A study was made of the concentration dependence of quantum yields of luminescence of the main substance (anthracene) and an impurity (naphthacene). The length of diffusion displacement of excitons l_0 was determined. It is concluded that localized excitons play a basic role in the migration of energy and luminescence.

1,212. **EFFECT OF ELECTRON IRRADIATION ON THE PHOTOLUMINESCENCE OF ANTHRACENE CRYSTALS**
Kucherov, I. Ya., Roskolodko, V. G., Faidysh, A. N.
***Visnik Kiivs'kogo Universitetu*, no. 3, *Seriya Fizika ta Khimiya*, no. 1, pp. 99–103, 1960**
(See also *Referativnyi Zhurnal, Khimiya*, 1962, #1B277)

The effect of electron irradiation (2 and 10 kev) on the intensity and spectra of photoluminescence of pure and im-ure anthracene crystals was investigated.

,213. THE ANISOTROPY OF HYPERFINE SPLITTING IN THE ELECTRON SPIN RESONANCE SPECTRA OF IRRADIATED ORIENTATED POLYMERS

Kiselev, A. G., Mokulskii, M. A., Lazurkin, Yu. S.
***Vysokomolekulyarnye Soedineniya*, v. 2, no. 11,**
pp. 1678–1687, 1960
(Translated from the Russian in *Polymer Science U.S.S.R.*, v. 3, no. 3, pp. 455–466, 1962; published January 1963)

The ESR spectra of irradiated, orientated polymers have een investigated. In polyethylene and polytetrafluorethylene t is possible to observe a strong dependence of the spectra n the orientation of the specimen in the magnetic field. It was found that for polyethylene irradiated at 77°K the hanges in the spectrum agree well with theory for an alkyl adical. For polyethylene irradiated at ~300°K it was possible o obtain an additional doublet splitting of all seven com-onents of the spectrum, which can be a serious argument n favor of the suggestion that an alkyl radical is formed. The SR spectra were obtained by means of a spectrograph at a requency of 9000 Mc with high frequency modulation of the magnetic field, and with automatic recording. The first derivative of the absorption curve was recorded. Theory is also presented.

,214. ON THE STRUCTURE OF PLASTIC SCINTILLATORS—III. INVESTIGATION OF THE TEMPERATURE DEPENDENCE OF THE REFRACTIVE INDEX AND DETERMINATION OF THE TRANSITIONS WITH RESPECT TO TEMPERATURE

Baroni, E. E.
***Vysokomolekulyarnye Soedineniya*, v. 3, no. 7,**
pp. 956–959, 1961

The internal structure of polystyrene scintillators (PS) is discussed on the basis of the optical determination of various ransition points. Refractive index data have confirmed the nvalidity of the proposition that the organic phosphors ad-mixed with styrene copolymerize with the latter. The meas-urements show that the additions do not affect the PS transi-tion points.

,215. ELECTRON DIFFRACTION STUDY OF A PLASTIC SCINTILLATOR

Aleksandriya, B. V., Baroni, E. E., Shvangiradze, R. R.
***Vysokomolekulyarnye Soedineniya*, v. 3, no. 8, p. 1285, 1961**

An electron diffraction study has been made of the state of aggregation of the luminescent addition p-terphenyl in poly-tyrene scintillators (PS). It has been shown that in PS the addition is in the form of minute crystals.

1,216. RADIOTHERMOLUMINESCENCE OF ORGANIC COMPOUNDS—II

Nikolskii, V. G., Buben, N. Ya.
***Vysokomolekulyarnye Soedineniya*, v. 4, no. 6, pp. 922–925, 1962**

The thermoluminescence of a number of polymeric specimens irradiated with fast electrons at 77°K has been investigated. The positions of the luminescence peaks have been shown to depend upon the preliminary cold drawing of the polymer and upon the degree of its crosslinkage. The heating rate ω and the position T_f of the peaks on the thermoluminescence curves were found to be correlated by the expression: $1/T_f = c_1 - c_2 \log \omega$. These results confirm the earlier conclusion that the shape of the thermoluminescence curve reflects structural changes in the solid during its defrosting. Values for the activation energies of a number of phase transitions in polyethylene and in technical paraffin have also been presented.

1,217. FORMATION AND RECOMBINATION OF FREE RADICALS ON γ-IRRADIATION OF POLYPROPYLENE—I

Milinchuk, V. K., Pshezhetskii, S. Ya., Kotov, A. G., Tupikov, V. I., Tsivenko, V. I.
***Vysokomolekulyarnye Soedineniya*, v. 5, no. 1, pp. 71–74, 1963**

The formation and recombination of free radicals on γ-irradiation of crystalline and amorphous polypropylene have been investigated. It has been established that at an irradiation temperature of 20°C more free radicals accumulate in crystalline than in amorphous polypropylene, whereas the reverse is true at −195°C. The temperature dependence of the free radical concentration in polypropylene irradiated at −195°C is of a different nature in the amorphous and crystalline specimens, and reflects a higher rate of combination of the radicals in the amorphous state. The EPR spectra of crystalline polypropylene have been observed to depend upon the temperature of measurement.

1,218. FLUORESCENCE DECAY TIMES OF ORGANIC CRYSTALS

Schmillen, A.
In "Luminescence of Organic and Inorganic Materials," International Conference Proceedings, New York University, N. Y., 1961, pp. 30–43
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N. Y., 1962

Fluorescence decay time measurements of several solid hydrocarbons and related compounds under α-particle, electron impact, and UV excitation are reported. Different methods of decay measurements are used for different excitations. Under α-excitation the decay time τ was determined from the Fourier spectrum of scintillations, under UV excitation by a phase-fluorometer. For electron impact excitation, a sampling method permitted the determination of the fluorescence intensity vs. time relation.

The samples investigated (polycrystalline powders) were carefully purified and freed from all fluorescing contaminants. Whereas the fluorometer reveals only one decay time, the Fourier analysis of α-excited luminescence gives several decay times for all purified hydrocarbon samples. For anthracene three components were determined with τ values (and relative intensities) of 18.8 (74%), 160 (17%), and 2100 (9%) nsec. The same fluorescence spectrum is emitted by all three components. On the other hand, most samples examined containing fluorescing host molecules (e.g., tetracene in chrysene) showed only one nearly exponential decay time.

The significance of the above for the excitation and energy transfer mechanism is discussed.

1,219. EFFECTS OF TEMPERATURE AND VISCOSITY ON SCINTILLATION DECAY TIMES OF SOLUTIONS

Weinreb, A.
In "Luminescence of Organic and Inorganic Materials,"
International Conference Proceedings, New York University,
N. Y., 1961, pp. 44–61
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N. Y., 1962

The efficiency of energy transfer (ε) from toluene to diphenyloxazole (PPO) is determined for solutions of PPO in (1) toluene, (2) a mixture of toluene and cyclohexane, and (3) a mixture of toluene and paraffin oil. It is found that ε is similar in systems 1 and 2, but considerably lower in system 3. For this last system, ε is further examined as a function of temperature and viscosity. The main part of the work deals with the fluorescence decay times of these systems when excited by electrons. The decay time is measured as a function of temperature in the presence and absence of PPO. In the latter case the measured decay time is that of toluene. In no case is the decay of the PPO solutions strictly exponential. Strong deviations from exponential decay are found in viscous solutions at low temperature. The transfer probabilities are determined from the results. The transfer probability in the viscous systems at low temperatures decreases remarkably with time. This effect becomes smaller with increasing temperature. The transfer efficiencies are computed and compared with the results obtained from intensity measurements of optically excited solutions. The decay of solutions of PPO in paraffin oil (without toluene) is studied. An explanation of the results is attempted.

1,220. ULTRAVIOLET AND LIFETIME STUDIES OF MECHANISMS IN THE SCINTILLATION PROCESS

Berlman, I. B.
In "Luminescence of Organic and Inorganic Materials,"
International Conference Proceedings, New York University,
N. Y., 1961, pp. 62–73
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N. Y., 1962

The technique of using a pulsed beam of electrons to excite an organic scintillation solution and the recording of the resultant pulse of emitted radiation are described. Sample pulse profiles are shown, and the values of the measured decay time of several solvents and solutes are presented. For specific solutions this technique is used to advantage to study the mechanism of nonradiative energy transfer from solvent to solute as a function of the solute concentration. Energy transfer values are determined which agree favorably with those obtained from other coordinated methods. One such method, involving the static excitation of the solution by monochromatic UV radiation and the recording of the fluorescence spectrum, is described. The anomalous changes in the measured value of the decay time and in the shape of the emission spectrum as the solute concentration is increased to a large value are investigated using the above methods.

1,221. FLUORESCENCE QUENCHING STUDIED BY FLASH SPECTROSCOPY

Leonhardt, H., Weller, A.
In "Luminescence of Organic and Inorganic Materials,"
International Conference Proceedings, New York University,
N. Y., 1961, pp. 74–82
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N. Y., 1962

Studies of fluorescence quenching by amines in solution have shown that, generally, an amine is the more efficient a quencher the smaller its ionization potential. This leads to the assumption that in these cases quenching occurs by univalent reduction of the excited molecules. A flash photolysis investigation carried out with solutions of perylene has confirmed this assumption. In the presence of strongly quenching amines, these solutions exhibit a transient absorption with a maximum at 580 mμ when irradiated under conditions such that only perylene absorbs light. The transient substance has been identified as the perylene monoanion radical. In addition to this radical spectrum which is very pronounced in polar solvents such as acetonitrile or dimethylformamide, a weaker absorption around 490 mμ is observed which is due to a triplet–triplet transition of perylene. This absorption is very much enhanced in nonpolar solvents (benzene, methylcyclohexane), where no 580-mμ absorption has been found. These results indicate that (1) stabilization by solvation of ionic radicals is strongly favored in polar solvents, and (2) additional triplet state population may take place by electron exchange.

1,222. QUENCHING OF ELECTRONIC ENERGY TRANSFER IN ORGANIC LIQUIDS

Lipsky, S., Helman, W. P., Merklin, J. F.
In "Luminescence of Organic and Inorganic Materials,"
International Conference Proceedings, New York University,
N. Y., 1961, pp. 83–99
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N. Y., 1962

In a previous publication bromobenzene was shown to quench the luminescence of a dilute air-equilibrated benzene p-terphenyl solution when the system was excited either with 2537 A light or with Co^{60} γ-rays. The quantitative results of this study indicated that:

1. The quenching by bromobenzene involves an interaction with the benzene solvent prior to the benzene-terphenyl transfer process.
2. The quenching efficiency is greater than would be expected on the basis of a diffusion-limited process with geometric cross sections for solvent and quencher.
3. The quenching is about 25% more efficient under high energy irradiation conditions.

These studies have been repeated now in the absence of molecular oxygen and have been extended to a benzene-cyclohexane mixture solvent and to a dibromomethane quencher. The mechanism of the energy transport process both under UV and high energy excitation conditions is discussed.

1,223. THE SENSITIZATION OF BIACETYL FLUORESCENCE IN FLUID SOLUTIONS

Dubois, J. T., Stevens, B.
In "Luminescence of Organic and Inorganic Materials,"
International Conference Proceedings, New York University, N. Y., 1961, pp. 115–131
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N. Y., 1962

The sensitization of biacetyl fluorescence in aerated cyclohexane solutions was studied at 25°C, using naphthalene, benzene, and acetone as donors. The simultaneous quenching of donor fluorescence by biacetyl was also investigated, and it is concluded that the energy transfer process involves the lowest excited singlet states of donor and acceptor in each case, and proceeds at a rate consistent with a diffusion-controlled process.

1,224. ENERGY TRANSFER FROM THE TRIPLET STATE

Porter, G., Wilkinson, F.
In "Luminescence of Organic and Inorganic Materials,"
International Conference Proceedings, New York University, N. Y., 1961, pp. 132–142
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N. Y., 1962

The transfer of electronic excitation energy from the triplet state of a donor molecule resulting in quenching of the donor and the elevation of the acceptor molecule from its singlet ground state to its triplet state has been observed between a number of donor–acceptor pairs in fluid solvents. Using the technique of flash photolysis, the mechanism of transfer has been unequivocally established by observation of the triplet state absorption spectra of both species in most of the cases studied. Energy transfer from excited singlet donors to the triplet state of the acceptor is not observed.

The transfer is diffusion controlled when the energy of the acceptor triplet is considerably lower than that of the donor, but there is no evidence for long-range resonance transfer of the kind found in the analogous singlet energy transfer processes. As the triplet energies become comparable the transfer probability is reduced, and no quenching is observed by molecules with triplet levels higher than that of the donor. Transfer of triplet energy between pairs of aromatic hydrocarbons has been illustrated, and it has been established that complex formation between donor and acceptor cannot be responsible for the transfer observed under the conditions of these experiments.

1,225. DELAYED FLUORESCENCE AND PHOSPHORESCENCE IN CRYSTALS OF AROMATIC MOLECULES AT 4.2°K

Sponer, H.
In "Luminescence of Organic and Inorganic Materials,"
International Conference Proceedings, New York University, N. Y., 1961, pp. 143–152
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N. Y., 1962

Delayed fluorescence has been observed in crystals of naphthalene, phenanthrene, and chrysene at 4.2°K. The naphthalene spectrum consists of two systems, one belonging to naphthalene and another belonging to β-methylnaphthalene. The 0,0 level of the first is placed at 31,574 cm^{-1}. The main portion of this spectrum originates at 30,964 cm^{-1}, which represents a 0–1 transition with a 610 cm^{-1} vibration excited in the ground state. The second system begins at 31,062 cm^{-1} with a strong 0,0 band. The view is confirmed that it belongs to β-methylnaphthalene, present as an impurity in naphthalene. This spectrum appears in delayed fluorescence. Phenanthrene crystals at 4.2°K emit a rather extended fluorescence spectrum originating at 28,636 cm^{-1}. Analysis confirms it as the true fluorescence. It also appears in the delayed emission. Chrysene crystals show a broad, diffuse fluorescence built upon the 25,180 cm^{-1} level. This system is of short extension, appears likewise in the delayed emission, and is the true fluorescence of chrysene. All three crystals exhibit extended phosphorescence spectra. The lifetimes of the emissions have been measured; in all three cases the decay is exponential for the phosphorescence in the absence of oxygen.

1,226. THE EFFICIENCY OF SOLUTION FLUORESCENCE

Bowen, E. J., Seaman, D.
In "Luminescence of Organic and Inorganic Materials,"
International Conference Proceedings, New York University, N. Y., 1961, pp. 153–160
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N. Y., 1962

Solutions of 1- and 2-naphthylamines and certain of their sulphonates in a number of solvents have been examined for fluorescence properties. Fluorescence yields were found to increase in general with a lowering of temperature to a constant value which in many cases is not unity. Such limiting yields of less than unity seem to arise from interaction of excited molecules with the solvent, since they are correlated with absorption and fluorescence band maxima separations.

Solutions of certain fluorescent molecules in paraffins of different viscosity show temperate quenching which correlates with diffusional characteristics of the solvents for flexible molecules, while for rigid molecules solvent viscosity has a much smaller influence.

1,227. FLUORESCENCE OF AROMATIC ALDEHYDES

Bredereck, K., Förster, Th., Oesterlin, H.-G.
In "Luminescence of Organic and Inorganic Materials,"
International Conference Proceedings, New York University, N. Y., 1961, pp. 161–175
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N. Y., 1962

The fluorescence properties of some aromatic aldehydes were investigated. Some higher members of the aromatic series fluoresce in inert as well as in hydroxylic solvents, others only in the latter or in mixtures with inert ones. This can be explained by the differences in energy of the fluorescent $\pi \rightarrow \pi^*$ and the quenching $n \rightarrow \pi^*$ states of these aldehydes together with the solvent dependence of these energies. For pyrene-3-aldehyde the existence of two different mechanisms of fluorescence activation was demonstrated by the dependence of fluorescence yields and spectra on temperature and solvent composition. In the case of moderately activating agents, solvent rearrangement during the lifetime of the excited molecule is most important. With a strong activator, ground-state interaction prevails at low concentration.

1,228. THE LUMINESCENCE SPECTRA OF SOME TRAPPED ORGANIC RADICALS

Leach, S.
In "Luminescence of Organic and Inorganic Materials,"
International Conference Proceedings, New York University, N. Y., 1961, pp. 176–185
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N. Y. 1962

Although important information on trapped organic radicals can be obtained from their luminescence spectra, this has hitherto been a neglected field of study. The fluorescence spectra of benzyl, deuterated benzyl, and triphenylmethyl radicals trapped in low-temperature rigid glasses are discussed. Some remarks are made concerning the sensitivity of the luminescence technique in observing trapped radicals and other species produced by low-temperature photolysis.

1,229. INTERDEPENDENCE OF EXCITED STATES OF DICHROIC MOLECULES

Oster, G., Oster, G. K.
In "Luminescence of Organic and Inorganic Materials,"
International Conference Proceedings, New York University, N. Y., 1961, pp. 186–195
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N. Y., 1962

Triphenylmethane dyes which lack trigonal symmetry of their substituent groups are colored green in solution. Apparently the two absorption bands at each end of the visible spectrum are associated with the two dichroic axes. Although the free dye is photochemically inactive, the dyes when bound to high polymers in solution are capable of being photoreduced. Futhermore, the bound dye is fluorescent while the free dye is not, due to competing internal conversion processes which are suppressed on binding.

Excitation with near ultraviolet light gives a green fluorescence (positively polarized), while excitation with red light gives a deep red fluorescence (negatively polarized). Hence, it appears that the two absorption bands are independent electronic systems. Excitation with blue light, on the other hand, gives green fluorescence plus a little red fluorescence. Flash spectroscopy of bound dye was carried out using extremely high intensity filtered light. Excitation with red light caused a reversible decrease of the long wavelength absorption band, while excitation with blue light resulted in a reversible decrease in both peaks.

The production of metastable species is not appreciably influenced by the presence of oxygen. Furthermore, no self-quenching of these species is observed. It is concluded that the excited molecule imbedded in the polymer is protected from external quenching influences.

1,230. *p*-OLIGOPHENYLENE STUDIES

Wirth, H. O.
In "Luminescence of Organic and Inorganic Materials,"
International Conference Proceedings, New York University, N. Y., 1961, pp. 226–229
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N. Y., 1962

It had been found that the solubility of the *p*-oligophenylenes could be greatly enhanced by substitution. With this knowledge it was possible to open a very interesting research field, especially interesting for systematic luminescence studies, since the fluorescence of these compounds is one of their identifying characteristics.

Because of the correlation between absorption and emission, the fluorescence bands of the *p*-oligophenylenes show a convergence. This fact not only diminishes the practical applications of these compounds, but also restricts systematic research.

If this spectral convergence phenomenon is caused by the inner rotations of the benzene rings, a blocking of this movement with the help of suitable substituents was thought to lead to an ideal coplanarity and, in connection with this, to a significant red shift of the spectral bands. Consequently, some bridged *p*-oligophenylenes were synthesized using, e.g., oxygen as bridging element, and expectations were confirmed.

1,231. FLUORESCENCE LIFETIME STUDIES OF PYRENE SOLUTIONS

Birks, J. B., Munro, I. H.
In "Luminescence of Organic and Inorganic Materials,"
International Conference Proceedings, New York University,
N. Y., 1961, pp. 230–234
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N. Y., 1962

The fluorescence emission spectrum of a solution of pyrene consists of two components: M, the normal emission from singlet excited molecules at $\lambda = 360\text{-}420$ mμ, and D, the emission from excited dimers (excimers) at $\lambda = 420\text{-}550$ mμ. Förster and Kasper have shown that as the pyrene concentration c is increased, the quantum intensity of M decreases and that of D increases. In the present investigation the rise and decay times of the two components have been studied, both in the absence and presence of dissolved oxygen, as a function of concentration c and of solvent viscosity η.

1,232. INTERNAL STRUCTURE OF POLYMER SOLUTIONS AS STUDIED BY A FLUORESCENCE POLARIZATION METHOD

Nishijima, Y.
In "Luminescence of Organic and Inorganic Materials,"
International Conference Proceedings, New York University,
N. Y., 1961, pp. 235–243
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N. Y., 1962

The fluorescence technique has been applied to study the internal structure of polymer solutions over a wide range of polymer concentrations. The relaxation time of rotation of fluorescent residues dispersed in a polymer solution is estimated from the degree of polarization of fluorescence emitted from the solution. The local viscosity, which is a measure of the internal architecture of the solution, can be obtained by dispersing free fluorescent molecules in the polymer solution. The micro-Brownian motion of a polymer chain in solution can directly be observed by placing fluorescent residues on the polymer chain by appropriate methods of chemical bond formation between the polymer chain and the fluorescent molecules. Measurements have been carried out under various conditions to investigate the effects of chain length and polymer concentration on the internal structure of polymer solution.

1,233. ENERGY TRANSFER PHENOMENA IN PURE AND MIXED CRYSTALS OF DURENE

Kallmann, H. P., Hayakawa, S., Magnante, P.
In "Luminescence of Organic and Inorganic Materials,"
International Conference Proceedings, New York University,
N. Y., 1961, pp. 244–251
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N. Y., 1962

Some energy transfer phenomena in pure and mixed crystals of durene are reported. The measurements and interpretation of absorption and fluorescence spectra of crystalline durene have been reported recently in detail by Schnepp and McClure. Their interest was related to the lower excited level of the simpler aromatic compounds. The present experimental results suggest the electronic interaction among luminescence centers introduced by guest molecules and photochemical reactions. The fresh pure-durene crystal showed no visible fluorescence. However, a visible green emission band appeared after long time irradiation by γ-rays, X-rays, and 254-mμ ultraviolet light.

Energy transfer phenomena were studied in anthracene-in-durene and in naphthalene-in-durene. It is concluded that the electronic transition between the traps introduced by naphthalene and the excited levels of the green emission centers is quite allowed in naphthalene-in-durene crystals, contrary to anthracene-in-durene crystals.

1,234. INVERSE CORRELATION BETWEEN LUMINESCENCE AND PHOTOCONDUCTIVITY OF DIAMOND

Halperin, A., Nahum, J.
In "Luminescence of Organic and Inorganic Materials,"
International Conference Proceedings, New York University,
N. Y., 1961, pp. 252–262
Kallmann, H. P., Spruch, G. M., Editors
John Wiley & Sons, Inc., New York, N. Y., 1962

The luminescence and photoconductivity excitation spectra of type I and IIa diamonds are described. The excitation spectra show a band structure near the absorption edge and at longer wavelengths. The photoconductivity excitation spectrum shows inverted peaks just at the wavelengths of maxima in the absorption and in the luminescence excitation spectrum. At temperatures above 240°K the inverted peaks in the photoconductivity excitation near the edge turn into real maxima, while those at longer wavelengths (in the region of the 415-mμ system) remain inverted.

A model is proposed to account for the results.

1,235. EINE ANORDNUNG ZUR MESSUNG VON LUMINESZENZSPEKTREN EINGEFRORENER LÖSUNGEN (AN APPARATUS FOR THE MEASUREMENT OF LUMINESCENCE SPECTRA OF FROZEN SOLUTIONS)

Brand, H., Doerr, F.
***Zeitschrift für Angewandte Physik*, v. 13, no. 8,**
pp. 390–395, August 1961

The details of construction of an apparatus designed for the quantitative measurement of luminescence spectra under monochromatic excitation are presented. Two Farrand monochromators containing reflection gratings are used to analyze the excitation radiation and the luminescence. A high pressure xenon lamp is used as the source of "continuous" radiation, while a high pressure mercury lamp is used for stimulation at discrete wavelengths. The detector is an eleven-stage quartz window photomultiplier. The samples to be studied are generally solutions of organic compounds solidified in a special quartz cell cooled by liquid air and placed in a thermostated enclosure. A solution of coronene in ethyl-tetrahydrofuran was used as a test sample and the luminescence spectrum was measured at 100 and 300°K. The fluorescence spectrum extends from about 4200 to 5300 Å, and at 100°K an additional phosphorescence component was observed in the range 5200 to 5800 A. (*PA*, 1962, #6627)

1,236. FLUORESZENZ- UND PHOSPHORESZENZ-AUSBEUTESOWIE LEBENSDAUERMESSUNGEN AN DIHALOGENIERTEN ACRIDINEN UND FLUORESZEINEN (FLUORESCENCE AND PHOSPHORESCENCE YIELD AND LIFETIME MEASUREMENTS FOR DIHALOGEN ACRIDINES AND FLUORESCEINS)

Zanker, V., Körber, W.
***Zeitschrift für Angewandte Physik*, v. 14, no. 1, pp. 43–48, January 1962**

The title data are reported for the cations and bases of 2,7-difluoro-, 2,7-dichloro-, and 2,7-dibromoproflavins, and for the dianions of 2,7-dichloro-, 2,7-dibromo-, and 4,5-diiodofluoresceins, in alcoholic solution at +20 and −180°C for an average molar concentration range of 5×10^{-3} to 10^{-4}. Apparatus and measurements are those of the method of Zanker and Rammensee. The results show, like the earlier work on tetrahalogenofluoresceins, that the fluorescence yields of the bases and cations rapidly decrease from the fluoro- to the bromoderivatives, and that the position of the halogen influences them. There is a decrease from the fluoro- to the bromo- and iododerivatives in the lifetimes of the phosphorescence. 9 references. (*PA*, 1962, #13,348)

1,237. DIE BEEINFLUSSUNG VON SINGULETT-TRIPLETT-ÜBERGÄNGEN AROMATISCHER KOHLENWASSERSTOFFE DURCH KOMPLEXBILDUNG (VARIATION IN THE SINGLET-TRIPLET TRANSITIONS OF AROMATIC HYDROCARBONS OWING TO FORMATION OF COMPLEXES)

Czekalla, J., Mager, K. J.
***Zeitschrift für Electrochemie*, v. 66, pp. 65–73, 1962**

The phosphorescence fading times and spectra of donator–acceptor complexes of dichloro-, tetrachloro- and tetrabromophthalic anhydride with naphthalene, phenanthrene, coronene, durene, and hexamethylbenzene have been measured and the spectra analyzed. The data obtained indicate an increase of the singlet–triplet transition probability owing to formation of complexes and a concurrent lowering of the frequencies of the Raman-active vibrations coupled with the electron jump. If the acceptor is varied, the magnitude of these effects increases with the number of the halogen substituents and their increasing atomic number (Z-effect); if, on the other hand, the donator is varied, the magnitude of these effects depends mainly on the dimension of the aromatic system. The observed increase in the singlet–triplet transition probability is, compared with the interaction with oxygen, some powers of ten smaller. Nevertheless, close parallels do exist between the two effects, and they are discussed with reference to the theoretical views developed on the oxygen effect.

1,238. EINFLUSS DES POLYMERISATIONSGRADES AUF DIE LUMINESZENZAUSBEUTE UND DIE ENERGIELEITUNG BEI KUNSTSTOFF-SZINTILLATOREN (INFLUENCE OF THE DEGREE OF POLYMERIZATION ON THE LUMINESCENCE YIELD AND ENERGY TRANSPORT IN SYNTHETIC SCINTILLATORS)

Heusinger, H.
***Zeitschrift für Naturforschung*, v. 15a, no. 12, pp. 1068–1072, December 1960**

Films of polystyrene and polyvinyl acetate about 0.3 mm thick, containing terphenyl or other organic phosphors, and with some residual solvent. were excited by Sr^{90}. The light output increased steadily with the degree of polymerization (between 10^2 and 10^4) provided that the phosphor was present in a quantity smaller than one mole to one mole of polymer. An excess of the phosphor caused a rapid decrease of the yield. Efficiency was altered by different solvents, aromatics being favorable. Some ultraviolet excitation experiments are described, and the scintillation mechanism is briefly discussed. (*PA*, 1961, #14,649)

1,239. ÜBER DIE FLUORESZENZ DES PYREN IN FESTEN KOHLENWASSERSTOFFEN (ON THE FLUORESCENCE OF PYRENE IN SOLID HYDROCARBONS)

Schmillen, A.
***Zeitschrift für Naturforschung*, v. 16a, no. 1, pp. 5–10, January 1961**

The fluorescence changes due to interassociation of the molecules were used to examine the influence of various host lattices on the luminescence spectrum. The decay characteristics were measured for the system pyrene in fluorene. The luminescence decay of fluorene is little influenced by pyrene concentration. The decay of monomolecular pyrene fluorescence is relatively short, but that of associated pyrene molecules approaches the value for fluorene for excitation by UV light. Excitation in the host lattice appears to be followed by an energy transfer to the pyrene molecule, probably associated with re-absorption of the fluorene emission. (*PA*, 1961, #10,127)

1,240. FLUORESZENZABKLINGDAUER VON EINIGEN AROMATISCHEN KOHLENWASSERSTOFFEN BEI α-STRAHLANREGUNG (FLUORESCENCE DECAY TIME OF SOME AROMATIC HYDROCARBONS FOLLOWING α-PARTICLE EXCITATION)

Schmillen, A., Kramer, K.
***Zeitschrift für Naturforschung*, v. 16a, no. 11, pp. 1192–1199, November 1961**

From an examination of the Fourier spectrum of scintillation pulses produced by α-particles in crystalline powders of aromatic hydrocarbons, some conclusions were produced about the decay-times (and also to a lesser extent about the rise times). It was found that the luminescence pulses from powders of the pure crystal exhibited a compound exponential decay. When the same crystals (anthracene, tetracene, pyrene and chrysene) were activated with various impurities, the luminescence pulses exhibited a decay which was almost exactly a single exponential. The measured values of the decay times (in the nsec range) are presented in two tables. Finally, some conclusions about the mechanism of stimulation of the emission in the various crystals are deduced from the experimental results. (*PA*, 1962, #6631)

1,241. QUALITATIVE PRÜFUNG DER FLUORESZENZÄNDERUNGEN ORGANISCHER LÖSUNGEN NACH EINWIRKUNG VON ULTRAVIOLETTEM LICHT (QUALITATIVE TEST OF THE FLUORESCENCE CHANGES OF ORGANIC SOLUTIONS AFTER THE ACTION OF ULTRAVIOLET LIGHT)

Ludwig, W., Herforth, L.
***Zeitschrift für Naturforschung*, v. 16b, no. 10, pp. 638–644, October 1961**

Luminescence intensity and pulse height of scintillation both decrease with irradiation of the luminescent material. In solution these changes often appear sooner than in the solid. In the experiments reported here, Hg light of 296–366 mμ wavelength was used, and changes visible to the eye in intensity or color of the fluorescence, or in the color of the solution, were recorded. The compounds were: seven condensed-ring systems, six hydrocarbons related to diphenylethylene, six diphenyl polyenes and analogs with triple bonds, four phenylmethanes and phenylchloromethanes, diphenylmethane and diphenylethane and four of their oxidation products, biphenyl and seven of its derivatives, naphthalene and six of its derivatives, anthracene and seven of its derivatives, 12 non-heterocyclic N compounds, 10 derivatives of heterocycles with five-membered rings, and 13 derivatives of heterocycles with six-membered rings. The solvents were, in most cases, MeOH, dioxane, tetrahydrofuran, acetone, $CHCl_3$, CCl_4, trichloroethylene, benzene, PhCl, Ac_2O, AcOH, and dimethylformamide.

1,242. ZUR SPIEGELSYMMETRIE DER ABSORPTIONS- UND LUMINESZENZBANDEN VON FARBSTOFFEN (REFLECTION SYMMETRY OF ABSORPTION AND LUMINESCENCE BANDS OF DYESTUFFS)

Kawski, A., Polacka, B.
***Zeitschrift für Naturforschung*, v. 17a, no. 4, pp. 352–354, April 1962**

When the absorption and emission spectra of rhodamine 6G, rhodamine B, and yellow eosine in glycerine and in polymethylmethacrylate are observed, essentially the same maxima in cm^{-1} and the same half-height width are obtained, whether $W_\nu(\mathrm{Lum})/\nu^4$ or $W(\mathrm{Lum})/\nu$ is plotted for absorption and whether χ/ν or χ is plotted for luminescence. (*PA*, 1962, #19,566)

1,243. STRAHLUNGSLOSER ÜBERGANG VON ELEKTRONENANREGUNGSENERGIE DURCH DÜNNE SCHICHTEN (RADIATIONLESS PASSAGE OF ELECTRON EXCITATION ENERGY THROUGH THIN LAYERS)

Zwick, M. M., Kuhn, H.
***Zeitschrift für Naturforschung*, v. 17a, no. 5, pp. 411–414, May 1962**

A monomolecular layer of a dye *S* (sensitizer) whose fluorescence maximum was 420 mμ was produced on a barium stearate (I) substrate, then overlaid by several monomolecular layers of I to a thickness *d*, and finally by a dye *A* (acceptor) for which trypaflavin was chosen (470-mμ absorption maximum). Excitation in the absorption region of *S* produces clear fluorescence of *S* if $d \geq 250$ Å, which disappears when $d \leq 100$ Å. A radiationless energy transfer between *S* and *A* has therefore occurred. This procedure, unlike those previously reported, does not involve trivial effects such as secondary absorption, energy transfer by impact, and presence of associates of S and *A*. (*PA*, 1962, #18,872)

1,244. DIE UV-ABSORPTIONSSPEKTREN EINIGER EINFACHER CHINOXALIN-DERIVATE (U.V. ABSORPTION SPECTRA OF SOME SIMPLE QUINOXALINE IN COMPOUNDS)

Perkampus, H. H.
***Zeitschrift für Naturforschung*, v. 17a, no. 7, pp. 614–621, July 1962**

The UV absorption spectra of 13 quinoxaline compounds (methyl-, chlor-, dimethyl-, dibrom-, etc.) were measured at 20°C in different solvents (heptane, hexane, methanol, sulphuric acid, hydrochloric acid, etc.). The particular compounds are similar in that the substitutes do not give rise to tautomeric and only little to mesomeric interactions. From the fine structure of the UV spectra of 2,3-dimethoxy- and isopropoxy-quinoxaline and from the solvent dependency of all the compounds, an attempt is made to assign the long-wavelength *L*-bands. (*PA*, 1962, #22,996)

1,245. ÜBER DIE FLUORESZENZ VON BINÄREN SYSTEMEN KRISTALLINER AROMATISCHER KOHLENWASSERSTOFFE (FLUORESCENCE OF BINARY SYSTEMS OF CRYSTALLINE AROMATIC HYDROCARBONS)

Schmillen, A., Legler, R.
***Zeitschrift für Naturforschung*, v. 18a, no. 1, pp. 1–9, January 1963**

The dependence of fluorescence spectra and lifetimes on the nature and concentration of the fluorescent heterogeneous molecule is investigated. Two mechanisms are suggested for the fluorescence due to UV radiation. A typical compound showing the mechanism of radiationless energy transfer is the system 2,3-dimethylnaphthalene with anthracene addition; one showing transfer by means of absorption of the parent fluorescence radiation is 2,3-dimethylnaphthalene with perylene.

1,246. ELEKTRONENSPINRESONANZ-UNTERSUCHUNGEN AN DPPH-HYDROPEROXYD-LÖSUNGEN (ELECTRON SPIN RESONANCE INVESTIGATION OF DPPH [DIPHENYLPICRYLHYDRAZIL] HYDROPEROXIDE SOLUTIONS)

Möbius, K., Schneider, F.
***Zeitschrift für Naturforschung*, v. 18a, no. 3, pp. 428–430,**
March 1963

1,247. TRIPLETTPHOSPHORESZENZ UND ELEKTRONENSPINRESONANZABSORPTION EINIGER ORGANISCHER MOLEKÜLE IN GLASIGEN LÖSUNGEN (TRIPLET PHOSPHORESCENCE AND ELECTRON SPIN RESONANCE ABSORPTION OF SOME ORGANIC MOLECULES IN GLASS-LIKE SOLUTIONS)

von Foerster, G.
***Zeitschrift für Naturforschung*, v. 18a, no. 5, pp. 620–626,**
May 1963

The phosphorescence and ESR of the triplet states of phenanthrene, chrysene, phenylenaphthylene oxide, fluoranthene, 2-methylnaphthalene, 2,3-dimethylnaphthalene, and 2,6-dimethylnaphthalene, dissolved in heptane or isopropanol, were investigated. Temperature dependence of the phosphorescence duration and intensity was determined. Experimental data are presented and explained.

1,248. LUMINESZENZUNTERSUCHUNGEN AN DOTIERTEN EINKRISTALLEN AROMATISCHER KOHLENWASSERSTOFFE (LUMINESCENCE INVESTIGATION OF DOPED SINGLE CRYSTALS OF AROMATIC HYDROCARBONS)

Schmillen, A., Kohlmannsperger, J.
***Zeitschrift für Naturforschung*, v. 18a, no. 5, pp. 627–632,**
May 1963

Changes in the luminescence spectra and quenching times with increased concentration are investigated for single crystals of 2,3-dimethylnaphthalene doped with perylene and dibenzyl doped with tetracene. The observed transfer of excited energy of the host lattice to the guest molecules is interpreted as exciton diffusion. From the decrease in host fluorescence quenching time, the mean diffusion range of the excitons in 2,3-dimethylnaphthalene is estimated at $l = 300a$, that in dibenzyl at $l = 31a$.

1,249. DAS FLUORESZENZSPEKTRUM VON NAPHTHALIN-KRISTALLEN ZWISCHEN 2 UND 100°K (THE FLUORESCENCE SPECTRUM OF NAPHTHALENE CRYSTALS BETWEEN 2 AND 100°K)

Pröpstl, A., Wolf, H. C.
***Zeitschrift für Naturforschung*, v. 18a, no. 6, pp. 724–734,**
June 1963

The spectrum (taken with resolving power of 10^4) is analyzed and found to contain almost exclusively the intrinsic fluorescence bands, starting at 31,476 cm^{-1}. Raman frequencies are assigned, and temperature dependence of bandwidth, band shape, quantum yield, and absorption edge is determined. Exciton theories seem applicable.

1,250. DIE TEMPERATURABHÄNGIGKEIT DER SENSIBILISIERTEN FLUORESZENZ IN NAPHTHALIN-KRISTALLEN ZWISCHEN 2 UND 100°K (TEMPERATURE DEPENDENCE OF THE SENSITIZED FLUORESCENCE IN NAPHTHALENE CRYSTALS BETWEEN 2 AND 100°K)

Pröpstl, A., Wolf, H. C.
***Zeitschrift für Naturforschung*, v. 18a, no. 7, pp. 822–828,**
July 1963

The relative quantum yields of the fluorescence of the host ($\bar{\nu}_0 = 31{,}474$ cm^{-1}), a shallow trap (X_1, $\bar{\nu}_0 = 31{,}444$ cm^{-1}), and a guest (β-methylnaphthalene, $\bar{\nu}_0 = 31{,}059$ cm^{-1}) have been measured from 2 to 100°K in naphthalene crystals as host. The temperature dependence can be described quantitatively by a hopping model for the exciton diffusion. The hopping time of the exciton ($t_H \cong 10^{-13}$ sec) is independent of the temperature. The freezing-in of the β-methylnaphthalene fluorescence at low temperatures is the result of the competition between the two traps. In addition, the fluorescence spectrum of β-methylnaphthalene as a guest in naphthalene has been measured and analyzed.

1,251. DIE ANISOTROPIE DER SZINTILLATIONSLICHT-AUSBEUTE ORGANISCHER MOLEKÜLEIN-KRISTALLE FÜR α-STRAHLEN (ANISOTROPY OF THE SCINTILLATION LIGHT YIELD OF ORGANIC MOLECULE SINGLE CRYSTALS FOR α-RAYS)

Kienzle, W. F., Flammersfeld, A.
***Zeitschrift für Physik*, v. 165, no. 1, pp. 1–11,**
October 18, 1961

It has been shown that the scintillation-light yield of single crystals of anthracene and *trans*-stilbene irradiated by α-particles exhibits a strong dependence on the impact direction of the α-particles with respect to the crystal orientation. Further investigations of 11 other compounds confirm this effect, which now seems to be a common feature of monocrystalline organic scintillators. A possible relation between the anisotropy of the scintillation-light yield and that of the electronic conductivity is proposed as an explanation. (*PA*, 1962, #726)

1,252. DIE SZINTILLATIONS-ANISOTROPIE VON ANTHRAZEN BEI TIEFEN TEMPERATUREN (SCINTILLATION ANISOTROPY OF ANTHRACENE AT LOW TEMPERATURES)

Heckmann, P. H., Sander, W., Flammersfeld, A.
***Zeitschrift für Physik*, v. 165, no. 1, pp. 12–16,**
October 18, 1961

An anthracene crystal was cooled down to liquid-hydrogen temperature and was bombarded with α-particles in two directions, parallel to the b and c' crystal axes. The ratio of maximum to minimum light yield (for α-particles parallel to

c' and b, respectively) was reduced to 1.23 at 20.4°K. This ratio is 1.46 for ThC′ and 1.53 for ThC α-particles at room temperature, and is measured as a function of temperature between 20.4 and about 90°K. (For Part II, see Entry #1,254.) (*PA*, 1962, #727)

,253. DIE TEMPERATURABHÄNGIGKEIT DER ENERGIEÜBERTRAGUNG IN ANTHRACEN-TETRACEN-MISCHKRISTALLEN (THE TEMPERATURE DEPENDENCE OF THE ENERGY TRANSFER IN ANTHRACENE–TETRACENE MIXED CRYSTALS)

Avakian, P., Wolf, H. C.
***Zeitschrift für Physik*, v. 165, no. 4, pp. 439–444,**
November 21, 1961

The transfer of excitation energy from one component to the other in mixed organic crystals can be "frozen" at low temperature. It is reported that, when the molar concentration of one of the components in the system anthracene–tetracene varies between 10^{-6} and 10^{-2}, the range of temperatures over which "freezing" occurs remains practically constant. The half-value temperature is (35 ± 2)°K. (*PA*, 1962, #4182)

1,254. DIE SZINTILLATIONS-ANISOTROPIE VON ANTHRAZEN BEI TIEFEN TEMPERATUREN. II (SCINTILLATION ANISOTROPY OF ANTHRACENE AT LOW TEMPERATURES. II)

Heckmann, P. H., Sander, W., Flammersfeld, A.
***Zeitschrift für Physik*, v. 169, no. 1, pp. 17–22,**
July 30, 1962

Continuing previous work (Entry #1,252), the scintillation anisotropy of anthracene bombarded with α-particles was measured as a function of temperature between 1.9 and about 80°K. With all crystal specimens investigated, a pronounced minimum was found between 20 and 30°K. The anisotropy is constant below about 9°K, whereas the light yield still increases with decreasing temperature down to 1.9°K. The light was found to be a nonlinear function of the temperature. (*PA*, 1962, #18,879)

1,255. THE FLUORESCENCE LIFETIMES OF FLUORESCEIN ANION

Rohatgi, K. K.
***Zeitschrift für Physikalische Chemie*, Leipzig, v. 217,**
no. 5–6, pp. 353–356, June 1961 (in English)

The fluorescence lifetimes of fluorescein anions in solutions of varying viscosity were measured using an electronic technique. Viscosity changes were brought about by using (1) water–glycerol mixtures, (2) a series of primary alcohols, and (3) temperature variation. In (1) the lifetime is independent of viscosity provided that the chemical nature of the solvent is unchanged. When alcohols are used the values decrease with viscosity increase; this effect is thought to be due primarily to changes in solvent. Variation in temperature has no effect on lifetime.

1,256. UNTERSUCHUNGEN ZUM ENERGIEÜBERTRAGUNGS-MECHANISMUS DURCH MESSUNG DER ABKLINGZEITEN AN ORGANISCHEN LUMINOPHOREN (AN INVESTIGATION OF THE ENERGY TRANSFER MECHANISM BY MEANS OF MEASUREMENT OF THE DECAY TIMES OF ORGANIC PHOSPHORS)

Wendel, G., Härtig, G.
***Zeitschrift für Physikalische Chemie*, Leipzig, v. 221,**
no. 1–2, pp. 17–28, 1962

The decay time of the luminescence was previously calculated from the measured phase difference between the sinusoidal (electron) stimulating beam and the consequent luminescence signal. The observed decay times of the solid and liquid organic phosphors were in the range 1 to 100 nsec. The results on the solid phosphors (e.g., tetracene in phenanthracene) are explained in terms of a model devised by Schmillen to account for the behavior of UV-stimulated luminescence. This model involves exciton diffusion. The decay times of the liquid phosphors are discussed separately for three different ranges of activator concentration, according to a scheme proposed by Kallmann. At concentrations $\geqslant 10^{-2}$ mole/l the dominant energy transfer mechanism involves dipole–dipole interaction. Between 7×10^{-4} and 10^{-2} mole/l the results are explicable in terms of intermolecular interaction. The measured value of the energy transport parameter Q in this range agrees reasonably well with previously determined values. For concentrations $\leqslant 5 \times 10^{-4}$ mole/l the nature of the characteristic energy transfer mechanism is not understood at present. At concentrations $< \sim 10^{-9}$ mole/l the decay time was comparable to that of the pure solvent. (*PA*, 1963, #6681)

1,257. FLUORESZENZMESSUNGEN AN DÜNNEN FILMEN AROMATISCHER KOHLENWASSERSTOFFE (FLUORESCENCE MEASUREMENTS ON THIN FILMS OF AROMATIC HYDROCARBONS)

Perkampus, H. H
***Zeitschrift für Physikalische Chemie, Neue Folge*,**
Frankfurt, v. 24, no. 1, pp. 1–10, April 1960

The principle of Ulbricht's sphere is used for measuring the fluorescence emission of thin films of aromatic hydrocarbons prepared in a high vacuum. By this method, the fluorescence spectra of thin films of anthracene, tetracene, pyrene, and perylene have been measured at room temperature and compared with the respective spectra in solution. Results are discussed.

1,258. MESSUNG DER WIRKUNGSQUERSCHNITTE VON BENZOL UND TULUOL GEGEN LANGSAM ELEKTRONEN (MEASUREMENT OF EFFECTIVE CROSS SECTIONS OF BENZENE AND TOLUENE FOR SLOW ELECTRONS)

Hartmann, H., Volpers, R., Euterneck, R.
***Zeitschrift für Physikalische Chemie, Neue Folge*,**
Frankfurt, v. 30, no. 3–4, pp. 201–214, November 1961

The effective cross sections of benzene (I) and toluene (II) are measured with an apparatus in which the effective cross sections could be taken vs. electron energies in the range 49–1.5 ev. The similarity in the slope of the effective cross sections of I and II as functions of the electron energy is noted. For certain electron energies, the effective cross sections show characteristic maxima which make probable an explanation as excitation or ionization resonance cross sections.

1,259. ÜBER DAS AUFTRETEN VON MEHREREN ELEKTRONENÜBERFÜHRUNGSBANDEN IN ELEKTRONEN-DONATOR–AKZEPTOR–KOMPLEXEN (OCCURRENCE OF SEVERAL ELECTRON TRANSFER BANDS IN ELECTRON DONOR–ACCEPTOR COMPLEXES)

Briegleb, G., Czekalla, J., Ruess, G.
Zeitschrift für Physikalische Chemie, Neue Folge,
Frankfurt, v. 30, no. 5–6, pp. 316–332, December 1961

The molecular complexes of $(CN)_2C{:}C(CN)_2$ and chloranil with perylene, coronene, fluorene, pyrene, 1,2-benzanthracene, 1,2,5,6-dibenzanthracene, chrysene, benzene, diphenyl, naphthalene, triphenylene, phenanthrene, and stilbene were studied. The charge transfer bands of these complexes were investigated.

1,260. MESOMERIEMOMENTE UND ELEKTRONENÜBERFÜHRUNGSBANDEN VON ELEKTRONEN–DONATOR–AKZEPTOR–KOMPLEXEN DES CHLORANILS UND TETRACYANÄTHYLENS MIT AROMATISCHEN KOHLENWASSERSTOFFEN (MESOMERIC [DIPOLE] MOMENTS AND ELECTRON TRANSFER BANDS OF ELECTRON DONOR–ACCEPTOR COMPLEXES OF CHLORANIL AND TETRACYANOETHYLENE WITH AROMATIC HYDROCARBONS)

Briegleb, G., Czekalla, J., Ruess, G.
Zeitschrift für Physikalische Chemie, Neue Folge,
Frankfurt, v. 30, no. 5–6, pp. 333–348, December 1961

1,261. EMISSION SPECTRA OF THE CHROMIUM (III) HEXAUREA COMPLEX

Porter, G. B., Schlaefer, H. L.
Zeitschrift für Physikalische Chemie, Neue Folge,
Frankfurt, v. 37, no. 1–2, pp. 109–114, April 1963
(in English)

The fluorescence $^4T_{2g} \rightarrow {}^4A_{2g}$ and phosphorescence $^2E_g \rightarrow {}^4A_{2g}$ of $Cr(urea)_6(ClC_4)_3$ in a rigid glass at a low temperature are discussed. Behavior of the Cr(III) complexes when excited in the spin-allowed quartet-quartet bands by radiation is illustrated.

1,262. X-RAY SCATTERING IN CRYSTALS WITH EXCITON FORMATION

Agranovich, V. M., Ginzburg, V. L.
***Zhurnal Eksperimentalnoi i Teoreticheskoi Fiziki,* v. 40,**
no. 3, pp. 913–919, March 1961
(Translated from the Russian in *Soviet Physics—JETP,*
v. 13, pp. 638–642, September 1961)

A study is made of Raman scattering of X-rays in crystals accompanied by the formation of excitons, i.e., "normal" electromagnetic waves in the given crystal. The plasmons (longitudinal plasma waves) in metals and dielectrics are a special case of excitons. The measurement of the energy of the scattered X-ray photons at various scattering angles may be an effective method of determining the energy of the excitons as a function of the wave vector. (*PA*, 1962, #536)

1,263. IONIC FORMS OF URANIN IN LIQUID AND SOLID SOLUTIONS

Adamov, V. S., Kantardzhyan, L. T.
***Zhurnal Fizicheskoi Khimii,* v. 36, no. 2, pp. 376–379,**
February 1962
(Translated from the Russian in *Russian Journal of Physical Chemistry,* v. 36, no. 2, pp 192–194, February 1962)

The luminescence spectra of aqueous solutions show pH dependence, but no effect of the anion, with three maximum regions observed: cation $(pH < 2)$ $(470\text{–}80\ m\mu)$, univalent anion $(4 < pH < 9)$ $(540\text{–}50\ m\mu)$, and bivalent anion $(pH > 9)$ $(515\ m\mu)$. Similar luminescence spectra were observed for uranin in sucrose solutions corresponding to the pH of the starting solutions. Spectra of borax solutions, pH insensitive, are like spectra of strongly acidic aqueous solutions.

1,264. LUMINESCENCE SPECTRA OF SOME ANTHRAQUINONE CARBOXYLIC ACID DERIVATIVES AT LOW TEMPERATURES

Shcheglova, N. A., Shigorin, D. N., Ryabchikova, T. S.,
Dokunikhin, N. S., Moiseeva, Z. Z.
***Zhurnal Fizicheskoi Khimii,* v. 37, no. 2, pp. 371–377,**
February 1963

The luminescence spectra of a number of anthraquinone carboxylic and dicarboxylic acid esters and their halogen derivatives in hydrocarbon media at 77°K possess a fine vibration structure. The most strongly manifested frequency is that of the anthraquinone carbonyl. A strong dependence between the multiplicity spectra and the length of the hydrocarbon chain of the solvent has been discovered. This property may be utilized for the analysis of the compounds. Each substituent which is an auxochrome makes its own specific contribution to the spectrum, manifested in line shifts and intensity changes of the major peaks. The luminescence spectra of the powdered halogen derivatives of the anthraquinone acids and their esters do not display fine structure, but are a system of rather narrow bands, shifted toward the longer wavelength region, with the difference between the centers of these bands equal to the carbonyl frequency of anthraquinone. Reversible self-extinction of luminescence has been found to take place in 1,4-anthraquinone dicarboxylic acid powder, disappearing in dioxane solution. The self-extinction of luminescence is apparently due to augmentation of intermolecular interaction (and photo-transfer) of a carboxyl proton with the *p*-electrons of the anthraquinone carbonyl oxygen, responsible for the electronic excitation (for the *p* to *π* transition). This assumption was confirmed by the results of IR frequency measurements of the carbonyl group.

1,265. LUMINESCENCE SPECTRA OF DIKETONIC VAT DYES IN LAVSAN AND IN SOLUTIONS

Nurmukhametov, R. N., Bondareva, L. V.
***Zhurnal Fizicheskoi Khimii*, v. 37, no. 5, pp. 1143–1148, May 1963**

Absorption and luminescence spectra of violanthrone, dimethoxyviolanthrone, isoviolanthrone, dichloroisoviolanthrone, and dibenzopyrenequinone were obtained at 293 and 77°K. The electronic transitions, corresponding to the long-wave absorption bands and fluorescence, are interpreted as $\pi \rightarrow \pi$ transitions. In solutions in which hydrogen bonds are formed, the appearance of wide, longer-wave absorption bands is observed, accompanied by a corresponding quenching of fluorescence. Fluorescence bands are displaced toward the red during transition from an inert medium to Lavsan.

1,266. PYRAZOLES. XXXV. THE FLUORESCENCE OF PYRAZOLES UNDER THE ACTION OF ULTRAVIOLET LIGHT

Grandberg, I. I., Tabak, S. V., Kost, A. N.
***Zhurnal Obshchei Khimii*, v. 33, no. 2, pp. 525–533, February 1963**
(Translated from the Russian in *Journal of General Chemistry of the USSR*, v. 33, no. 2, pp. 517–524, February 1963)

Ultraviolet fluorescence colors are reported for 300 pyrazoles. Results are tabulated.

1,267. NEW MAGNETIC PROPERTIES OF MACROMOLECULAR COMPOUNDS CONTAINING CONJUGATED DOUBLE BONDS

Blyumenfeld, L. A., Berlin, A. A., Slinkin, A. A., Kalmanson, A. E.
***Zhurnal Strukturnoi Khimii*, v. 1, no. 1, pp. 103–108, May–June 1960**
(Translated from the Russian in *Journal of Structural Chemistry*, v. 1, no. 1, pp. 93–97, May–June 1960)

A summary is given of published and new data concerning the electron paramagnetic resonance (EPR) and the static paramagnetic susceptibility of polymers having conjugated double bonds in the main chain.

Polymers with conjugated double bonds give narrow electronic paramagnetic resonance signals with the free spin g-factor. The intensity of the signals increases with increase in the conjugation. The effect is an intramolecular one, independent of dissolution, and characterizes the fundamental state of the π-electron cloud of the molecule. In the solid state, polymers with conjugated double bonds, especially those containing nitrogen atoms and polar groups in the macromolecular chain, are characterized not only by the narrow lines mentioned above, but also by the broad asymmetrical EPR lines of very great integral intensity. These structures possess positive static magnetic susceptibility, though with increase in the magnetic field intensity, the susceptibility diminishes; the magnetizability, however, remains constant, which makes it permissible to speak of the ferromagnetic properties of the systems under discussion. The effect referred to appears to be purely structural.

1,268. ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF RADICALS FORMED IN IRRADIATED POLYPROPYLENE

Lebedev, Ya. S., Tsvetkov, Yu. D.
***Zhurnal Strukturnoi Khimii*, v. 2, no. 5, pp. 607–609, September–October 1961**
(Translated from the Russian in *Journal of Structural Chemistry*, v. 2, no. 5, pp. 558–560, September–October 1961)

Electron paramagnetic resonance spectra of radicals produced in polypropylene by Co^{60} γ-rays or fast electrons were studied. Spectral data are given for a polycrystalline specimen irradiated at 77°C and cooled in vacuum to 25°C, a specimen kept in a vacuum for 5 hr at 25°C, and a specimen kept for 1.5 min after admitting oxygen. (*NSA*, 1962, #7601)

1,269. THE UNIVERSAL FLUORESCENCE OF POLYMERS. I. QUALITATIVE RESULTS

Gachkovskii, V. F.
***Zhurnal Strukturnoi Khimii*, v. 4, no. 3, pp. 424–432, May–June 1963**

1,270. ELECTRONIC PARAMAGNETIC RESONANCE SPECTRA OF BIOPOLYMERS

Blyumenfeld, L. A.
***Zhurnal Vsesoyuznogo Khimicheskogo Obshchestva imeni D. I. Mendeleeva*, v. 6, pp. 319–324, 1961**
(36 references)

SYNTHESIS AND PREPARATION

1,271. SYSTEMS CAPABLE OF LUMINESCENCE BASED ON CRYSTALLINE INORGANIC SUBSTANCES AND ORGANIC ACTIVATORS

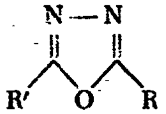
Chomse, H., Arend, I.
In "Zur Physik und Chemie der Kristallphosphore (Physics and Chemistry of Crystalline Phosphors)," pp. 243–254
Ortmann, H., Witzmann, H., Editors
Akademie Verlag, Berlin, Germany, 1960
(Paper presented at the Conference on Crystalline Phosphors—Entry #496)

Results are given of a systematic investigation of various inorganic bases activated by various organic substances, the activators and their concentrations, colors of fluorescence and phosphorescence, and phosphorescent decay times. Conditions under which inorganic compounds can act as host lattices for organic phosphors are discussed, as well as the type of interaction which must be assumed to exist between activator and host material. (*PA*, 1962, #8562)

1,272. NEW ORGANIC SCINTILLATING AGENTS; 1,3,4-OXADIAZOLE DERIVATIVES

Grekov, A. P., Shvaika, O. P.
In "Stsintillyatory i Stsintillyatsionnye Materialy, Vsesoyuznyi Nauchno-Issledovatelskii Institut Khimicheskikh Reaktivov, Materialy 2-go [i.e., Vtorogo] Koordinatsionnogo Soveshchaniya po Stsintillyatoram (Scintillators and Scintillation Materials, All-Union Scientific Research Institute of Chemical Reagents, Materials of the 2nd Coordination Conference on Scintillators), Moscow, USSR, 1957," pp. 105–114
Akademii Nauk SSSR, Moscow, 1960

The effect of radicals in the p-position on the scintillating activity of 2-phenyl- and 2,5-diphenyl-1,3,4-oxadiazole was studied. Syntheses of the 2-monosubstituted 1,3,4-oxadiazoles and of the 2,5-disubstituted 1,3,4-oxadiazoles (I) are presented. The introduction of a group into the p-position of 2-phenyl- or 2,5-diphenyl-1,3,4-oxadiazoles changed the scintillating activity; an electron donor increased it. The same substituent in the phenyl ring of mono- or disubstituted I caused the same changes. Monoaryl derivatives of I were weaker scintillators than the corresponding disubstituted derivatives. Among asymmetrical 2,5-diaryl-substituted I, the biphenyl group was the most effective. 2,5-Substituted I were more stable toward hydrolysis than monosubstituted I.



(I)

1,273. PREPARATION OF DIARYLPOLYENIC HYDROCARBONS

Mikhailov, B. M., Povarov, L. S., Ter-Sarkisyan, G. S.
In "Stsintillyatory i Stsintillyatsionnye Materialy, Vsesoyuznyi Nauchno-Issledovatelskii Institut Khimicheskikh Reaktivov, Materialy 2-go [i.e., Vtorogo] Koordinatsionnogo Soveshchaniya po Stsintillyatoram (Scintillators and Scintillation Materials, All-Union Scientific Research Institute of Chemical Reagents, Materials of the 2nd Coordination Conference on Scintillators), Moscow, USSR, 1957," pp. 155–170
Akademii Nauk SSSR, Moscow, 1960

A new synthesis of arylpolyenic hydrocarbons, based on the condensation of aromatic acetals and ketals with α,β-unsaturated ethers, is described. The resulting phenylpolyethoxyalkanes treated with aromatic Mg organic compounds form diarylpolyethoxyalkanes; the latter, on splitting off alcohol and water, yield diarylpolyenic hydrocarbons. The compounds prepared and methods of preparation are detailed. These compounds are of interest as luminophores.

1,274. STRUCTURE OF PLASTIC SCINTILLATORS

Baroni, E. E., Shoniya, V. M.
In "Stsintillyatory i Stsintillyatsionnye Materialy, Vsesoyuznyi Nauchno-Issledovatelskii Institut Khimicheskikh Reaktivov, Materialy 2-go [i.e., Vtorogo] Koordinatsionnogo Soveshchaniya po Stsintillyatoram (Scintillators and Scintillation Materials, All-Union Scientific Research Institute of Chemical Reagents, Materials of the 2nd Coordination Conference on Scintillators). Moscow, USSR, 1957," pp. 212–220
Akademii Nauk SSSR, Moscow, 1960

Solubility in styrene and polystyrene of the additives p-terphenyl, 1,1,4,4-tetraphenyl-1,3-butadiene, 1,3,5-triphenylpyrazoline, and anthracene was investigated. Heat polymerization of styrene containing luminescent additives proceeds without marked copolymerization and without substantial catalytic influence of additives on styrene polymerization. Anisotropy found in plastic scintillators is due to inhomogeneity of polystyrene itself owing to internal strains originating during heat polymerization, while optical inhomogeneity of polystyrene with additives is due to heterogeneous microcrystalline states of the additives.

1,275. PRODUCTION AND USE OF ORANGE-RED LUMINOGEN II, 4-(4-DIMETHYLAMINOBENZYLIDENE)-2-PHENYL-5-OXAZOLONE

Matveev, V. K.
In "Metody Lyuminestsentnogi Analiza Materialy VIII Soveshchaniya po Lyuminestsentsii," pp. 75–78
Akademiya Nauk Belorusskoi SSR, Institut Fiziki, 1960
(Paper presented at the Eighth Conference on Luminescence —Entry #497)

A review of existing organic luminophors and luminescent materials having orange-red and red luminescence is presented and a new method is proposed for the synthesis of luminogen II. 18 references.

1,276. MIXED ORGANIC SINGLE CRYSTALS, THEIR LUMINESCENCE AND SCINTILLATION PROPERTIES

Naboikin, Yu. V., Dobrokhotova, V. K., Uglanova, V. V.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya, **v. 24, no. 6, pp. 744–748, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 6, pp. 747–751, 1960)

In connection with the widespread investigation of energy transfer in mixed organic crystals, it is now possible to prepare new scintillation crystals from readily available substances, the luminescence properties of which vary substantially as a result of deliberately introducing impurities. This paper discusses the nature of the effects resulting from these impurities – not only on the nature of the impurity molecule itself, but also by distortion of the host lattice around this molecule. All the experiments described deal with single crystals, the degree of purity being evaluated from the luminescence spectra of the crystals. Some of the crystals studied were naphthalene, and naphthalene with (1) phenylbiphenylethylene, (2) salicylamide, and (3) α,α'-dinaphthylethylene. The concentration of the impurity was added to the melt before growing the crystals. The question of solubility of the impurities in the solid phase is discussed. (*PA*, 1962, #14,748)

1,277. REASONS FOR ELIMINATION OF INTERNAL NONRADIATIVE TRANSITIONS IN ORGANIC MOLECULES INCIDENT TO FORMATION OF INTRACOMPLEX COMPOUNDS WITH CATIONS

Bozhevolnov, E. A.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 6, pp. 762–766, 1960**
(Paper presented at the Eighth Conference on Luminescence —Entry #497; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 6, pp. 765–768, 1960)

It is stated that the most sensitive luminescence analysis reagents for determination of cations are compounds in which intramolecular nonradiative transitions are suppressed or eliminated as a result of formation of an intracomplex compound with cations. An example of this type is furnished by the formation of an intracomplex compound by salicylal-*o*-aminophenol with aluminum. After discussing the properties and molecular arrangements of organic compounds which show or do not show fluorescence in solution, it is concluded that to discover new luminescent reagents molecules with a nonrigid structure should be sought. Among the practical applications of this research is the discovery of new luminescent reagents for the determination of gallium, magnesium, and a number of other metals. (*PA*, 1962, #15,604)

1,278. SYNTHESES OF 2,5-DIARYLOXAZOLES FOR ORGANIC SCINTILLATORS

Hashimoto, S., Kato, S., Kano, T., Hashimoto, J.
***Kogyo Kagaku Zasshi*, v. 62, pp. 1406–1409, 1959**

Condensation of some ω-aminomethyl aryl ketone hydrohalides with aromatic carboxylic chlorides, and cyclization of resulting 1,4-diaryl-2-aza-1,4-diketones produced 2,5-diaryloxazoles, which were then purified by chromatography. When used as plastic scintillator solutes, they had sufficient quality as organic fluors.

1,279. ORGANIC OXIDE LUMINOPHORES

Dvorovenko, V. K.
***Nauchnye Zapiski, Odesskii Gosudarstvennyi Pedagogicheskii Institut imeni K. D. Ushinskoyo, Kafedry Matematiki, Fiziki i Estestvoznaniya*, v. 22, no. 1, pp. 43–46, 1958**
(See also *Referativnyi Zhurnal, Fizika*, 1961, #4V382)

A method is described for preparing a new group of organic phosphors, based on MgO, CaO, SrO, or BaO, which are to a considerable extent free of the shortcomings previously noted, such as complexity in production; decomposition on recrystallization, oxidation, or hydration; and heat-treatment requirements. The activators used are phenanthrene, carbazole, *p*-aminobenzoic, anthranilic, sulfanilic, salicylic, and other organic acids, and it is possible to vary concentration widely. Up to a temperature of 100°C, phosphorescence is produced for a minute or less depending on the oxide used; cooling to low temperatures increases afterglow.

1,280. GROWTH OF ANTHRACENE SINGLE CRYSTALS FOR SCINTILLATOR

Nakada, I.
***Ōyô Butsuri*, v. 30, pp. 560–569, 1961**

Optimum conditions were studied for growing a single crystal of anthracene from its melt by the Bridgman method. Furnace design, rates of growth and cooling are related mathematically. Scintillating characteristics of the irradiated cylindrical crystals (about one inch high and one inch in diameter) were determined.

1,28 GROWTH OF STILBENE SINGLE CRYSTAL

Nakada, I.
***Ōyô Butsuri*, v. 30, pp. 679–682, 1961**

The method (preceding abstract) is applied to stilbene, which is not as good a scintillator as anthracene.

1,282. THE OPTICAL PROPERTIES OF ANTHRACENE SINGLE CRYSTALS

Nakada, I.
***Physical Society of Japan, Journal of the*, v. 17, no. 1, pp. 113–118, January 1962**

The preparation of single crystals of anthracene is described, and optical measurements made on these crystals are reported. A single crystal of anthracene with (010) orientation can be grown from the melt by the Bridgman method. A large, transparent crystal with a mirror-like cleavage plane can be obtained with a seed. From double refraction and the optical axis, three axes of the crystal have been determined. The three principal indices obtained from 5893 Å are 1.550 ± 0.010, 1.775 ± 0.010, and 2.04 ± 0.08. The absorption coefficients in the fundamental absorption tail have been measured for polarized radiation along the various crystal axes. The absorption coefficient measured along the *b*-axis is five times larger than that of the *a*-axis. The absorption along the *c*-axis is different from absorption on the other axes. All of the absorption coefficients decrease exponentially with wavelength. (*SSA*, #15,204)

1,283. PREPARATION AND PROPERTIES OF PLASTIC SCINTILLATORS OF LARGE VOLUME

Kirdina, G. A., Pereyaslova, N. K.
***Pribory i Tekhnika Eksperimenta*, v. 1959, no. 5, pp. 47–51, September–October 1959**
(Translated from the Russian in *Instruments and Experimental Techniques*, v. 1959, no. 5, pp. 745–749, September–October 1959)

A method of preparing scintillating polystyrene blocks up to 10 liters in volume is described. Some of the measured properties of the prepared phosphors are given.

1,284. MAKING OF SCINTILLATORS BY PRESSING
Balats, M. Ya., Krivitskii, V. V., Leksin, G. A., Trebukhovskii, Yu. V.
***Pribory i Tekhnika Eksperimenta*, v. 1961, no. 2, p. 171, March–April 1961**
(Translated from the Russian in *Instruments and Experimental Techniques*, v. 1961, no. 2, p. 380, December 1961)

Plastic scintillators can be prepared from a bar of scintillation plastics material (polystyrene + terphenyl + POPOP) in a press die under a pressure of 100–200 g cm^{-2} and at a temperature of 140–150°C. (*PA*, 1962, #16,863)

1,285. PRESSED PLASTIC SCINTILLATORS WITH HETERO-ORGANIC ADDITIVES
Andreeshchev, E. A., Baroni, E. E., Kursanova, N. S., Rozman, I. M.
***Pribory i Tekhnika Eksperimenta*, v. 1961, no. 4, p. 151, July–August 1961**
(Translated from the Russian in *Instruments and Experimental Techniques*, v. 1962, no. 4, pp. 775–776, February 1962)

The results are described of attempts to prepare loaded plastic scintillators by pressing a split metal mold press at 2.5 kg cm^{-2} and 125–130°C. The resulting scintillators containing mercury and arsenic were transparent, while those containing lead and tin were cloudy. This difference is attributed to differences between the melting points of the different organometallic compounds in the polystyrene. However, the extent of the quenching of the luminescent efficiency for the lead and tin compounds was found to be much lower than for the mercury and arsenic compounds. It is concluded that plastic scintillators containing certain hetero-organic compounds and having a high luminescent efficiency can be prepared by the pressing technique. (*PA*, 1962, #23,610)

1,286. SUBSTITUTED *p*-OLIGOPHENYLENES. PART I. SYNTHESES AND PROPERTIES OF SUBSTITUTED *p*-OLIGOPHENYLENES
Wirth, H. O.
In "Proceedings of the University of New Mexico Conference on Organic Scintillation Detectors, August 15–17, 1960," pp. 78–91
U.S. Atomic Energy Commission, Office of Technical Information, Oak Ridge. Tenn.
(Available in TID-7612, U.S. Dept. of Commerce, Office of Technical Services, Washington, D.C.)

The Ullmann and organometallic carbonyl methods of synthesis of substituted *p*-oligophenylenes are discussed. The solubility in toluene, melting point, and UV absorption spectrum of these compounds are also discussed. (For Part II, see Entry #1,205.) (*NSA*, 1961, #29,406)

1,287. PLASTIC SCINTILLATORS
Baroni, E. E., Rozman, I. M., Shoniya, B. M.
January 25, 1960 (application date)
U.S. Department of Commerce, Washington, D.C.
USSR Patent 139,830
(See also *Byulleten Izobretenii*, no. 14, p. 48, 1961)

A claim is made for compounds from vinyl toluene polymers with an additive of *trans*-1,3,4,5-tetraphenyl-2-pyrazoline as a phosphor.

1,288. FLUORESCENT LIQUID BASED ON KEROSINE FOR FLAW DETECTION
Shuikin, N. I., Bekauri, N. G., Klimov, A. I.
May 9. 1960 (application date)
U.S. Department of Commerce, Washington, D.C.
USSR Patent 138,084
(See also *Byulleten Izobretenii*, no. 9, p. 51, 1961)

The claim concerns rearrangement of kerosine with the aid of a catalyst in H at an elevated temperature and pressure to form luminescent, polycyclic hydrocarbons. Toxicity and fire hazard are decreased and technological properties improved.

1,289. PHOSPHOR
Bozhevolnov, E. A., Lukin, A. M., Zavarikhina, G. B.
November 3, 1960 (application date)
U.S. Department of Commerce, Washington, D.C.
USSR Patent 139,388
(See also *Byulleten Izobretenii*, no. 13, p. 34, 1961)

The application of salicylidene-*p*-nitroaniline as an orange fluorescing phosphor of improved lightfastness is claimed.

1,290. SOLVENT FOR LIQUID SCINTILLATORS
Grekov, A. P., Aleksandrova, D. M., Titskii, G. D.
November 9, 1960 (application date)
U.S. Department of Commerce, Washington, D.C.
USSR Patent 139,390
(See also *Byulleten Izobretenii*, no. 13, p. 34, 1961)

A claim is made for an improvement in scintillation properties by the use of 1-methylnaphthalene as a solvent.

1,291. PHOSPHOR
Bozhevolnov, E. A., Drapkina, D. A., Brudz, V. G., Yarovaya, G. D., Kushnir, L. S.
November 29, 1960 (application date)
U.S. Department of Commerce, Washington, D.C.
USSR Patent 139,389
(See also *Byulleten Izobretenii*, no. 13, p. 34, 1961)

The application of the substance salicylidene-*p*-aminobenzoic acid as a yellow fluorescing phosphor of improved lightfastness in near ultraviolet is claimed.

1,292. SCINTILLATORS
Bezuglyi, V. D., Mukhina, S. A.
March 2, 1962 (patent application, June 10, 1961)
U.S. Department of Commerce, Washington, D.C.
USSR Patent 145,356

A mixture of methylmethacrylate and naphthalene is polymerized with luminophor-forming material. Peroxide initiators are used.

1,293. OPTICAL SCINTILLATORS

Bezuglyi, V. D., Grachev, N. M.
April 23, 1962 (patent application, May 26, 1961)
U.S. Department of Commerce, Washington, D.C.
USSR Patent 146,489

Poly(2,4-dimethylstyrene) is used in obtaining the scintillators.

1,294. SCINTILLATION SOLUTION ENHANCERS

Kallman, H. P., Furst, M., Brown, F. H.
December 11, 1962 (patent application, October 14, 1959)
U.S. Department of Commerce, Washington, D.C.
U.S. Patent 3,068,178 (assigned to Leonard E. Rauich)

An intermediate solvent added to a known efficient solvent to increase the fluorescence efficiency of the liquid transfers much or most of the energy originally present in the major solvent efficiently to the fluorescing material. The lowest energy level of excitation of the intermediate solvent is less than that of the primary solvent and greater than the energy level of excitation of the solute. An example is explained of the addition of naphthalene to dioxane-with-water solvent with the fluorescent solute of 2,5-diphenyloxazole. Intermediate solvents can be used to enhance scintillation solutions which contain $\geqq 5\%$ water, which may also contain compounds of elements whose atomic number is >10; rigid plastic scintillators, such as rods, can also be enhanced. Intermediate solvents increase fluorescence only if the bulk solvent is "poor" or if quenching materials are present in the scintillation solution. Intermediate solvents cannot increase fluorescence if it is caused by poor or weak light emitting solutes.

APPLICATION

1,295. USES OF LUMINESCENCE IN BIOLOGICAL RESEARCH

Tumerman, L. A.
***Akademiya Nauk, Izvestiya, Seriya Fizicheskaya*, v. 26, no. 1, pp. 84–93, January 1962**
(Paper presented at the Tenth Conference on Luminescence —Entry #500; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 26, no. 1, pp. 84–92, January 1962; published 1963)

Examples are used to show that investigation of the luminescence of biological objects may be useful in determining the physical mechanisms of some fundamental life processes.

In dealing with the problems of luminescence analysis, where certain substances must be identified or detected and (in some cases) their states determined, the researcher is concerned primarily with investigating the spectral composition of the luminescence or, in simpler cases, with determining its color. In contrast, when an attempt is made to utilize luminescence for investigating the mechanisms of biological processes, these purely spectral characteristics of the emission lose their importance, and attention must be focused on such attributes as the lifetime of the excited state of the luminescing atoms and molecules and the quantum yield of luminescence and its polarization, as well as the dependence of all these on the wavelength of the exciting light. It is natural to wonder whether the presence of a π-electron system (and all that ensues therefrom) is not responsible for the exceptional role played by aromatic compounds and polyenes in all important vital processes and, in particular, in the processes of accumulation and utilization of energy in cells.

A fundamental but little known physical fact is that in the entire world of living organisms there exists a kind of universal "energy currency," the chemical energy of the so-called macroergic bond in one definite and unique compound, namely, adenosine triphosphate (ATP). This compound serves as the accumulator and transformer of all forms of energy involved in life processes. In ATP, a phosphate chain is linked with adenine, a compound having a ring of conjugated bonds (i.e., a system of π-electrons). The role played by aromatic compounds in bioenergetic processes is discussed. Photosynthesis as well as emission spectra is considered.

1,296. SPECTRAL INVESTIGATION OF THE LUMINESCENCE OF MALIGNANT TUMORS

Karyakin, A. V.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya*, v. 26, no. 1, pp. 94–99, January 1962**
(Paper presented at the Tenth Conference on Luminescence —Entry #500; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 26, no. 1, pp. 93–97, January 1962; published 1963)

Luminescence (fluorescence) has been used for several years as a method of diagnosing cancer. Many of the uses of the method for tumors in different organs are described. After reviewing the published results, it is concluded that the method cannot yet be recommended for general adoption in clinical practice. Experiments were carried out by (1) staining excised tissues with fluorescein, and (2) staining intravitam where the dye is introduced three to six hours prior to operation. For several different organs the spectral characteristics of the fluorescent radiation are the same for normal and malignant tissues, though the intensity might vary considerably. Details of the results on many different tissues are described and some definite conclusions presented. (*PA*, 1963, #11,618)

1,297. LUMINESCENT METACHROMASY

Savostyanova, M. V.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,
v. 26, no. 1, pp. 100–102, January 1962
(Paper presented at the Tenth Conference on Luminescence —Entry #500; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 26, no. 1, pp. 98–99, January 1962; published 1963)

A brief statement is given of some applications of luminescence in biology, in particular the change of color of solutions of ionic dyes in the presence of high molecular weight substances. Some of the limitations of the technique are pointed out. Absorption and luminescence curves are given for aqueous solutions of trypaflavine in the presence of a surface-active agent. (*PA,* 1963, #9469)

1,298. STUDY OF FINE STRUCTURE OF FLUORESCENCE SPECTRA OF A SERIES OF POLYCYCLIC AROMATIC HYDROCARBONS AS A METHOD OF ANALYSIS OF CARCINOGENIC COMPOUNDS

Dikun, P. P.
Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,
v. 27, no. 1, pp. 9–11, January 1963

1,299. DERIVADOS LUMINISCENTES DEL BORAZOL, SU APLICACION AL CONTAJE DE NETRONES TERMICOS (LUMINESCENT DERIVATIVES OF BORAZOL AND THEIR APPLICATION IN COUNTING THERMAL NEUTRONS)

Videla, G. J., Molinari, M. A., Rojo, E. A., Lires, O. A., Casas, L. H.
1962
Comision Nacional de Energia Atomica, Buenos Aires, Argentina
Informe 77

The method of general purification is modified and used to prepare the luminescent derivatives of Borazol, and the spectra of fluorescent excitation are determined. The thermal neutron count, determined from tables of relative efficiency and various gamma-ray strengths, is given. Some results were obtained from experiments with solid borazols. Results showed that there are some advantages in measuring thermal neutrons by this method as compared to methods that use conventional counters. (*STAR,* N63-16,038)

1,300. FLUORESCENCE OF PLASMOCHINE AND ITS USE AS A FLUORESCENT INDICATOR

Buric, I. U., Draskovic, B.
***Glasnik Hemiskog Drustva, Beograd,* v. 27, no. 5–6, pp. 271–277, 1962**

1,301. A THIN PLASTIC RADIATION DOSIMETER

Harris, K. K., Price, W. E.
***International Journal of Applied Radiation and Isotopes,* v. 11, no. 2–3, pp. 114–122, September 1961**

Because of their very short range, radiation doses of low-energy particles and X-rays are difficult to measure by the usual methods. To perfect a dosimeter to measure low-energy radiation doses, the change in optical transmission of thin plastic films was studied as a function dose. A survey of 20 types of film placed in γ-radiation fields up to 10^7 r was made. Saran No. 7 was found to have the most suitable characteristics. The curve of optical densities of saran at 2600 Å vs. exposure dose was found to be a straight line on a log–log plot from 5×10^4 r to 10^7 r when irradiated by γ-radiation. A dose of 10^4 r was detectable and the range may extend above 10^7 r. The change in absorption of saran caused by radiation is only slightly reduced when irradiated in vacuum and measured in an inert atmosphere. (*PA,* 1962, #7798)

1,302. PHOSPHORESCENCE AND STIMULATED EMISSION IN ORGANIC MOLECULES

Morantz, D. J., White, B. G., Wright, A. J. C.
***Journal of Chemical Physics,* v. 37, no. 9, pp. 2041–2048, November 1, 1962**

Stimulated emission of light was demonstrated using aromatic organic molecules in a rigid glass matrix, e.g., acetophenone, benzaldehyde, benzophenone, α-bromonaphthalene, and pyrazine. This system is compared with the inorganic crystalline light masers. The experimental technique is described, and characteristic properties of the emitted light are given in detail and discussed. The conditions for achieving the stimulated emission threshold are described. The possibility of [illegible]enting molecules in a maser cell is proposed. (*PA,* 1963, #2610)

1,30[illegible] A NEW METHOD FOR STUDYING PORE SIZES BY THE USE OF DYE LUMINESCENCE

Rosenberg, [illegible] [illegible]bert, D. J.
***Journal of Physical Chemistry,* v. 65, no. 11, pp. 2103–2105, November 1961**
(Paper presented at the 138th National Meeting of the American Chemical Society, New York, N. Y., September 16, 1960)

A suitable phosphorescent dye was adsorbed on the porous substance. The principal criteria in the selection of the dye were high adsorbability (minimum of 10^{-8} mole of dye per gram of adsorbent) and a phosphorescence, of convenient mean life (about 1 sec), quenched readily by oxygen. Typical systems are acriflavine silica gel and fluorescein-alumina. The adsorbate sample was placed on a vacuum line, where it was baked out. Its phosphorescence, excited with a flash lamp, was intercepted by a photomultiplier tube, and the intensity–time curve was displayed on an oscilloscope. While the phosphorescence was still decaying, oxygen was admitted to the sample through a solenoid-operated mercury valve. By a proper choice of optical filters between the sample and the photomultiplier, it was possible to observe either the direct triplet to ground delayed emission of β-phosphorescence or the chemiluminescence accompanying the oxygen–dye reaction. The former process could be observed readily at any temperature from −160°C to room temperature; the latter was most conveniently studied at −100°C. The rate of either type of luminescence decay following admission of oxygen was found to depend on the rate of penetration of oxygen through the pores of the adsorbent. This fact was proved by two types of observations on adsorbates of acriflavine on silica gel.

It is proposed that these differences in luminescence decay rate might be used to determine the internal pore sizes of adsorbent substances. The method is applicable to any substance which can adsorb a suitable phosphorescent dye, so long as the adsorbent transmits the dye's excitation and luminescent bands.

1,304. ORGANOMETALLIC COMPOUNDS AS POSSIBLE LASER MATERIALS

Schimitschek, E. J., Schwarz, E. G. K.

***Nature*, v. 196, no. 4857, pp. 832–833, December 1, 1962**

The use of organometallic rare-earth compounds is proposed for laser action. The feasibility of the proposed approach is estimated numerically, using europium salicylaldehyde as an example.

The output power attainable in laser action is limited in practice by the energy transfer from the pump to the emitting system. Optically pumped systems in existence today are characterized by narrow absorption bands, resulting in poor utilization of the energy content of the spectra emitted by the pumping light source. A molecular system capable of absorption over a broad spectral band, in conjunction with sharp emission lines, is sought in order to obtain laser action at higher power outputs than those presently accessible.

The optical properties of the organometallic compounds discussed render them very attractive as potential laser materials. The pump power required to start laser oscillation is estimated, using the complex compound $Eu(5\text{-}NO_2\text{–}C_6H_3OCHO)_3$, and turns out to be $P_{uv} = (dN_{uv}/dt)\ (h\bar{\nu}) = 8.5$ w. This estimate indicates that organometallic lasers are feasible in principle. Experimental realization, however, will depend on overcoming various problems, the most prominent of which might be the photodecomposition under intense ultraviolet irradiation frequently observed in organic compounds.

1,305. PHOSPHORESCENCE IN PLASTICS

Forster, C. F., Rickard, E. F.

***Nature*, v. 197, no. 4873, pp. 1199–1200, March 23, 1963**

In a search for less costly forms of phosphors suitable for mail-coding applications, various organic systems were examined. It was found that enhanced intensities and prolonged decay periods were given at room temperatures when certain types of activating molecule were reacted simultaneously with the major components of aminoplastic resins. Since the resins formed from cyanuric acid and formaldehyde were more easily ground to a fine powder (suitable for use in printing inks, etc.), most of the results were obtained with this system. The amino-resin phosphors have been patented, and two such powders have been successfully used in field trials of automatic mail facing and sorting.

1,306. THE γ-RAY PERFORMANCE OF A LARGE VOLUME PLASTIC SCINTILLATOR

Iinuma, T. A., Burch, P. R. J.

***Nuclear Instruments & Methods*, v. 16, no. 2, pp. 247–261, July 1962**

The γ-ray spectral spread and the background count of a large plastic scintillator (20 × 10 × 6½ in.) viewed by two 7-in.-D photomultipliers (20th Century VMP/11/170 or EMI 9623) were investigated. The spectral spread on the high energy side was compounded of three independent factors (statistical, geometrical, and intrinsic), and the contribution of each factor to the total spread was calculated from experimental γ-ray spectra. The first two factors were then independently estimated by (1) determining the average number of photoelectrons released by a known energy deposition in the scintillator, and (2) directing collimated beams of γ-rays (from a Cs^{137} source) into the scintillator. It was found that the optimum performance could be obtained by applying proper distribution of high voltage on the photomultiplier and by using short light guides. The background spectrum (0–3 Mev γ-ray energy) was obtained inside a steel cubicle (5 in. thick wall), and additional 1-in. lead shielding reduced the background by 25%. The radioactivity of the photomultiplier was measured, and its contribution to the total background was assessed. The perspex light guide (1 or 1½ in. thick) reduced the background by about 10%, which was due to the photomultiplier radioactivity. The photomultiplier noise, which determines the lowest measurable energy, was found to be an increasing function with the voltage between photocathode and first dynode. The two types of 7-in. photomultipliers showed almost the same performances at their best conditions. (*PA*, 1962, #20,294)

1,307. UNTERSUCHUNGEN ÜBER DAS KURZZEITIGE ABKLINGEN EINIGER ORGANISCHER SZINTILLATOREN BEI ANREGUNG MIT γ-STRAHLUNG, PROTONEN ODER α-TEILCHEN (INVESTIGATIONS OF THE SHORT-LIVED DECAY OF ORGANIC SCINTILLATORS EXCITED BY γ-RAYS, PROTONS OR α-PARTICLES)

Peuckert, K.

***Nuclear Instruments & Methods*, v. 17, no. 3, pp. 257–260, December 1962**

The scintillation decay properties for the organic scintillators stilbene, NE 102, NE 150, NE 211, NE 213, NE 314, and anthracene were investigated in the time range from 3 to 200 nsec by observing the current pulses at the anode of a 56 AVP multiplier with a sampling oscilloscope of 500-Mc bandwidth. The results show that the scintillators stilbene, NE 211, and NE 213 are practically applicable for pulse shape discrimination. (*PA*, 1963, #6682)

1,308. DIRECTIONAL ANISOTROPY IN THE CHARACTERISTICS OF THE ORGANIC-CRYSTAL SCINTILLATORS

Tsukada, K., Kikuchi, S.
***Nuclear Instruments & Methods*, v. 17, no. 3, pp. 286–288, December 1962**

Scintillators for detecting fast neutrons were investigated. The directional anisotropies in the scintillation responses of the anthracene and *trans*-stilbene scintillators were measured by changing the direction of the incident neutrons to those scintillators. For anthracene, the directions of the neutrons which correspond to the maximum and minimum scintillation yields coincide with the *c'*- and *b*-axes, respectively, where the *c'*axis is defined as the axis perpendicular to the *ab*-plane. The directional anisotropy of the fast decay component is much more significant than that of the slow decay component. For *trans*-stilbene, no definite correlation was established between anisotropies in the scintillation responses and the crystal structure because of the complexity of the crystal used.

1,309. MESURE DE LA COMPOSANTE LENTE DE L'EMISSION DE LUMIERE DANS LES SCINTILLATEURS ORGANIQUES; APPLICATION A LA DISCRIMINATION DES PARTICULES SELON LEUR POUVOIR IONISANT (MEASUREMENT OF THE SLOW COMPONENT OF THE EMISSION OF LIGHT IN ORGANIC SCINTILLATORS. APPLICATION TO THE DISCRIMINATION OF PARTICLES ACCORDING TO THEIR IONIZING POWER)

Walter, G., Coche, A.
***Nuclear Instruments & Methods*, v. 23, no. 1, pp. 147–151, May 1963**

A method to study the rate of decay of the slow component of luminescence in organic scintillators is discussed. The results for stilbene, anthracene, diphenylacetylene (tolan), terphenyl, plastic scintillator NE 102, and one liquid scintillator are presented. The same principle is applied for the design of a circuit useful for discrimination between particles of differing specific ionization.

1,310. LIGHT COLLECTION IN PLASTIC SCINTILLATORS

Baroni, E. E., Rozman, I. M., Shoniya, V. M.
***Pribory i Tekhnika Eksperimenta*, v. 1961, no. 3, p. 159, May–June 1961**
(Translated from the Russian in *Instruments and Experimental Techniques*, v. 1961, no. 3, p. 571, December 1961)

A simple method is described for depositing a reflecting layer onto a plastic scintillator in order to improve the light collection. A MgO suspension in an ethyl alcohol-acetone mixture is sprayed onto the scintillator and allowed to dry; this process is repeated several times. A solution of cellophane in collodion and acetone is then sprayed on to fix the MgO deposit. Layers produced in this way have been found to be as good as conventional magnesium oxide powder reflectors. Measurements have shown that, with this new reflector, the Compton peak amplitude can be increased by a factor of 1.56 and the resolution improved from 55 to 25%. (*PA*, 1962, #19,689)

1,311. TRACKS OF CHARGED PARTICLES IN HIGH POLYMERS

Fleischer, R. L., Price, P. B.
***Science*, v. 140, no. 3572, pp. 1221–1222, June 14, 1963**

Heavily ionizing particles create trails of damage as they move through materials. In both addition and condensation polymers these trails can be selectively dissolved so that the sites and the directions taken by the moving particles are revealed. These materials thus serve as simple detectors of heavily charged particles.

1,312. THE EFFICIENCY OF ORGANIC SCINTILLATORS

Birks, J. B.
In "Proceedings of the University of New Mexico Conference on Organic Scintillation Detectors, August 15–17, 1960," pp. 12–36
U.S. Atomic Energy Commission, Office of Technical Information, Oak Ridge, Tenn.
(Available in TID-7612, U.S. Dept. of Commerce, Office of Technical Services, Washington, D. C.)

The factors determining the scintillation efficiency of various types of organic scintillators are discussed. Competitive processes in pure crystals and in binary and ternary solutions are considered. (*NSA*, 1961, #29,403)

1,313. HEXAFLUOROBENZENE LIQUID SCINTILLATORS AND THEIR APPLICATION TO GAMMA AND FAST NEUTRON DOSE RATE MEASUREMENTS

Williams, D. L.
In "Proceedings of the University of New Mexico Conference on Organic Scintillation Detectors, August 15–17, 1960," pp. 121–140
U.S. Atomic Energy Commission, Office of Technical Information, Oak Ridge, Tenn.
(Available in TID-7612, U.S. Dept. of Commerce, Office of Technical Services, Washington, D. C.)

Because C_6F_6 contains no hydrogen, it can be used as the solvent for a gamma-sensitive liquid scintillator in a paired detector system. Methods for synthesis and purification of C_6F_6 are given. Solutes in C_6F_6 were evaluated as liquid scintillators; 9,10-diphenylanthracene in oxygen-free C_6F_6 is considered to be the best choice for monitoring high gamma dose rates. The design of photovoltaic cell detectors for use with gamma-sensitive scintillators is discussed, as is the calibration of paired detectors. The factors affecting detector response are discussed in detail. (*NSA*, 1961, #29,409)

1,314. THE PERFORMANCE OF LARGE-VOLUME PLASTIC SCINTILLATORS WITH REFERENCE TO WHOLE BODY COUNTING

Burch, P. R. J.

In "Proceedings of the University of New Mexico Conference on Organic Scintillation Detectors, August 15–17, 1960,"
pp. 329–343
U.S. Atomic Energy Commission, Office of Technical Information, Oak Ridge, Tenn.
(Available in TID-7612, U.S. Dept. of Commerce, Office of Technical Services, Washington, D. C.)

The factors affecting the resolution of large plastic scintillators used for γ-ray detection are discussed, and it is shown that the pulse height observed for a given event depends on its position in the scintillator. Light guides and scintillator thickness are discussed. Preliminary counting statistics are presented for a three-unit plastic scintillator apparatus. (*NSA*, 1961, #29,420)

1,315. LUMINESCENT SCREENS

Reschauer, E.
December 19, 1958 (application date)
U.S. Department of Commerce, Washington, D. C.
German Patent 1,106,600 (addition to German Patent 1,032,068)

The process of coating luminescent layers with an aqueous solution or dispersion of synthetic resins containing gelling agents (alginates, proteins, or pectins), which is fixed by gelling and by H_2O evaporation, is claimed. The resultant reflection or electroluminescent layers provide workable screens.

1,316. ORGANIC ELECTROLUMINESCENT MATERIALS

The Dow Chemical Company
February 22, 1963 (patent application, January 5, 1962)
U.S. Department of Commerce, Washington, D. C.
French Patent 1,318,673

Organic materials are claimed which have a longer life than the usual inorganic electroluminescents. They may be used to give to the television screen, for example, a number of differently colored tints. An example is given of anthracene with 1 wt. % tetracene dissolved in hot C_6H_6 and evaporated to dryness. A thick paste is prepared by crushing this material with 1 wt. % coal and silicone oil, and a layer 25μ in thickness is spread on a flat electrode plated with Cr. A layer of polystyrene 25μ in thickness is applied, and then covered with a conducting glass plate. When a voltage of 800 v at 6,000 cps is applied across the metal plate and glass, a green light shines through the glass plate.

1,317. RADIATION DOSIMETRY AND PLASTICS COMPOSITIONS THEREFOR

Acitelli, M. A., Blair, G. E.
August 27, 1963 (patent application, December 12, 1960)
U.S. Department of Commerce, Washington, D. C.
U.S. Patent 3,102,197 (assigned to Bausch and Lomb, Inc.)

The method of radiation dosimetry described consists of (1) subjecting to radiation a body of transparent organic plastic containing an organic dye throughout its mass, and (2) measuring the resultant change in optical density. Preparation of several suitable internally dyed plastics is described, and curves illustrate the changes in absorption coefficients of the materials produced by exposure to radiation. The materials are more nearly tissue equivalent than previous inorganic dosimeter materials; they are inexpensive to manufacture and simple to use. (*NSA*, 1964, #5685)

1,318. UNTERSUCHUNGEN AN EINEM GASSZINTILLATIONSZÄHLER (STUDIES WITH A GAS SCINTILLATION COUNTER)

Lorenz, W., Lauterjung, K. H.
***Zeitschrift für Physik*, v. 165, pp. 74–78, October 18, 1961**

Anthracene, Na salicylate, quaterphenyl, and diphenylstilbene were used as energy converters to transform the scintillation light of the Ar into wavelengths of maximum sensitivity of the photomultiplier. Gradual decrease in sensitivity with time was noticed, perhaps caused by organic vapors originating from the energy converters or seals. The effect of gas pressure on quantum yield and on energy resolution was studied for the argon scintillation counter

DIELECTRIC EFFECTS

GENERAL REFERENCES

1,319. MODERN DIELECTRIC MATERIALS

Birks, J. B., Editor
Academic Press Inc., New York, 1960

Electrical properties are included in the following chapters: "Hydrocarbon Insulating Oils," by N. Pilpel and E. H. Reynolds; "Chlorinated Hydrocarbons," by J. B. Birks; "Natural and Synthetic Rubbers," by W. J. Green and S. Verne; "Synthetic High Polymers," by J. B. Birks; and "Silicones," by D. J. Dowling.

1,320. PHYSIK DER KUNSTSTOFFE (THE PHYSICS OF PLASTICS)

Holzmuller, W., Altenburg, K., Editors
Akademie-Verlag, Berlin, Germany, 1961

This book covers in detail the physical properties of macromolecules in the solid and liquid states, and includes both theory and experimental work. After an introduction (1), chapters are devoted to (2) synthesis of polymers (66 pages); (3) macromolecular solutions (158 pages); (4) macromolecular structure (90 pages); (5) mechanical behavior of plastics (120 pages); (6) thermal (32 pages), (7) electrical (74 pages), and (8) optical properties (26 pages); and (9) suitability for industrial purposes (43 pages). Chapter 3, which is very comprehensive, contains material on thermodynamic properties, transport phenomena, and methods of determining molecular weights. It also deals with light scattering and X-ray scattering. Chapter 4 is concerned with binding forces, structural determination by X-ray analysis and transformation properties. The elastic and viscous behavior of plastics is treated in chapter 5, while in chapters 6, 7 and 8 thermal expansion, specific heat determination, dielectric properties, ultraviolet and infrared absorption, and artificial double refraction are considered. Mechanical strength and hardness are considered in chapter 9. Each chapter is separately supplied with references, totaling some 700 in all, together with 370 diagrams. There are a number of tables, including one which lists all the journals dealing with plastics, and a summary of the most important technical expressions in German, English, French, and Russian.

1,321. TRANSACTIONS OF THE THIRD CONFERENCE ON FERROELECTRICITY

Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,
v. 24, no. 10, pp. 1176–1306; no. 11, pp. 1308–1342, 1960
(Translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 24, no. 10, pp. 1179–1301; no. 11, pp. 1307–1431, 1960)

This conference was held in Moscow on April 25–30, 1960 Topics discussed included the theory of ferro- and antiferroelectrics; investigation of ferroelectrics by NMR and X-ray diffraction methods; and preparation and properties of ferroelectric substances. (*PA*, 1962, #12,561)

1,322. SURVEY OF THE DIELECTRIC PROPERTIES OF SEMICRYSTALLINE POLYMERS: POLYCHLOROTRIFLUOROETHYLENE

Hoffman, J. D.
American Chemical Society, Washington, D. C.
Paper 19, Division of Polymer Chemistry, presented at the 144th Meeting, ACS, Los Angeles, Calif., March 31–April 5, 1963

A survey of the dielectric phenomena exhibited by a dipolar semicrystalline polymer is given using PCTFE as an example. Discussion is presented for systems where independent motions of side chains do not enter. Comparison with the corresponding dynamic mechanical data is given where relevant.

Semicrystalline polymers of the general type under discussion exhibit three distinct loss peaks when the loss index e' is plotted as a function of temperature at a constant frequency. (The mechanical loss data show similar peaks.) The origin of each of these peaks is discussed with reference to the phase of origin and the possible molecular mechanisms. The high temperature peak is a crystal contribution. The intermediate temperature peak is an amorphous phase contribution, and appears just above T_g. The low temperature peak occurs in the glassy phase well below T_g.

The three peaks mentioned do not exhaust the bulk dielectric processes of interest. For example, PCTFE crystals exhibit a very high frequency (microwave) contribution to the dielectric constant, which is as yet unexplained. Also, PCTFE specimens of equal density (i.e., a similar degree of crystallinity) exhibit large differences in dielectric behavior depending on the type and size of crystals. These and related subjects are considered.

1,323. SPACE-RADIATION EFFECTS ON ELECTRICAL INSULATION AND SEMICONDUCTORS. ELECTRICAL INSULATION 1961-62

Weller, J. F., Campbell, F. J., Kallander, J. W.
***Electro-Technology,* v. 69, pp. 116–124, February 1962**

The interaction of organic materials with radiation (ionization and excitation) leaves an environment of free electrons, ionized molecules, and free radicals. Whether produced by electrons, protons, X-rays, or gamma rays, the reactions depend primarily on the total radiation absorbed by the material. The free ions and electrons have a transient effect on properties such as conductivity, capacitance, dissipation factor, and electric strength, which varies with the rate, time, and temperature of the exposure. The transient effect decays at an exponential rate to constant value after the material is removed from the radiation field. The resistivity of polystyrene and polyethylene decreases by a factor of 10^8 on exposure to 4000 PRE (physical roentgen equivalent) of X-rays. Shortly after polytetrafluoroethylene is placed in a gamma-ray field, a small decrease in resistivity occurs which varies with exposure rate and thickness. After exposure to 57 Mrad there is no change in dielectric constant or electric strength. In vacuum the volume resistivity decreases slightly; however, significant increases in the 60-cps dielectric constant and dissipation factor result. The latter properties reach maximum peaks during early stages of irradiation, and with continued exposure decrease to approach the initial values. When irradiated in air, both TFE-6 and TFE-7 attain approximately the same dielectric constant and dissipation factor, and no decline is noted due to continued exposure. Under similarly irradiated vacuum conditions, however, TFE-6 has higher peak values. Permanent effects of electron radiation on capacitance and on the dissipation factor of polyethylene increase linearly with dosage. Insulation resistance of polyethylene terephthalate decreases by a factor of 10^7 at 300-Mr electron radiation.

The effect of temperature on irradiated materials is a critical factor affecting their stability. A comparison of radiation effects on tensile strength of silicone rubber shows that 18 Mrad at 200°C produces the same damage as 55 Mrad at 23°C. Similarly, equivalent values of electric strength are reached for silicone varnish on magnet wire irradiated with 196 Mrad at 200°C and with 2000 Mrad at 23°C. The descending order of electric strengths of wire enamels (modified to include radiation exposure) is: polyesters, silicones, polyvinyl formal, epoxy, and polytetrafluoroethylene.

The crystalline structure of a semiconductor will change upon displacement of an atom from its normal position. This results in the establishment of impurity levels in the forbidden region, and provides locations where carriers can recombine or become trapped, altering both the conductivity and the lifetime of the carrier. The number of lattice displacements is a function of flux, energy, and specific nature of the radiation.

1,324. PROGRESS IN DIELECTRICS, VOLUME III
Birks, J. B., Hart, J., Editors
Heywood & Company, Ltd., London, and
John Wiley & Sons, Inc., New York, N. Y., 1961

1,325. PROGRESS IN DIELECTRICS, VOLUME IV
Birks, J. B., Hart, J., Editors
Heywood & Company, Ltd., London, and
Academic Press, New York, N. Y., 1962

1,326. PROGRESS IN DIELECTRICS, VOLUME V
Birks, J. B., Hart, J., Editors
Heywood & Company, Ltd., London, and
Academic Press, New York, N. Y., 1963

1,327. DIELECTRIC BEHAVIOR AND STRUCTURE
Smyth, C. P.
McGraw-Hill Book Co., Inc., New York, N. Y., 1955

1,328. TRENDS IN DIELECTRIC RESEARCH DURING 1960
Parks, A. M
In "Digest of Literature on Dielectrics—1960," Volume 24, pp. 1–6
Callinan, T. D., Parks, A. M., Editors
National Academy of Sciences, National Research Council, Washington, D. C., 1961 (available as Publication 917)

Interest in polymers and plastic films centered around studies of the damaging effects caused by radiation and corona discharge. Polyethylene continued to be of primary interest although more and more data on epoxy resin systems were becoming available. The changes in electrical properties were used to follow polymerizations, but most of the literature on epoxies involved new compounding techniques to improve one or another specific property, rather than new materials. Other generally studied polymer systems included polyvinyl chloride, the polymethacrylates, and the silicones. The newer fluorocarbon resins were being investigated for high temperature applications.

In the area of fibrous insulation, perhaps the most significant contribution was the observation that the temperature dependence of the conductivity of dry cellulose is similar to that of an inorganic crystal. The data showed the conductivity could be represented by the sum of two terms: one due to ionic conduction and the other to absorbed water. The results were in excellent agreement with the theoretical calculations which include the usual water-cellulose complex. From studies of the conductivity of cellulose containing known amounts of water, a second equation was derived. This equation involved saturation conductivities and an integer which is believed to be associated with the number of vacant or water-occupied sites within the cellulose molecules.

Interest in synthetic fiber papers and nonwoven fibrous structures centered on preparation rather than electrical characteristics. Some promising results were obtained with acrylics, certain butadiene copolymers, and glass fibers.

The trends in natural and synthetic rubbers were again toward increasing their stability to temperature, aging, and radiation. The majority of work was done on actual cable installations. Butyl rubbers were still preferred for their good resistance to weathering, but the use of silicone, fluoro-, and nitrile-polyvinyl chloride rubbers for high temperature applications had increased. Polyethylene blends were still considered desirable because of their advantages in mechanical properties.

1,329. TRENDS IN DIELECTRIC RESEARCH DURING 1961

Parks, A. M.
In "Digest of Literature on Dielectrics—1961," Volume 25, pp. 1–5
Parks, A. M., Editor
National Academy of Sciences, National Research Council, Washington, D. C., 1962 (available as Publication 1034)

The increased attention given dielectrics and insulation systems as shown by the phenomenal growth in the volume of literature in the field during 1961, especially in the areas of ferroelectrics and conduction processes, is pointed out. One very evident trend noted is the increasing contribution of foreign scientists both to fundamental research and to application work in the areas of dielectrics and insulation. Mention is made of the organic as well as inorganic materials.

1,330. GENERAL THEORETICAL AND EXPERIMENTAL WORK

Hart, J.
In "Digest of Literature on Dielectrics—1961," Volume 25, pp. 109–130
Parks, A. M., Editor
National Academy of Sciences, National Research Council, Washington, D. C., 1962 (available as Publication 1034,

Pages 118 and 119 present résumés of the following: electrical conduction as a dielectric phenomenon; static electrification; and electrets.

1,331. HIGH POLYMERIC MATERIALS

Mayer, R., Zaring, M., Palinchak, S.
In "Digest of Literature on Dielectrics—1961," Volume 25, pp. 299–343
Parks, A. M., Editor
National Academy of Sciences, National Research Council, Washington, D. C., 1962 (available as Publication 1034)

Publications on the electrical insulating properties of elastomeric and plastic materials during 1961 are reviewed. Because of the vast amount of information on this subject, it was necessary to be selective in the choice of publications in order to avoid repetition of data and references to purely commercial announcements. Numerous studies on electrical insulating materials, including methods of testing, applications in components, and the influence of environments, are reported. Some new polymers are being developed for use in cryogenic and high-temperature applications, and as semiconductors. These and a variety of other pertinent subjects are discussed.

1,332. INSULATING FILMS AND FIBROUS MATERIALS

Kasarda, D. D.
In "Digest of Literature on Dielectrics—1961," Volume 25, pp. 345–358
Parks, A. M., Editor
National Academy of Sciences, National Research Council, Washington, D. C., 1962 (available as Publication 1034)

Literature concerned with the dielectric properties and insulation applications of polymer films and fibrous materials is reviewed. Although the primary concern is with articles which appeared in 1961, reference is also made to some earlier work not mentioned previously in this publication. Some articles, e.g., those concerned with water absorption, are mentioned because of their important relation to the insulating properties of fibers and films.

Relatively little study directly related to the electrical properties of fibers was reported in 1961. Water absorption and crystallinity received almost equal attention.

The importance of paper as a capacitor dielectric and insulating material has resulted in continued efforts to control quality and to classify those variables which affect the dielectric properties.

A considerable amount of work concerned with polymer films was published, and the trends established in the past few years were continued. Especially worthy of note are a new polyester—poly(1,4-cyclohexylenedimethylene terephthalate)—which has improved resistance to hydrolysis, and two new classes of polymers—polyimides and polybenzimidazoles—which show promise for high temperature applications. The electrical conductivity of polyethylene terephthalate has been related to molecular structure, degree of crystallinity, and crystallite orientation.

1,333. DIELECTRIC PROPERTIES (EXCLUDING DILUTE SOLUTIONS)

de Brouckère, L.
March 1962
National Academy of Sciences, National Research Council, Washington, D. C.
Technical Report, "Unsolved Problems in Polymer Science," pp. 172–175, ASD TR-62-283, AF 33(616)-1861
AD-282,067

Past achievement, present problems, and foreseeable advancements in the field of polymer dielectrics are reviewed.

1,334. FERROELEKTRISCHE UND PIEZOELEKTRISCHE EIGENSCHAFTEN BIOLOGISCH BEDEUTSAMER STOFFE (FERROELECTRIC AND PIEZOELECTRIC PROPERTIES OF BIOLOGICALLY SIGNIFICANT SUBSTANCES)

Athenstaedt, H.
***Naturwissenschaften*, v. 48, pp. 465–472, July 1961**

This review demonstrates the many similarities in properties between ferroelectrics, electrets, and liquid crystals. The nematic phase of the liquid crystals is considered analogous to the ferro- or ferrielectric state, while the smectic phase is considered equivalent to an antiferroelectric state. Emphasis is placed throughout on the fact that most of the substances under discussion either are organic chemicals occurring in nature or are related to naturally occurring substances. (*PA*, 1961, #17,831)

1,335. PLASTIC CRYSTALS AND ROTATION IN THE SOLID STATE

***Physics and Chemistry of Solids*, v. 18, no. 1, pp. 1–92,**
January 1961

The proceedings of a symposium held in the Inorganic Chemistry Laboratory, Oxford University, April 5 and 6, 1960, are presented. The symposium was supported by the U.S. Department of the Army through its European Research Office. Nine invited papers were presented, followed by eight contributed papers. (*PA*, 1961, #14,144)

1,336. PLASTIC CRYSTALS: A HISTORICAL REVIEW

Timmermans, J.
***Physics and Chemistry of Solids*, v. 18, no. 1, pp. 1–8,**
January 1961
(Paper presented at the Plastic Crystals Symposium,
Oxford University, England, April 5–6, 1960)

Tables are given classifying organic compounds as either "globular" (low entropy of melting) or "non-globular" (high entropy of melting). Properties such as heat capacity and dielectric constant are discussed in relation to their changes on the transition of the substance from ordinary to plastic crystalline state. (*PA*, 1962, #10,306)

1,337. CHEMICAL STRUCTURE AND DIELECTRIC PROPERTIES OF HIGH POLYMERS

Reddish, W.
***Pure and Applied Chemistry*, v. 5, no. 1–2, pp. 723–742,**
1962

This note is not an attempt to review the vast literature of experimental and theoretical investigations which is directed toward the interpretation of electrical properties in terms of structure. This is not necessary at present as a number of authoritative review articles have appeared within the last few years, covering polymers specifically, the relevant dielectric theory, and the broader field of dielectric properties of solids. Instead, the intent is to submit for consideration a selection of results, some of them new data, which are considered to be typical of the phenomenology of the subject; some ideas which provide its conceptual framework; and some thoughts on future possibilities and objectives.

A rough map is presented to show the logical steps and areas of theoretical ideas which must be traversed in order to connect electrical properties to chemical structure. Ionic and electronic conduction studies are briefly discussed, and, in addition, extensive consideration is given the dc and ac dielectric properties and their dependence on structure.

It is concluded that, although there are links (of the general nature indicated in the range map mentioned) connecting measured electrical properties of solid polymers with concepts of their molecular structure, these links are often tenuous, involve a wide range of related experience, and are often post-rationalizations rather than *a priori* predictions. 29 references.

1,338. FUNDAMENTAL WORK ON DIELECTRIC PROPERTIES OF PLASTICS AND CERAMICS

***R & D (Research and Development for Industry)*,**
Great Britain, no. 8, pp. 55–58, April 1962

Research being carried out at present in the U.S.A. is reviewed. Topics discussed include electric polarization, controlled conductivities, dielectric measurements on ceramics, and degree of crystallinity. (*PA*, 1962, #16,766)

THEORY

1,339. DIELECTRIC SATURATION THEORY FOR MOLECULES WITH TWO AXES OF INTERNAL ROTATION

Kluk, E.
***Acta Physica Polonica*, v. 20, pp. 845–851, 1961**
(in English)

Previous work in the field of dielectric saturation in rotational isomers was generalized to include rotational isomers with 3-C chains and two axes of rotation. Calculations were carried out for the case of two Me groups at either end, or halogen substituents, which give rise to a rotating group with a dipole moment. A continuous potential barrier for the interaction between groups during rotation was constructed; $V = kTY\ (\cos \theta_{1,2} - 3 \cos \theta_1 \cos \theta_2)$, where Y is the interaction energy in kT units, $\theta_{1,2}$ is the angle between the dipoles, and θ_1, θ_2 are the angles between either dipole and the line connecting them. By assuming the Onsager model, values were calculated for dielectric properties of several compounds.

1,340. THE MECHANISM OF A FERROELECTRIC PHASE TRANSITION IN THIOUREA AT 133°K

Vainshtein, B. K., Dvoryankin, V. F.
***Akademiya Nauk SSSR, Doklady*, v. 140, no. 1, pp. 111–114,**
September 1, 1961
(Translated from the Russian in *Soviet Physics—Doklady*,
v. 6, no. 9, pp. 747–749, March 1962)

The X-ray and electron diffraction structure determinations of thiourea are discussed in relation to the phase transitions in the material. The ferroelectric properties of the lowest-temperature phase are attributed to the nonplanar nature of the molecule and to the development of strong hydrogen bonding at low temperatures. (*PA*, 1962, #667)

1,341. A NEW SECOND-ORDER TRANSITION TEMPERATURE RELATIONSHIP FOR COPOLYMERS

Dyvik, G. K., Bartoe, W. F., Steck, N. S.
American Chemical Society, Washington, D. C.
Paper 22, Division of Polymer Chemistry, presented at the 144th Meeting, ACS, Los Angeles, Calif.,
March 31–April 5, 1963

Recent measurements at 60 cps have shown a good correlation among α-peak, Vicat, and dilatometric T_g temperatures. Other measurements of copolymer systems have suggested a restudy of existing second-order transition temperature relationships. This study has revealed that the most common of these equations are mathematically equivalent and not fully satisfactory for explaining all observations. A relationship is proposed which is capable of fitting either linear or nonlinear second-order transition relationships for compatible copolymer systems. Some mechanics of this relationship are suggested.

1,342. CHARGE DECAY OF CARNAUBA-WAX ELECTRETS

Perlman, M. M., Meunier, J.-L.
American Physical Society, New York, N. Y.
Paper T5, presented at the American Physical Society Winter Meeting, California Institute of Technology,
Pasadena, Calif., December 19–21, 1963

Wiseman, et al., have developed a phenomenological theory, based on a superposition principle and a specific polarization function, to explain the typical charge reversal of electrets in the shielded state. In a previous paper, it has been shown that the charge decay of a carnauba-wax electret in the unshielded state can be attributed mainly to self-polarization due to its own internal field. Wiseman's theory has been extended, the effects of internal field and finite resistivity have been included, and the charge decay of the electret in the unshielded state has been accounted for quantitatively. Experimental results on carnauba wax at 40°C and 10^{-5} mm Hg are consistent with (1) a low-frequency dielectric constant of 3.28 ± 0.10, and (2) a volume resistivity of $(8.7 \pm 0.5) \times 10^{17}$ Ω-cm. The results confirm the validity of the authors' phenomenological theory and of Gross's hypothesis concerning the nature of the charges present in the electret phenomenon.

1,343. MECHANISCHE UND DIELEKTRISCHE RELAXATIONSERSCHEINUNGEN UND IHRE MOLEKÜLPHYSIKALISCHE INTERPRETATION (MECHANICAL AND DIELECTRIC RELAXATION PHENOMENA AND THEIR MOLECULAR PHYSICAL INTERPRETATION)

Zeil, W.
***Angewandte Chemie*, v. 74, no. 8, pp. 271–290,**
April 21, 1962

The measurement of mechanical and dielectric relaxation phenomena yields information about the intermolecular interactions. In the case of gases, these are quite clear, whereas in the case of liquids and amorphous solids (high polymers), one must rely on simplifying models. Although the emphasis in terms of technical application today is on high polymers in relaxation studies, the intention here is to indicate the common physical bases for the mechanical and dielectric relaxation phenomena. In addition, a review of the relaxation behavior of gases, liquids, and amorphous solids (high polymers) is presented. These questions were the main theme of the 60 meetings of the German Bunsen Society for Physical Chemistry. Relaxation phenomena subject to chemical equilibria are not discussed, nor is the entire field of magnetic relaxation phenomena.

1,344. INTERPRETATION OF THE DIELECTRIC PROPERTIES OF GLYCOLS AS COMPARED WITH MONO-ALCOHOLS

Moriamez, C.
***Archives des Sciences*, v. 13, Special Number, pp. 48–53, 1961**
(Paper presented at the Ninth Ampere Colloquium, Pisa, September 12–16, 1960 — Entry #501)

A polymeric model is given for alcohol "association." The Kirkwood calculation method is used to obtain a g-factor of 2.67 for the two-dimensional polymer. When this is compared with known values for g of 1.92 for ethanediol, 2.30 for propanediol, 2.56–2.79 for 1,3-butanediol, 1.71 for 2,3-butanediol, and 2.64–2.84 for 1,5-pentanediol, good agreement is found. The kinetics of association was also considered.

1,345. THE THEORY OF DIELECTRIC POLARIZATION IN AMORPHOUS POLYMERS

Gotlib, Yu. Ya., Salidhov, K. M.
***Fizika Tverdogo Tela*, v. 4, no. 9, pp. 2461–2467, September 1962**
(Translated from the Russian in *Soviet Physics — Solid State*, v. 4, no. 9, pp. 1804–1808, March 1963)

An approximate kinetic equation for the motion of a polymer molecule in an amorphous sample has been used to show that the spectrum of the low-frequency dipole-elastic relaxation times is equivalent to the long-wave branch of the spectrum of the squares of the normal frequencies of an irregular molecular crystal with a complicated unit cell, and is of a universal nature, being independent of the structure of the particular polymer. The theory explains the value of width parameter in the dipole-elastic relaxation spectrum found experimentally. The defect structure of real amorphous polymers is responsible for the existence of different incoherent types of motion of small defect chain segments. The high-frequency dipole-radical relaxation in polymers may be related to intracellular motions and incoherent types of motion in the defects.

1,346. CALCULATION OF DEPOLARIZATION RATIOS, ANISOTROPIES, AND AVERAGE DIMENSIONS OF n-ALKANES

Smith, R. P., Mortensen, E. M.
***Journal of Chemical Physics*, v. 35, no. 2, pp. 714–721, August 1961**

A general scheme is outlined for the calculation of the polarizability and the depolarization ratio for alkane chains.

Computed results are given for these quantities and also for the mean-square end-end distance and the mean-square radius, for chains of up to 10 carbon atoms. The effects of various weighting-factor approximations, of excluded volume, of temperature, and of *trans-gauche* energy difference are discussed. The theoretical and experimental depolarization ratios are compared and discussed.

1,347. DIELECTRIC SATURATION AND HYDROGEN BONDING

Piekara, A.

***Journal of Chemical Physics*, v. 36, no. 8, pp. 2145–2150, April 15, 1962**

A new type of effect of dielectric saturation, as found by Malecki (Entry #1452) in alcohols and their solutions in nondipolar solvents, consists in the fact that an external electric field raises the dielectric permittivity of solutions of low concentration and lowers that of strong ones. The rise in permittivity (positive saturation effect) is due to the presence of dimers, whereas its decrease (negative saturation effect) is attributed to multimers, chiefly tetramers. The latter effect is essentially one of orientation of the multimers in the electric field. In addition, the proton shift due to the electric field introduces a small variation in the electric moment of the multimers, but raises that of the dimers very considerably, leading to the positive saturation effect in alcohol solutions of low concentration. (*PA*, 1962, #13,350)

1,348. DIELECTRIC LOSS IN "NONPOLAR" POLYMERS

Curtis, A. J.

***Journal of Chemical Physics*, v. 36, no. 12, pp. 3500–3501, June 15, 1962**

The small dielectric loss peak seen in so-called nonpolar polymers may be directly interpreted in terms of orientation of small dipole moments characteristic of the structure, rather than through the presence of impurity groups. Significantly higher dielectric loss is expected for polymers with methyl or other side-groups. (*PA*, 1962, #18,763)

1,349. DIELECTRIC DISPERSION OF POLAR POLYMERS

Bueche, F.

***Journal of Polymer Science*, v. 54, no. 160, pp. 597–602, October 1961**

A simple molecular theory is presented for the dielectric dispersion behavior of polar polymers. It is shown that the α-dispersion involves movement of the chain backbone. The relaxation time for this dispersion is given by a relation of form $\tau_a = a^2 f_0/4kT$, where a and f_0 are, respectively, the jump distance and friction factor for a chain segment. Although the numerical factor in this relation will depend somewhat on the exact model used for the computation, the general form of the relation is independent of the model as long as the chain can be considered a statistical coil. If the dipole is not rigidly attached to the chain backbone, a second region (β-dispersion) will result. The causes of the broadening of the dispersions are discussed.

1,350. DIELECTRIC CONSTANT AND DIPOLE MOMENT

Jatkar, S. K. K., Deshpande, C. M.

***Journal of the University of Poona, Science and Technology*, no. 12, pp. 61–73, 1957**

Theoretical and empirical equations developed by other workers for calculating dipole moments are critically reviewed. On the basis of theories of hindered rotation and anisotropy of the molecule, Jatkar has derived a simple equation applicable, by suitable substitution, to gases, liquids, and solids. The new equation seems to give better results than either the Debye–Clausius–Mosotti equation or that of Onsager and Kirkwood.

1,351. DIELECTRIC α_a AND β_c ABSORPTIONS IN SOME AMORPHOUS AND SEMICRYSTALLINE POLYMERS

Yamafuji, K., Ishida, Y.

***Kolloid-Zietschrift*, v. 183, no. 1, pp. 15–37, May 1962**
(in English)

The dielectric α_a- and β_a-absorptions in the linear high polymers whose dipoles are short and rigidly attached to their main chains are investigated theoretically and compared with observed data. Suffix "*a*" indicates that dielectric absorption comes from the amorphous part. Examples of this kind are polyvinyl chloride, polyvinyl bromide, polyethylene isophthalate, polyethylene terephthalate, and polyoxymethylene. The α_a-absorptions are attributed to the reorientations of their dipoles due to the segmental micro-Brownian motions of the polymer chains in the amorphous part. The β_a-absorptions seem to be caused by local micro-Brownian motions of the polymer chains. The β_a-absorptions are described by a model of local viscoelastic relaxations of the "dipoles" in the vicinity of their equilibrium directions. Here, the term "dipole" represents the resultant dipole of the permanent dipoles in the motional unit which has about the same order of magnitude as the monomer unit. Thus, the various properties of α_a- and β_a-absorptions are calculated and agree with observed values at least semi-quantitatively.

In the second section the equations of α_a- and β_a-absorptions are derived. The properties of the α_a-absorptions are calculated and compared with observed data. The magnitudes of α_a-absorptions of the semicrystalline polymers are smaller than those of the amorphous polymers even in the amorphous samples of the semicrystalline polymers. The temperature dependence of the magnitude of α_a-absorption is far gentler in the crystalline polymer as compared with the amorphous at temperatures higher than glass transition temperature (T_g). These observed tendencies are explained by the theory presented. The calculated values of the activation energies of α_a-absorptions are 50 ≈ 150 kcal/mole, the same orders as the observed values. The shape of the α_a-absorption is given by the form

$$[\varepsilon(i\nu) - \varepsilon_\infty]/[\varepsilon_0 - \varepsilon_\infty] = [(1 + i\omega\tau_1)(1 + i\omega\tau_2)^{-1}]^2$$

at temperatures higher than T_g. This is in good agreement with the observed shape in the amorphous polymer, not only for the order of breadth but also for the order of asymmetry. The shape of the α_a-absorption in the semicrystalline polymer is given by a superposition of the above formula and leads to the same order of breadth as the observed shape.

The properties of β_c-absorptions are also calculated with the aid of the above-mentioned model. The calculated values of the magnitude of β_a-absorptions show fairly good agreement with the observed values too. The temperature dependence of the magnitude of β_a-absorption is discussed. The calculated values of the activation energies of the β_a-absorptions are of the order 10 ≈ 20 kcal/mole, in good agreement with the observed values. The shape of β_a-absorption is also given by a superposition of the above formula and leads to the same order of breadth as the observed shape. The order of asymmetry of the theoretical absorption curve agrees with that of the observed curve.

1,352. PIEZOELECTRIC POLYMERS

Rez, I. S.
***Kristallografiya*, v. 6, no. 4, pp. 646–649, July–August 1961**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 6, no. 4, pp. 521–523, January–February 1962)

Past work is reviewed and interpreted theoretically. The conclusion is reached that piezoelectric activity may occur in conjunction with other properties under certain conditions; this is characteristic of many biological polymers (nucleic acids, nucleoproteins, and proteins). Such behavior may be understood on the basis of linearly ordered and partly delocalized systems of electrons in the presence of a spiral skeleton, as in Crick and Watson's model of DNA. Blyumenfeld and Benderskii have explained the electrical and magnetic anomalies in terms of these structures. The ferroelectric behavior may also be explained by using Cochrane's theory of directional labilization in relation to certain modes of oscillation in such structures.

1,353. THE ELECTRIC POLARIZATION OF ROD-LIKE, CHARGED MACROMOLECULES

Mandel, M.
***Molecular Physics*, v. 4, no. 6, pp. 489–496, November 1961**

The polarizability in the longitudinal direction of rod-like, highly charged macromolecules was evaluated. A simple model, emphasizing the discrete distribution of the fixed charges along the macromolecule, but neglecting interionic repulsion, was used to calculate the statistical distribution of the counterions which gives rise to this polarization. For weak electric fields, the expression obtained for the polarizability is analogous to that previously derived by Schwartz (1959), although it contains less implicit information about the temperature dependence and the influence of the valency of the counterions. The possibility that saturation effects may appear with high electric fields is left open. An approximate formula for the relaxation time of the longitudinal polarization is also derived. (*PA*, 1962, #3802)

1,354. TRIBOELECTRICITY IN POLYMERS

Henniker, J.
***Nature*, v. 196, no. 4853, p. 474, November 3, 1962**

A triboelectric series of well-defined polymers is presented, but there is no correlation with dielectric constant, dipole moment, luminescent color, or intensity. The Fermi levels remain the most reasonable property for correlating with the series. (*PA*, 1963, #6623)

1,355. CALCULATION OF THE POLARIZABILITY OF CONJUGATED MOLECULES, TAKING INTO ACCOUNT THE ELECTROSTATIC INTERACTION OF THE π-ELECTRONS

Rebane, T. K.
***Optika i Spektroskopiya*, v. 8, no. 4, pp. 458–464, April 1960**
(Translated from the Russian in *Optics and Spectroscopy*, v. 8, no. 4, pp. 242–245, April 1960)

The effect of electrostatic interaction of π-electrons on the polarizability of molecules with conjugated single and double bonds is considered. Appropriate equations of perturbation theory are derived by the self-consistent field method. The theory is applied to ethylene and benzene molecules with the use of simplifying assumptions taken from the semiempirical modification of the self-consistent molecular orbital method.

1,356. NATURE OF THE FERROELECTRIC TRANSITION IN TRIGLYCINE SULFATE

Blinc, R., Detoni, S., Pintar, M.
***Physical Review*, v. 124, no. 4, pp. 1036–1038, November 15, 1961**

The occurrence of linewidth transitions in the proton magnetic resonance spectra of triglycine sulphate, selenate, and fluoberyllate at the corresponding Curie points demonstrates that the ferroelectric transitions in these crystals are connected with a rearrangement of the basic ionic units in the unit cell. The results of a combined proton magnetic and infrared study confirm the crystal structure proposed by Pepinsky and coworkers. Further, the results show that the ferroelectric transition in triglycine sulphate and its isomorphs is of the order–disorder type and basically of the same nature as that in KH_2PO_4. The chief difference is the strong coupling of the protonic motion in triglycine sulphate with the motions of heavier groups. (*PA*, 1961, #17,833)

1,357. THEORIES OF THE DIELECTRIC PROPERTIES OF MACROMOLECULAR SOLUTIONS

Ingram, P., Jerrard, H. G.
***Science Progress*, London, v. 49, pp. 651–676, October 1961**

An accepted theory for the exact nature of the mechanism by which electric polarization occurs in macromolecular solutions is lacking. In this paper a number of theories are considered and critically examined. A general mathematical theory for the variation of dielectric constant with frequency is presented and discussed with reference to the molecular rotation theory of Debye (1954), the ionic atmosphere theory of Debye and Falkenhagen (1928), the interfacial polarization theory of Maxwell–Wagner (1913), the mobile proton theory of Kirkwood and Shumaker (1952), and the water structure hypothesis of Jacobson (1955). In discussing molecular rotation theories, the cases of gaseous polar molecules, and solutions of polar molecules in both a nonpolar and a polar solvent, are considered separately. The theories are discussed in connection with experimental results. It is concluded that molecular rotation alone is not sufficient to explain the dielectric properties of most macromolecular solutions, and that it is necessary to include charge transport processes arising from the motion of ions or other charge carriers in the solvent, in the ion atmosphere, and in the solute or suspended phase. (*PA*, 1962, #1162)

1,358. DIELECTRIC PROPERTIES OF SOLUTIONS OF HYDROPHILIC, HIGH-MOLECULAR-WEIGHT POLYMERS

Kurilenko, O. D.
***Trudy Kiloskogo Tekhnologicheskogo Instituta Pischevoi Promyshlennosti*, no. 17, pp. 151–160, 1957**
(See also *Referativnyi Zhurnal, Fiziki*, 1958, #27,389)

An attempt was made to ascertain the causes for dispersion in ε for aqueous solutions of high-molecular-weight polymers. It is indicated that the particles have a rigid dipole moment.

1,359. DEPENDENCE OF DIELECTRIC CONSTANT ON TEMPERATURE IN THE CRITICAL-POINT REGION

Shakhparonov, M. I.
***Vestnik Moskovskogo Universiteta, Seriya II: Khimiya*, v. 16, no. 4, pp. 25–30, 1961**

The theory previously given by Semenchenko and Azimov is critically analyzed, and the problem is treated thermodynamically.

1,360. RELAXATIONSUNTERSUCHUNGEN ZUM STUDIUM DER MOLEKULAREN VORGÄNGE IN HOCHPOLYMEREN (RELAXATION INVESTIGATIONS FOR THE STUDY OF THE MOLECULAR PROCESSES IN HIGH POLYMERS)

Wolf, K. A.
***Zeitschrift für Elektrochemie*, v. 65, no. 7–8, pp. 604–615, July–August 1961**

This is a review which deals mainly with the dependence of relaxation processes on temperature. After discussing the variation of dielectric constant and power loss with frequency, the temperature dependence of the relaxation times is considered. Graphs are given for polyvinyl acetate. The influence of dipole moments and of the steric hindering of the side-groups on the variation of the shear modulus and on the damping factor for torsional vibrations with temperature is considered with special reference to polyvinylmethyl ether, polyvinyl acetate, polyvinyl chloride, polyvinyl-*n*-butyl ether, polyvinyl-iso-butyl ether, and polyvinyl tertiary butyl ether. The temperature dependence of the real and imaginary parts of the complex shear modulus and of the logarithmic decrement of the damping of torsional vibrations is reviewed for linear and branched polymers. The effect of crystallinity on relaxation processes is also dealt with. (*PA*, 1962, #8141)

1,361. ZUR THEORIE DES DIELEKTRISCHEN VERHALTENS VON POLAREN HOCHPOLYMEREN IN LOSUNGEN (THEORIES ON THE DIELECTRIC BEHAVIOR OF POLAR HIGH POLYMERS IN SOLUTION)

Kaestner, S.
***Zeitschrift für Elektrochemie*, v. 65, no. 7–8, pp. 669–671, July–August 1961**

No satisfactory agreement has been found between existing theories and experimental results regarding the dielectric relaxation behavior of solutions of poly(methyl methacrylate) and poly(vinyl acetate). A new statistical segment model which is in better agreement with the experimental results is proposed.

EXPERIMENT

1,362. QUANTITATIVE MEASUREMENTS ON DISCHARGES IN SOLID INSULATORS IN AN INHOMOGENEOUS FIELD

Schmidt, J.
***Abhandlungen der Deutschen Akademie der Wissenschaften zu Berlin, Klasse für Mathematik, Physik und Technik*, no. 1, pp. 47–48, 1960**

The pre-breakdown currents from a point embedded in plexiglas (polymethylmethacrylate) were measured and the accompanying visual phenomena studied. It is suggested that microcracks in the plastic are widened by the gas pressure due to discharges from the electrode, and that further discharges and carbonization then follow in the widened passages. (*PA*, 1961, #17,849)

1,363. THE BREAKDOWN VOLTAGE OF EPOXY RESINS IN AN INHOMOGENEOUS FIELD

Eberhardt, M.
***Abhandlungen der Deutschen Akademie der Wissenschaften zu Berlin, Klasse für Mathematik, Physik und Technik*, no. 1, pp. 49–50, 1960**

Using an embedded point and a plane electrode, plots of ac breakdown voltage against electrode separation were obtained which were similar to those of gaseous breakdown. (*PA*, 1961, #17,850)

1,364. COMMENTS ON THE PROPERTIES OF TRIGLYCINE SULPHATE

Ballato, A. D.
***Acta Crystallographica*, v. 14, pt. 1, p. 78, January 1961**

Criticism is given the methods of Konstantinova, et al., (AI/LS 341, Entry #563) for deriving the piezoelectric (d) constants and the elastic compliances (s) from the experimental measurements. The possible errors in the d values are estimated, and corrected s values are given.

1,365. DIELECTRIC PARAMETERS OF BINARY LIQUID SYSTEMS IN THE CRITICAL REGION

Arkhangelskii, K. V.
In "Fizika Dielektrikov Sbornik," pp. 49–56;
(discussion) pp. 77–90
Akademii Nauk SSSR, Moscow, 1960
(See also *Referativnyi Zhurnal, Fizika*, 1961, #5D33)

For binary systems in the critical region, the variation of dielectric constant and of the angle of dielectric losses was studied as a function of temperature, concentration, and frequency. The system $PhNO_2$-heptane was investigated, and the effect of impurities on the properties of both the system and its components was studied. Results are given in the form of graphs.

1,366. DIELECTRIC PROPERTIES OF HETEROGENEOUS DIELECTRICS AT ULTRAHIGH FREQUENCIES

Parnas, Ya. M., Lebedeva, K. I.
In "Fizika Dielektrikov Sbornik," pp. 65–76;
(discussion) pp. 77–90
Akademii Nauk SSSR, Moscow, 1960
(See also *Referativnyi Zhurnal, Fizika*, 1961, #4E162)

The dielectric constant (ε) and loss factor ($\tan \delta$) were studied at high frequencies in the temperature range 20 to 200°C. The dependence of the parameters on the volume content of components of a heterogeneous dielectric was found. The dielectric constant of foam plastic and foam ceramics, which are mixtures of a solid phase and air, satisfies both the Lichtenecker and the Lorentz-Lorenz formulas for matrix systems with an air matrix phase. The dependence of $\tan \delta$ for epoxide resin–TiO_2 mixture, on the content of TiO_2, satisfies the Lichetenecker formula, as does ε of a mixture of epoxy resin with C black. The frequency dependence of ε for the dielectrics studied was found.

1,367. THE DIELECTRIC CONSTANT AND LOSS FACTOR OF POLYMERS AT ULTRAHIGH FREQUENCIES AS A FUNCTION OF TEMPERATURE

Mikhailov, G. P., Lobanov, A. M.
In "Fizika Dielektrikov Sbornik," pp. 91–96;
(discussion) pp. 105–108
Akademii Nauk SSSR, Moscow, 1960
(See also *Referativnyi Zhurnal, Fizika*, 1961, #5D95)

The temperature and frequency dependence of the dielectric constant and loss factor was measured for a series of polymers at −160 to +240°C. Measurements were made at ultrahigh frequencies of 420, 3000, and 10,000 Mc, and at low frequencies. The polymers studied included poly(methyl methacrylate), poly(vinyl acetate), polycaprolactam, poly(ethylene terephthalate), and poly(methyl acrylate).

1,368. USE OF COAXIAL RESONATORS FOR MEASURING DIELECTRIC LOSSES AND DIELECTRIC CONSTANT OF POLYMERS IN RELATION TO TEMPERATURE

Dmitrochenko, D. A., Shevelev, V. A.
In "Fizika Dielektrikov Sbornik," pp. 132–138
Akademii Nauk SSSR, Moscow, 1960
(See also *Referativnyi Zhurnal, Fizika*, 1961, #5D99)

Apparatus using a semi-coaxial resonator for studying the temperature dependences of the dielectric constant ε and dielectric losses $\tan \delta$ at 10-cm wavelengths is described. The design of a resonator for 536 Mc is given. Formulae are presented for calculating ε from the measured resonance frequency, and $\tan \delta$ from the Q-factor of the empty resonator and the resonator with a specimen. Graphs showing the dependence of ε and $\tan \delta$ on temperature are given for quartz and teflon. For teflon, ε changes linearly from 2.074 at +20°C to 2.020 at 160°C; $\tan \delta$ of teflon has a maximum at +50°C.

1,369. PHOTOELECTRETS AND ELECTROPHOTOGRAPHY

Zheludev, I. S. Fridkin, V. M.
In "Fizika Dielektrikov Sbornik," pp. 139–149;
(discussion) pp. 164–169
Akademii Nauk SSSR, Moscow, 1960
(See also *Referativnyi Zhurnal, Fizika*, 1961. #5E159)

The piezoelectric effect in polarized single crystals of anthracene and S was studied. Cubes cut from the crystals were polarized in a capacitor at a voltage of 20 kv/cm, and at the same time they were illuminated with the lamp PRK-2. The electrodes were then removed and the specimens kept in the dark. The charge density was measured either by measuring the discharge current during depolarization with light, or with an electrometer. To determine the piezo modulus the electret was compressed in the direction of polarization. When the load was removed, the deflection of the filament in the electrometer was observed. The effect was compared with the piezo effect for an X-cut quartz plate. A parallel study of the drop in the piezo modulus and the charge of the photoelectret with time showed that the values are proportional. The study of piezoelectric phenomena in S single crystals was only qualitative owing to the brittleness of S. 25 references.

1,370. EFFECT OF ADSORBED WATER ON THE ELECTRIC PROPERTIES OF ORGANIC DIELECTRICS

Rodionova, N. A.

In "Fizika Dielektrikov Sbornik," pp. 194–202;
(discussion) pp. 215–219
Akademii Nauk SSSR, Moscow, 1960
(See also *Referativnyi Zhurnal, Khimiya*, 1961,
#6R76 and #4D110)

Tan δ was measured from 400 cps to 100 Mc for a number of polymers in which adsorption of water occurs by a mechanism of activated diffusion: polyethylene, polystyrene, poly(tetrafluoroethylene), poly(trifluorochloroethylene), polycaprolactam, poly(hexamethyleneadipamide), poly(hexamethylenesebacamide), and polyurethan. Electrical conductivity in the last four polymers increased with increase in the amount of adsorbed water. In the last three polymers an increase in tan δ and a shift of maxima toward lower frequencies were observed, while in polycaprolactam only an increase in tan δ was noted. For amorphous polystyrene or partially crystalline polyethylene, a new maximum of tan δ appeared at 10^7 cps; this maximum is associated with H_2O sorption. For highly crystalline specimens of poly(trifluorochloroethylene) and poly(tetrafluoroethylene), no effect of H_2O sorption was observed. Change in electrical properties is associated with the density of the packing of the polymer.

1,371. PULSE BREAKDOWN OF CERTAIN POLYMERS AND MICA

Melnikov, M. A.
In "Fizika Dielektrikov Sbornik," pp. 256–261;
(discussion) p. 280
Akademii Nauk SSSR, Moscow, 1960
(See also *Referativnyi Zhurnal, Fizika*, 1961, #3D146)

Polystyrene, styroflex, fluoroplast-4, organic glass, and muscovite were studied. Electric potential-time characteristics were obtained at voltage exposures of 5×10^{-9} to 10^{-6} sec. These dielectrics exhibited a discharge delay at a voltage exposure of 5×10^{-9} sec, with this delay greater with lower dielectric strength. Breakdown in these dielectrics is thought to be due to impact ionization.

1,372. CERTAIN POST-BREAKDOWN PROCESSES IN LIQUID DIELECTRICS

Balygin, I. E.
In "Fizika Dielektrikov Sbornik," pp. 262–270
Akademii Nauk SSSR, Moscow, 1960
(See also *Referativnyi Zhurnal, Fizika*, 1961, #4D34)

A study is reported of the electric breakdown of liquids (an organosilicon compound, unoxidized and oxidized aniline, CCl_4, toluene, and a 3% solution of ethylcellulose in toluene) during an impulse discharge between two polished spherical electrodes with gap of 0.2 mm. Breakdown oscillograms were obtained whose characteristics depended on the physical-chemical properties of the liquid. Phenomena due to the very high temperature of the spark played the main role in the dynamics of the breakdown processes.

1,373. DIELECTRIC PROPERTIES OF GUANIDINE-ALUMINUM SULFATE HEXAHYDRATE

Zheludev, I. S., Rez, I. S., Sonin, A. S., Gladkii, V. V., Gurevich, V. M., Meleshina, V. A., Filimonov, A. A.
In "Fizika Dielektrikov Sbornik," pp. 393–403;
(discussion) pp. 429–431
Akademii Nauk SSSR, Moscow, 1960
(See also *Referativnyi Zhurnal, Fizika*, 1961, #5E200)

Data are reported on: the shape of hysteresis loops, spontaneous polarization, coercive field, time of repolarization, the effective dielectric constant, dc conductivity, and activation energy. The effects of temperature, crystal thickness, pulse intensity, and frequency are considered.

1,374. CONNECTION OF ELECTRIC CONDUCTIVITY OF FERROELECTRICS WITH FERROELECTRICITY

Rez, I. S., Gurevich, V. M.
In "Fizika Dielektrikov Sbornik," pp. 410–414;
(discussion) pp. 429–431
Akademii Nauk SSSR, Moscow, 1960
(See also *Referativnyi Zhurnal, Fizika*, 1961, #5E170)

The change in the resistance with time and temperature of rochelle salt single crystals, as well as $BaTiO_3$, was studied. In the ferroelectric phases of the materials, resistance increases with time, to saturation. This "transitional conductivity" does not occur in paraelectric phases, and it is hypothesized that this is associated with a 180-deg shift of the domain walls and with the growth of embryonic domains.

1,375. DIELECTRIC PROPERTIES OF ACETONE-CARBON TETRACHLORIDE SOLUTIONS IN ULTRAHIGH-FREQUENCY ELECTROMAGNETIC FIELDS AND CONCENTRATION FLUCTUATIONS

Kasimov, R. M., Akhadov, Ya. Yu., Shakhparonov, M. I.
Akademiya Nauk Azerbaidzhanskoi SSR, Doklady,
v. 17, pp. 207–211, 1961

Dielectric constants and loss factors for CCl_4-Me_2CO solutions were measured at 3.21 cm and 8.15 mm, with temperature from 0 to 40°C. Data are explained by assumption of concentration fluctuations; the results are not thought to be due to formation of molecular complexes.

1,376. DIELECTRIC PROPERTIES AND MOLECULAR STRUCTURE OF SOLUTIONS OF NITROBENZENE, METHYL ALCOHOL, AND WATER IN ACETONE

Kasimov, R. M., Akhadov, Ya. Yu., Shakhparonov, M. I.
Akademiya Nauk Azerbaidzhanskoi SSR, Doklady,
v. 17, pp. 687–690, 1961

Dielectric constants and losses of the title solutions were determined at wavelengths of 3.21 cm and 8.15 mm and temperatures between 0 and 40°C. Enthalpies and entropies of activation are considered. The semicircular complex dielectric constant plots of the pure components become circular arcs in the solutions.

1,377. THE DISPERSION OF THE DIELECTRIC CONSTANT IN THE CRITICAL REGION OF BINARY LIQUID SYSTEMS
Arkhangelskii, K. V.
***Akademiya Nauk SSSR, Doklady,* v. 143, no. 6, pp. 1378–1379, April 21, 1962**

It was found that, in the case of the system $C_6H_5NO_2$–C_6H_{14}, there exists in the ultracritical region not only a temperature but also a frequency dispersion of dielectric constant (especially for a mixture with 41.167% $C_6H_5NO_2$ and for audio frequencies). For the same system the dispersion of ε and tan δ begins at more than 5°C before the temperature of division into layers is attained. (*PA*, 1962, #15,611)

1,378. ELECTRIC CHARGES ARISING ON DEFORMATION OF POLYMERS
Gul, V. E., Lushcheikin, G. A., Dogadkin, B. A.
***Akademiya Nauk SSSR, Doklady,* v. 149, no. 2, pp. 302–304, March 11, 1963**

Cylindrical samples of poly(vinyl chloride), polystyrene, polypropylene, and polyethylene were molded from the powdered polymers, and one of poly(Me methacrylate) was cut from the bulk polymer. The samples were subjected to a compressive stress of 125 kg/cm² at 110°C for 3 hr. After cooling to 50°C, the stress was removed and the electric charge and its distribution along the surface of the samples were measured. The data indicate that mechanical deformation of polymers causes a rise of electric polarization accompanied by the buildup of an electric charge of reverse sign on the opposite surfaces. The magnitude of the charge is proportional to the degree of compression and depends on the cooling conditions; the charge distribution along the surfaces depends mainly on the strain heterogeneity. The usual charge-decay with time is accelerated by addition of plasticizers. Heating of the oriented samples removes the electrical polarization.

1,379. POLYCOMPONENT ORGANIC ELECTRETS
Yanson, Yu. Ya.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,* v. 22, no. 3, pp. 359–360 1958**

1,380. PREPARATION AND FERROELECTRIC PROPERTIES OF DEUTERATED TRIGLYCINE SULPHATE CRYSTALS
Konstantinova, V. P., Silvestrova, I. M., Shuvalov, L. A., Yurin, V. A.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,* v. 24, no. 10, pp. 1203–1208, 1960**
(Paper presented at the Ferroelectricity Conference — Entry #1,321; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 24, no. 10, pp. 1206–1211, 1960)

The replacement of hydrogen by deuterium raises the Curie point of the triglycine sulphate (DTGS) by ~10°C. The domain structure could not be observed by polarized light. Etched crystals, however, showed ellipse-shaped domains. The characteristic dielectric peak was observed. Under an ac field the dielectric constant showed nonlinear behavior, with a peak at E ~ 300 v cm⁻¹. Similar results were obtained with dc biasing. The temperature variation of the spontaneous polarization and coercive field was also measured with similar results to the hydrogen salt. The switching time of DTGS showed a strong temperature dependence only above 40°C —which is explicable by the increase in the Curie point. With their higher elastance, however, the activation field is greater and the mobility lower. (*PA*, 1962, #16,775)

1,381. EFFECT OF GAMMA-RADIATION ON THE FERROELECTRIC PROPERTIES OF TRIGLYCINE SULPHATE
Yurin, V. A., Baberkin, A. S., Kornienko, E. N., Gavrilova, I. V.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,* v. 24, no. 11, pp. 1334–1336, 1960**
(Paper presented at the Ferroelectricity Conference — Entry #1,321; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 24, no. 11, pp. 1334–1336, 1960)

The effect of gamma radiation on the ferroelectric properties of triglycine sulphate was investigated by observing the change in the hysteresis loops during irradiation. The stable states formed were either polydomain having double loops, or single-domain with biased single loops. These states were thought to arise from the internal bias fields established within the specimens during irradiation. (*PA*, 1962, #14,622)

1,382. FERROELECTRIC PROPERTIES OF TRIGLYCINE SULPHATE SINGLE CRYSTALS IN THE 0.01 TO 50 c/s FREQUENCY RANGE
Gurevich, V. M., Zheludev, I. S.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,* v. 24, no. 11, pp. 1342–1346, 1960**
(Paper presented at the Ferroelectricity Conference — Entry #1,321; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 24, no. 11, pp. 1341–1344, 1960)

This is a continuation of the study of the hysteresis loops of triglycine sulphate single crystals at infralow frequencies. The coercive field and the squareness of the loops increase with frequency between 0.01 and 50 cps, and with applied field strength up to 600 v/cm. (*PA*, 1962, #14,624)

1,383. EFFECT OF ULTRASOUND ON SOME PHYSICAL PROPERTIES OF ROCHELLE SALT CRYSTALS
Chormonov, T. Kh.
***Akademiya Nauk SSSR, Izvestiya, Seriya Fizicheskaya,* v. 24, no. 11, pp. 1347–1349, 1960**
(Paper presented at the Ferroelectricity Conference — Entry #1,321; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series,* v. 24, no. 11, pp. 1345–1347, 1960)

Ultrasonic energy (21.5 kc) is applied to growing rochelle salt crystals. The microhardness of crystals grown with ultrasonic radiation is higher than that of ordinary crystals. Data are given showing the temperature dependence of the dielectric constant and the loss tangent of sonicized and ordinary rochelle salt. The dielectric constant changes at all temperatures investigated if the crystal is treated ultrasonically, and the dielectric loss is substantially reduced. Study of X-ray diffraction lines shows that for sonicized rochelle salt crystals the diffusion width of the interference lines increases with large glancing angles while the intensity of the lines is weakened. (*PA*, 1962, #16,972)

1,384. STATIC ELECTRICITY IN POLYMERS: CHEMICAL STRUCTURE AND ANTISTATIC BEHAVIOR

Shashoua, V. E.
American Chemical Society, Washington, D. C.
Paper 6, Division of Polymer Chemistry, presented at the 140th Meeting, ACS, Chicago, Ill., September 3–8, 1961

A very sensitive method for measuring the antistatic properties of polymers was developed for use in a study of the relationship of chemical structure to antistatic behavior. In this method, the experimentally determined half-lives of charge decay for positive (τ_+) and negative (τ_-) applied potentials are used to calculate the root mean square half-life of charge decay (τ_{rms}). τ_{rms} was found to be related by an exponential law to the relative humidity conditions of measurement. From observation of the τ_{rms} values for some fifty vinyl and condensation polymers, certain functional groups, such as -COONa, -SO_3Na, -$HCONCH_3$, $CONEt_2$, -P-$(NMe_2)_2$, and imidazole, were found to confer good antistatic properties to polymers. These functional groups were more effective in improving the antistatic properties when they were used as side-chain substituents than when they were employed as part of the main polymer chain. A number of highly water-sensitive and water-soluble polymers were found to have extremely poor antistatic properties—indicating no direct correlation of antistatic properties with hydrophilic character.

A new parameter, the charge selective power of a substance, was devised to describe the charge polarity preference of a given substance. It is defined by the following equation:

$$\sigma = \frac{\tau_+ - \tau_-}{\tau_{rms}}$$

The charge selective power of substances was found to correlate well with their assignments in the tables of triboelectric series. The effect of impurities on the charge decay properties and the charge selective power was found to be extremely important in influencing antistatic behavior of polymers.

1,385. DIELECTRIC MEASUREMENTS ELUCIDATE STRUCTURE OF ACRYLIC POLYMERS

Steck, N. S.
American Chemical Society, Washington, D. C.
Paper 21, Division of Polymer Chemistry, presented at the 144th Meeting, ACS, Los Angeles, Calif., March 31–April 5, 1963

Dielectric measurements made at 60 cps over a temperature range of −40 to 200°C on small (0.2 g) samples are most useful in studying acrylic polymers. Not only has this method elucidated structure, but the study of some structures has led to new interpretations emphasizing the value of this type of measurement.

Data on a number of acrylic polymers are shown, and several copolymer systems are discussed. It is suggested that, at 60 cps, measurements of stereospecific PMMA samples can show more about molecular arrangements than has previously been revealed.

1,386. H-FILM — A NEW HIGH TEMPERATURE DIELECTRIC

Amborski, L. E.
American Chemical Society, Washington, D. C.
Paper 23, Division of Polymer Chemistry, presented at the 144th Meeting, ACS, Los Angeles, Calif., March 31–April 5, 1963

Polyimide polymers have shown exceptional mechanical and electrical properties over a wide temperature range. Specifically, polyimides resulting from the polycondensation reaction between pyromellitic dianhydride and aromatic diamines are infusible and intractable. A film of this type, designated as H-Film, exhibits useful mechanical and electrical properties from below liquid nitrogen temperature (flexible at 4°K) to beyond 500°C (tensile strength of 5000 psi). H-Film does not melt or burn, but will char above 800°C. The highly aromatic character of this polymer contributes to its extremely good thermal and radiation resistance and results in a fairly stiff but extremely tough film, having mechanical properties equal to or greater than any known organic polymeric film. H-Film has high electrical resistivity, low dielectric loss, and outstanding electrical breakdown strength. After 3000 hr at 300°C, H-Film retains over 90% of its original dielectric strength. Dielectric properties which have been investigated from −60 to +250°C are essentially constant over the useful temperature range. From the Arrhenius plots, the activation energies have been calculated for the dc conductivity and the dielectric loss process.

1,387. GENERATION OF STATIC ELECTRICITY BY CONTACT BETWEEN SOLIDS

Montgomery, D. J.
American Chemical Society, Washington, D. C.
Paper 24, Division of Polymer Chemistry, presented at the 144th Meeting, ACS, Los Angeles, Calif., March 31–April 5, 1963

The fundamental processes involved in the generation of electrostatic charge between solids are discussed according to the following scheme: When two objects are placed into contact so that their intermolecular fields may interact, charge will flow so as to equalize the electrochemical potentials within the objects. During separation of the objects, as the capacitance of the object diminishes, some of the transferred charge will return. When both objects are good conductors, the retained charge is small, and ordinarily is without consequence. However, when at least one of the objects is a good insulator, the retained charge may be large, and may have serious static-electricity effects. To analyze the transfer process, it is assumed that q, the net charge retained, may be considered as the product q_0, the charge transferred upon contact, times a quantity f, the fraction retained upon separation. The initial charge q_0 is determined by the chemical nature of the materials in contact, and by the impressed forces and the geometrical factors involved in the contact. The fraction f is determined by the ratio of the contact time (controlled by the relative velocity of the objects and by some distinct characteristic of the object) to a relaxation time (controlled by the electrical properties that affect the rate of charge dissipation). In the present paper, the factors q_0 and f are analyzed briefly, and the results of recent experiments are discussed.

1,388. STATIC ELECTRICITY IN POLYMERS

Shashoua, V. E.
American Chemical Society, Washington, D. C.
Paper 25, Division of Polymer Chemistry, presented at the 144th Meeting, ACS, Los Angeles, Calif., March 31–April 5, 1963

The antistatic behavior of a substance may be defined as its capacity to dissipate electrostatic charges quickly. The relationship of relative humidity, temperature, and chemical structure to the behavior of electrostatic charges on polymer surfaces was studied by measuring the rate of buildup and decay of known charges on a series of polymers. The instrumentation for obtaining such measurements and the theory for interpreting the results are discussed. The factors influencing assignment of a substance in a given triboelectric series are found to correlate closely with the difference in the rates of charge decay for positive and negative charges. The charge decay method was found to be the most satisfactory means of investigating the antistatic behavior of substances. A comparison of results from electrical resistivity measurements and charge decay measurements was made for a number of antistatic agents and their end-use performance. A general review of the theory and mechanism of charge decay from polymer surfaces is given.

1,389. MICROWAVE ABSORPTION AND MOLECULAR STRUCTURE IN LIQUIDS. XLI. THE DIELECTRIC RELAXATION OF THREE SUBSTITUTED NAPHTHALENES IN A SLIGHTLY VISCOUS AND A VERY VISCOUS SOLVENT

Grubb, E. L., Smyth, C. P.
***American Chemical Society, Journal of the*, v. 83, no. 20, pp. 4122–4124, October 20, 1961**

The dielectric constants and losses at wavelengths of 1.2, 3.2, 10, 25, and 50 cm and 575 m and temperatures of 20, 40 and 60°C have been measured for α-chloronaphthalene and α-bromonaphthalene in dilute solution in decalin and in Nujol, and for β-methylnaphthalene in dilution solution in Nujol. The data have been used to calculate the relaxation times of the polar solute molecules in the solutions. They all show a considerable distribution of relaxation times, both the distribution and the relaxation times decreasing with rising temperature. β-Methylnaphthalene, the longest molecule of the three, shows the largest distribution parameter and the largest relaxation time The activation energies and entropies for the dielectric relaxation processes have been calculated.

1,390. MICROWAVE ABSORPTION AND MOLECULAR STRUCTURE IN LIQUIDS. XLII. MOLECULAR AND GROUP ROTATION IN AROMATIC METHOXY AND ETHOXY COMPOUNDS

Grubb, E. L., Smyth, C. P.
***American Chemical Society, Journal of the*, v. 83, no. 24, pp. 4873–4878, December 20, 1961**

The dielectric constants and losses at wavelengths of 1.2, 3.2, 10, 25 and 50 cm, and 575 m, at temperatures of 20 and 40°C or 20, 40 and 60°C, have been measured for anisole, *p*-dimethoxybenzene, and α- and β-methoxy and α- and β-ethoxynaphthalene in solution in decalin and in Nujol, and for *p*-methyl-, *p*-chloro-, and *p*-phenylanisole in solution in Nujol. The two solvents were used in order to facilitate the analytical separation of the effects of the molecular and the intramolecular relaxation processe The equations used by Bergmann, Roberti, and Smyth to calculate the relaxation times for simultaneously occurring molecular and intramolecular relaxation processes have been employed in analyzing the results for the decalin solutions, but the equations have been modified to take care of the large distribution of molecular relaxation times occurring in the Nujol solutions. The calculated molecular relaxation times show dependence on the liquid viscosity, the dependence being greater the larger the molecule. The much smaller relaxation times for the rotation of the polar methoxy group within the molecule are virtually equal in the two solvents, and the same is true for the ethoxy group. The larger size of the ethoxy group gives it a relaxation time longer than that of the methoxy group. The shorter relaxation times of the methoxy and ethoxy groups in the 2-position as compared to the 1-position in the substituted naphthalenes give evidence of steric hindrance exerted by the hydrogen in the 8-position upon the rotation of a group in the 1-position.

1,391. MICROWAVE ABSORPTION AND MOLECULAR STRUCTURE IN LIQUIDS. XLIII. DIELECTRIC RELAXATION AND INTRAMOLECULAR ROTATION IN TEN AROMATIC AMINES

Grubb, E. L., Smyth, C. P.
***American Chemical Society, Journal of the*, v. 83, no. 24, pp. 4879–4883, December 20, 1961**

The dielectric constants and losses at all or most of the wavelengths of 1.2, 3.2, 10, 25 and 50 cm, and 575 m, at tempera tures 20, 40 and 60°C, have been measured for pure aniline and *N*,*N*-dimethylaniline, for dilute benzene solutions of aniline, p-toluidine, benzidene, N,N,N',N'-tetramethylbenzidene, α-naphthylamine, β-naphthylamine, diphenylamine, N-phenyl-1-naphthylamine and N-phenyl-2-naphthylamine and for dilute solutions of diphenylamine in Nujol and N-phenyl-1-naphthylamine and N-phenyl-2-naphthylamine in decalin. The refractive indices for the D sodium line have also been measured for most of the solutions. The data have been used to calculate the most probable dielectric relaxation times and have been analyzed to obtain relaxation times for dipole orientation by molecular and intramolecular rotation. The molecular relaxation times calculated from the measurements are of the magnitudes to be expected from the sizes and shapes of the molecules. A second relaxation time obtained for each substance in solution is associated with intramolecular motion—the slightly hindered rotation of an NH_2 or $N(CH_3)_2$ group, or the more hindered rotation of a phenyl or naphthyl group, or a combination of the two relaxation times of a phenyl and a naphthyl group rotation.

1,392. THE DIELECTRIC PROPERTIES OF PALMITIC ACID AND ALEURITIC ACID

Sen, A. K., Bhattacharya, G. N.
***Applied Physics Quarterly*, v. 7, no. 2, pp. 16–20, 1961**

The dielectric properties of palmitic acid are compared with those of aleuritic acid in the temperature range 30–100°C and over a frequency range of 1–500 kc. Palmitic acid behaves as a nonpolar substance, forming double molecules at ordinary temperatures. Permittivity-temperature and loss-temperature curves for aleuritic acid indicate a polar nature; neither a completely anomalous dispersion range nor loss peaks can be pin-pointed because of high conductivity. It is suggested that OH groups in aleuritic acid may have some freedom of rotation even in the solid state.

1,393. DIELECTRIC RELAXATION IN PHENYL ALCOHOLS AT LOW TEMPERATURES

Bennett, R. G.
***Archives des Sciences*, Geneva, v. 13, Special Number,**
pp. 62–64, 1960
(Paper presented at the Ninth Ampere Colloquium, Pisa,
September 12–16, 1960 — Entry #501)

Measurements were made from 1 kc to 3 Mc at −60 to −20°C for the complex dielectric constants of 3-phenylpropanol, 2-phenylethanol, and 1-phenylpropanol. Relaxation time, ϵ_0, and ϵ_∞ are reported; Cole–Cole plots are presented.

1,394. DIELECTRIC PROPERTIES OF SOME α–ω DIBROMOALKANES

Price, A. H.
***Archives des Sciences*, Geneva, v. 13, Special Number,**
pp. 71–76, 1960
(Paper presented at the Ninth Ampere Colloquium, Pisa,
September 12–16, 1960 — Entry #501)

The dielectric properties of 1,4-dibromobutane, 1,6-dibromohexane, and 1,8-dibromooctane were measured at 1000–8000 Mc. The activation energy for dielectric relaxation for the three compounds is 2.5, 1.8, 1.8 kcal/mole, respectively.

1,395. MOLECULAR ROTATIONAL RELAXATION IN LIQUIDS AND SOLIDS

Clemett, C., Davies, M.
***Archives des Sciences*, Geneva, v. 13, Special Number,**
pp. 77–81, 1960
(Paper presented at the Ninth Ampere Colloquium, Pisa,
September 12–16, 1960 — Entry #501)

The dielectric properties of 2-chloro-2-nitropropane were investigated at 250–897 Mc. Values for dielectric constant and activation energy are presented and results compared with those of other compounds. Interpretation is given in terms of free rotation in the solid.

1,396. EXCESS NOISE IN SEMICONDUCTORS

Brophy, J. J.
November 14, 1962
Armour Research Foundation, Chicago, Ill.
Annual Summary Report 7 for November 15, 1961–
November 14, 1962, Nonr-180,000
AD-288,874

Critical point polarization fluctuations in ferroelectric triglycine sulfate crystals were measured at the Curie temperature by observing noise voltages between electrodes applied to the crystal.

1,397. EFFECTS OF IRRADIATION AND THERMAL TREATMENT ON THE DIELECTRIC DISPERSIONS IN NYLON

Stein, M. N.
November 1960
Army Signal Research and Development Laboratory,
Fort Monmouth, N. J.
TR 2149
AD-248,864

The effect of irradiation and thermal treatment on the dielectric properties of several long chain polymers was studied in the temperature region from −160 to +480°C for frequencies from 0.1 to 100 kc. The dielectric data show one or more dispersion regions which were correlated with the onset of various modes of internal motion within the polymers. The changes in dielectric properties are interpreted in terms of the alteration in structure produced by irradiation, absorbed moisture, and thermal treatment. The concept of radiation damage as a thermal spike phenomenon is introduced to explain the similar results produced by thermal quenching and irradiation. The two low temperature dispersion regions in nylon were studied extensively and are discussed in detail.

1,398. MEASUREMENT OF THE DIELECTRIC CONSTANT OF FILAMENT NYLON IN A TRANSVERSE FIELD

Ward, F. S.
***British Journal of Applied Physics*, v. 12, no. 9, pp. 450–455, September 1961**

An instrument was designed for measuring the dielectric constant of a material in the form of a single cylindrical filament, and experiments are described in which it is used for measurements on nylon. The filament is placed centrally between two silvered optical flats, which form a parallel-plate capacitor and serve as the tuning capacitor of a radio-frequency oscillator. According to an existing theory, the change in capacity due to the presence of the dielectric is given by:

$$\delta C = \left(\frac{b^2H}{2D^2}\tanh\frac{\pi B}{2D}\right)\Big/\left(\frac{\varepsilon+1}{\varepsilon-1}-\frac{\pi^2b^2}{3D^2}\right)$$

(where b is the radius of the filament, H the length of the capacitor and B the width and D the distance between the plates), and δC can be determined from the corresponding change in oscillator frequency, if the electrical parameters of the circuit are known. The experimental observations confirmed the general form of the equation, but were not sufficiently accurate to verify the second-order term $-\pi^2b^2/3D^2$. A value of 3.0 was found for the dielectric constant of nylon at 6 to 7 Mc, which is in reasonable agreement with values of 3.1 to 3.4 recorded by other workers for both filament and bulk nylon. (*PA*, 1961, #16,232)

1,399. DIELECTRIC PROPERTIES OF CERTAIN HETEROGENEOUS MIXTURES OF FERRITE AND PARAFFIN OIL

Luca, E., Reus, N.
***Buletinul Institutului Politehnic din Iasi*, v. 7, no. 1–2, pp. 205–210, 1961**

The dielectric properties of several heterogeneous mixtures of paraffin oil and powder ferrites (Mn–Zn and Ba + 1.5% Bi_2O_3 ferrites) were examined; the variations of the dielectric constant ε' and the tan δ were studied as functions of the ferrite concentration (5–25%), of the frequency (100 cps–10 Mc), and of the temperature −30 to + 15°C. Data are compared with theory. 12 references.

1,400. EFFECT OF γ Co⁶⁰ RADIATION ON THE DIELECTRIC PROPERTIES OF TRIGLYCINE SULPHATE

Hilczer, B.
***Bulletin de l'Académie Polonaise des Sciences, Série des Sciences, Mathématiques, Astronomiques et Physiques*, v. 9, no. 3, pp. 229–234, 1961**

The Curie point was found to shift linearly with irradiation time to lower temperatures, and at the same time the peak permittivity fell. The D/E hysteresis loops first became constricted, then single straight lines. The results are attributed to lattice defects blocking the movement of domain walls. (*PA*, 1961, #17,832)

1,401. DIELECTRIC PROPERTIES OF SOLID POLYMERS

de Brouckere, L., Geuskens, G., Robert, G.
***Bulletin des Sociétés Chimiques Belges*, v. 70, pp. 410–414, 1961**

Dielectric constants and loss factors of poly(vinyl formal) were determined from 400 cps to 1 Mc and −10 to + 150°C. Although α-dispersion (attributed to movement of segments of the polymer chain) is noted, no β-dispersion is evident, which indicates that there is no independent motion of polar side-groups. This can be anticipated by the bridged structure of the polymer segments.

1,402. DIELECTRIC PROPERTIES OF POLYMERS IN DILUTE SOLUTION. III. INFLUENCE OF THE SOLVENT ON THE DIPOLE MOMENT AND ON THE DIELECTRIC RELAXATION

de Brouckere, L., Lecocq-Robert, A.
***Bulletin des Sociétés Chimiques Belges*, v. 70, pp. 549–575, 1961**

Dielectric properties of dilute solutions of poly(methylmethacrylate) in toluene, $CHCl_3$, and 1,2-dichloroethane, and of poly(butylmethacrylate) in CCl_4, dioxane, toluene, $CHCl_3$, and 1,2-tetrachloroethane were measured at 0.5 kc to 30 Mc, and − 30 to + 25°C. Solvent effects are considered for dipole moments, critical frequencies, average relaxation times, and activation energies.

1,403. THE DIELECTRIC BEHAVIOR AT LOW TEMPERATURES OF SEVERAL GASES ADSORBED ON POROUS VYCOR GLASS

Chapman, I. D., McIntosh, R.
***Canadian Journal of Chemistry*, v. 40, no. 1, pp. 92–103, January 1962**

The complex dielectric constants of several systems comprising a gas adsorbed on Vycor glass have been measured at temperatures between 0 and −180°C and frequencies between 3 kc and 4 Mc. The real and imaginary parts of the dielectric constant of the adsorbed phase have been computed. Loss maxima occurring at low temperatures are observed for some of the matter in the monolayer and are assumed to be due to complexes formed between the gas first admitted and hydroxyl groups which are covalently attached to the surface of the glass. The complexes may be considered either as dipoles having two equilibrium positions, or as highly damped oscillators. Ethyl chloride adsorbed in the first molecular layer and not bonded to OH behaves as an oscillatory system for which no loss is observed in the frequency and temperature ranges studied. Ethyl chloride adsorbed in the multilayers behaves similarly, but shows a slightly greater temperature coefficient of ε'. Both these types of adsorbed ethyl chloride interact with the complexes and reduce the threshold temperature at which loss is observed in the complex. Methyl chloride interacts with OH groups in a similar fashion, but n-butane does not.

1,404. PIEZOELECTRIC TEXTURES AND PERSPECTIVES FOR THE FURTHER DEVELOPMENT OF PIEZOELECTRICITY

Shubnikov, A. V.
Československy Časopis pro Fysiku, Sekce A**, v. 12, pp. 172–174, 1962**

Piezoelectric materials belonging to only three groups are known, although textures (arrangements of building blocks such as small crystals, long molecules, electric or magnetic dipoles, etc.) important in piezoelectricity fall into seven groups, depending on their elements of symmetry. The textures of rochelle salt and $BaTiO_3$ used in practice are discussed. Piezoelectric effects in a deformed organic glass are reported.

1,405. DIELECTRIC PROPERTIES OF MONOHALOGENOBENZENES IN THE MICROWAVE REGION

Okabayashi, H.
Chemical Society of Japan, Bulletin of the**, v. 35, no. 1, pp. 163–170, January 1962**

The dielectric constants and the loss factors of liquid monohalogenobenzenes were measured in the microwave region by the free wave method (developed by Yasumi) and the waveguide method (developed by Surber). The experimental results were discussed on the basis of the formula of the local field previously proposed by Yasumi and Komooka. In the cases of liquid monohalogenobenzenes, the experimental facts can be explained by a single relaxation time.

1,406. DIELECTRIC RELAXATION AND MOLECULAR STRUCTURE. I. RELAXATION TIME AND VISCOSITY

Chitoku, K., Higasi, K.
Chemical Society of Japan, Bulletin of the**, v. 36, no. 9, pp. 1064–1068, September 1963**

Stokes' simple formula for a rigid sphere rotating in a viscous liquid was assumed by Debye to be applicable to a sphere of molecular dimensions surrounded by other molecules of a similar size:

$$\tau = \frac{4\pi\eta a^3}{kT}$$

in which η is the ordinary viscosity of the liquid, a is the radius of the sphere, k is the Boltzmann constant, and T is the absolute temperature.

The object of this paper is to postulate an empirical relation between the viscosity and the relaxation time and to compare it with the above equation. The ordinary viscosity alone is considered, since it seems desirable to deal only with measurable quantities. The dielectric measurements have been limited to dilute solutions, because the relaxation time measured in the liquid state is accompanied with ambiguity due to the choice of an arbitrary conversion factor. From the study it is concluded that:

(1) Stokes' formula for a rotating sphere in a viscous medium cannot be applied to a sphere of molecular dimensions.

(2) There exists an empirical relation between the relaxation time, τ, and the viscosity, η:

$$\log \tau = A + x \log \eta$$

in which the x parameter has a value $0 < x \leqslant 1$.

(3) Through the x parameter, some insight into the mechanism of rotation (internal rotation vs. overall rotation) can be obtained and the shape of the rotating unit can be discussed.

1,407. THE CAUSE OF THE VARIATION OF DIELECTRIC CONSTANT AND CONDUCTIVITY OF SUSPENSIONS BY TORSION

Nasuhoglu, R.
Communications de la Faculté des Sciences de l'Université d' Ankara**, v. 9, no. 1, pp. 1–19, 1957**

A deformation perpendicular to the field causes a change in dielectric constant and conductivity. This change is investigated on iron, carbon black, and graphite suspensions in mineral oil. The change, found to be independent of the direction of deformation, is probably due to a partial destruction and orientation of elongated agglomerates.

1,408. VARIATION WITH FREQUENCY OF DIELECTRIC CONSTANT AND CONDUCTIVITY OF HETEROGENEOUS SOLID MIXTURES

Nasuhoglu, R.
Communications de la Faculté des Sciences de l'Université d'Ankara**, v. 9, no. 1, pp. 20–42, 1957**

An investigation was made of the change with frequency of the dielectric constant and conductivity of graphite polystyrene mixtures. A dispersion with a relaxation time of 0.8×10^{-7} sec was observed at 2 Mc; a second dispersion in the variation of conductivity with the frequency is shown above 10 Mc. Changes in the agglomeration of the particles apparently cause these dispersions.

1,409. THE DIELECTRIC RELAXATION TIME OF SEVERAL DIPOLE MOLECULES IN RELATION TO THEIR STRUCTURE

Fischer, E.
Communications de la Faculté des Sciences de l'Université d'Ankara**, v. 9, no. 1, pp. 43–48, 1957**

Measured relaxation times are compared with calculated times for the following inflexible molecules: acetal, tetrahydrofuran, iso-Pr_2O, thianthrene, pyrrole, indole, and carbazole. The effective values were obtained by measurements of calorimetric and dilatometric loss in dilute benzene solutions at 25°C. Slight deviations in all cases are noted. The results are interpreted.

1,410. CONDITIONS DETERMINING THE PRESERVATION IN THE DARK OF PHOTOPOLARIZATION IN PHOTOELECTRETS

Nadzhakov, G., Antonov, A., Zadorozhnÿi, G.
Comptes Rendus de l'Académie Bulgare des Sciences**, v. 14, no. 4, pp. 329–332, 1961 (in Russian)**

Specimens of monocrystal and polycrystal sulphur, as well as of polycrystal anthracene, were investigated. The following results were established: (1) Photoelectrets preserve most of their initial polarization if, when kept in the dark, the electrodes are short-circuited. (2) The preservation of photopolarization improves when the polarizing electric field increases. (3) The preservation of photopolarization in photoelectrets of polycrystal anthracene improves and its sensitivity decreases when the pressure under which the specimens are produced increases. With a pressure exceeding 2 ton/cm², at which the substance of the photoelectret attains its maximum of density, these dependences cease to be observed. The explanation for this may be the fact that part of the electrons adhere firmly to the free surface of the different monocrystals on comparatively shallower surface traps. (*PA*, 1962, #10,562)

1,411. INFLUENCE D'UN CHAMP ÉLECTRIQUE SUR CERTAINES CONSTANTES ÉLASTIQUES DU SULFATE DE GLYCOCOLLE (INFLUENCE OF AN ELECTRIC FIELD ON SOME ELASTIC CONSTANTS OF GLYCINE SULFATE)

Gilletta, F.

***Comptes Rendus Hebdomadaires des Séances de l Académie des Sciences*, v. 250, no. 19, pp. 3162–3164, May 9, 1960**

Glycine sulfate is ferroelectric up to 50°C, the elastic constants are then able to be determined from the resonance frequencies of plates or of bars subjected to an alternating electric field. A report is given of preliminary results obtained on bars perpendicular to the ferroelectric axis. Curves are presented showing both temperature dependence and dependence on electric field of the compliances. The results below the transition point are related to a first electrification; there also seem to be some remarkable phenomena of hysteresis.

1,412. ABSORPTION DIÉLECTRIQUE DISSYMÉTRIQUE DANS LES LIQUIDES EN SURFUSION (ASYMMETRIC DIELECTRIC ABSORPTION IN SUPERCOOLED LIQUIDS)

Gaoubert, E., Caillon, P.

***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 251, no. 1, pp. 82–84, July 4, 1960**

Dielectric properties of glycerol and its substituted Cl and AcO derivatives (both mono- and di-) are examined.

1,413. INFLUENCE DE FAIBLES QUANTITÉS D'EAU SUR LE COMPORTEMENT DIÉLECTRIQUE DE L'ACIDE ACÉTIQUE SOLIDE (INFLUENCE OF TRACES OF WATER ON THE DIELECTRIC BEHAVIOR OF SOLID ACETIC ACID)

Raczy, L., Constant, E., Gabillard, R.

***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 252, no. 17, pp. 2523–2525, April 24, 1961**

The use of a new type of automatic bridge circuit for measurement of complex permittivity at 100 kc showed certain unusual features of the acetic acid–water mixture in the solid phase. The solid phase with added water possesses very different dielectric properties from those of the solid pure acid. (*PA*, 1961, #17,826)

1,414. DÉTERMINATION DES COMPLIANCES ÉLASTIQUES ET DES MODULES PIEZOÉLECTRIQUES DU SULFATE DE GLYCOCOLLE (DETERMINATION OF THE ELASTIC COMPLIANCES AND PIEZOELECTRIC MODULI OF GLYCINE SULPHATE)

Gilletta, F.

***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 253, no. 15, pp. 1556–1558, October 9, 1961**

The purpose of this note is to complete the partial results previously published (Entry #1,411). (*PA*, 1962, #4104)

1,415. SUR L'ABSORPTION DIPOLAIRE DEBYE DE LIQUIDES ORGANIQUES CONGELÉS RENFERMANT LES LIAISONS $C = O$, $S = O$ OU NO_2; CAS DES ACÉTYLACÉTATES (DIPOLAR DEBYE ABSORPTION IN FROZEN ORGANIC LIQUIDS CONTAINING C:O, S:O, NO_2 BONDS AND IN ACETYLACETATES)

Freymann, M.

***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 253, no. 19, pp. 2061–2063, November 6, 1961**

Dipolar Debye absorption of ionic crystals and metal semiconductors has been studied experimentally many times; the concept of defects in the lattice and the possible role of phase change have been considered. This report extends the work to the case of organic compounds (solids or congealed liquids). Absorption at 100 kc was studied in (1) aldehydes, e.g., AcH, paraldehyde, BzH, and furaldehyde, (2) ketones, e.g., fenchone, camphors, and cyclohexanone, (3) esters, e.g., methyl and ethyl acetylacetates, methyl benzoate, and methyl salicylate, (4) Me_2SO, and (5) nitroethane and nitropropane. The dielectric constant ε' and dielectric loss factor tan δ are plotted as functions of temperature.

1,416. ÉTUDE DE L'ÉVOLUTION AU COURS DU TEMPS D'UN MONOCRISTAL DE SULFATE DE GLYCOCOLLE (A STUDY OF THE GROWTH WITH TIME OF A MONOCRYSTAL OF GLYCINE SULPHATE)

Taurel, L., Lauginie, P.

***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 253, no. 22, pp. 2511–2513, November 27, 1961**

Ferroelectric domains in glycine sulphate single crystals were made visible by surface etching with water. Crystals which had had no thermal treatment for several days gave large domains approximating to cylinders parallel to the ferroelectric axes. On heating the crystals above 45°C, and cooling in air, a large number of small needle-shaped domains appeared, which, over several days, coagulated into large domains similar to those existing originally. The effects of weak ac and strong dc fields on the domain growth were studied. Thin plates were cut from the crystals perpendicular to the ferroelectric axis and the change in dielectric constant with time was studied at a weak field of 1 kc and at a temperature of 28.5°C. When the crystal had just undergone thermal treatment, ε' and ε'' decreased with time, where $\varepsilon' = \varepsilon_L + A\varepsilon''$ with $\varepsilon_L = 40$ and $A = 4.74$. After several days, ε' was equal to ε_L, a value of 40 being obtained for each of three different plates. (*PA*, 1962, #4094)

1,417. DOMAINE DE VALIDITÉ DE L'EXPRESSION ANALYTIQUE DU COURANT D'ABSORPTION D'UN CHLORURE DE POLYVINYLE (RANGE OF VALIDITY OF THE ANALYTICAL EXPRESSION FOR THE ABSORPTION CURRENT OF A CHLOROPOLYVINYL)

Couget, A., Lacoste, R.

***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 254, no. 10, pp. 1750–1752, March 5, 1962**

The variation of the absorption current of a chloropolyvinyl as a function of time is found to be represented by an expression of the form $i = at^{-n}$ (where $n = -0.93$), which is valid within a period of 0.5 min to 1–2 hr after the initial application of the electric field. The photographic method of investigation is described and six diagrams are presented.

1,418. SUR L'ABSORPTION DIPOLAIRE DEBYE DES LIQUIDES ORGANIQUES CONGELÉS. LIQUIDES ORGANIQUES RENFERMANT DES LIAISONS C = O (ON THE DIPOLAR DEBYE ABSORPTION IN FROZEN ORGANIC LIQUIDS. ORGANIC LIQUIDS CONTAINING C:O BONDS)

Jaffrain, M., Marin, C.

***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 254, no. 16, pp. 2958–2960, April 18, 1962**

The dielectric constant ε' and dielectric loss factor tan δ were studied as functions of temperature in the ketones Me_2CO, Et_2CO, Pr_2CO, iso-Bu_2CO, MeEtCO, Me(iso-Pr)CO, Me(iso-Bu)CO, and cyclopentanone; in isobutyl and isoamyl formates; and in the Et esters of HCO_2H, HOAc, $H_2C_2O_4$, and malonic, succinic, and glutaric acids. The data are presented and discussed.

1,419. SUR L'ABSORPTION DIPOLAIRE DEBYE DE LIQUIDES ORGANIQUES CONGELÉS. SOLUTIONS CONGELÉES DANS CCl_4 OU $CHCl_3$ (DEBYE DIPOLAR ABSORPTION OF FROZEN ORGANIC LIQUIDS. FROZEN SOLUTIONS IN CCl_4 OR $CHCl_3$)

Jaffrain, M., Charles, J.

***Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, v. 254, no. 19, pp. 3343–3345, May 7, 1962**

The authors extend their previous research. The dielectric properties of frozen organic compounds containing C:O are investigated. For pure ethylacetate, the Debye dipolar absorption (DDA) is very low (tan $\delta < 0.0010$, $\nu = 100$ kc); upon dilution with CCl_4 or $CHCl_3$, the DDA appears to be very high (tan $\delta \sim 0.1500$–0.3000). Solutions of acetone, Et malonate, etc., are examined in the same way.

1,420. PERMITTIVITY IN THE PROCESS OF POLARIZATION REVERSAL OF FERROELECTRIC TRIGLYCINE SULPHATE

Mísařová, A., Janoušek, V.

***Czechoslovak Journal of Physics*, v. 10, no. 9, pp. 687–688, 1960**

Values of ε and tan δ were measured at frequencies of 10 to 300 kc while the crystal traversed its *D*–*E* hysteresis loop at 30 cps. As in $BaTiO_3$, ε passed through anomalously high values during polarization reversal, but ε was not a unique function of the repolarizing current in this case. (*PA*, 1961, #17,335)

1,421. PERMITTIVITY OF ROCHELLE SALT DURING SWITCHING

Fousková, A., Janoušek, V.

***Czechoslovak Journal of Physics*, v. 12, no. 5, pp. 413–415, 1962**

The complex permittivity was measured over the frequency range 10 to 200 kc, while the crystal was being switched at 40 cps with a field of 15 kv/cm. As in $BaTiO_3$ and other ferroelectrics, the permittivity reached a high value, several times that measured without switching. The frequency dependence of the permittivity could be fitted to a Debye relaxation process. (*PA*, 1962, #18,771)

1,422. DIELECTRIC ABSORPTION IN LONG-CHAIN SECONDARY ALCOHOLS AND THEIR SOLID SOLUTIONS

Meakins, R. J.

***Faraday Society, Transactions of the*, v. 58, no. 478, pt. 10, pp. 1953–1961, October 1962**

It has been shown theoretically that when dipoles are associated to form a chain, the magnitude of the dielectric absorption increases with n and the relaxation time increases with n^2, where $(n-1)$ is the number of dipoles in the chain. In the present work, this theory is applied to long-chain secondary alcohols to calculate the average lengths of the hydrogen bond chains from the experimental results. Separate calculations are made from the frequency of the maximum f_{max} and from the magnitude of the absorption.

In the former it is necessary to determine f_{max} for the rotation of individual hydroxyl groups, or preferably, for hydrogen-bonded chains of known lengths. Some values for these are obtained from microwave measurements of solid solutions of the secondary alcohol 16-hentriacontanol in the long-chain hydrocarbon n-dotriacontane. With the aid of infrared data and the solid-liquid phase diagram, it is possible to relate different dielectric absorption maxima to individual hydroxyls groups (monomers), pairs (dimers), and chains (polymers).

In a calculation from the magnitude of the absorption, there is an energy difference between the equilibrium positions of the hydroxyl groups to be taken into account. This is obtained from measurements of the dielectric absorption at various temperatures.

1,423. ASYMMETRIC DISPERSION IN PROPYLENE GLYCOL

Rao, V. M.
***Faraday Society, Transactions of the*, v. 58, no. 479, pt. 11, pp. 2139–2143, November 1962**

The dielectric dispersion in pure propylene glycol and in solution has been studied in the ultra-high frequency and microwave region at room temperature. The present and the previously published results on glycerol can be well represented by the Davidson–Cole type of skewed arcs. They agree closely with the theoretical curves drawn from the Glarum function derived on the basis of a defect diffusion model.

1,424. DIELECTRIC BEHAVIOR OF DIMETHYLSULPHOXIDE AND ITS BINARY MIXTURES WITH ALCOHOLS AND BENZENE

Lindberg, J. J., Hakalax, R.
***Finska Kemistsamfundets Meddelanden: Suomen Kemistiseuran Tedonantaja*, v. 71, no. 4, pp. 97–103, 1962**

1,425. THE PROBLEM OF INORGANIC ELECTRETS

Gubkin, A. N., Skanavi, G. I.
***Fizika Tverdogo Tela*, v. 3, no. 1, pp. 297–304, January 1961**
(Translated from the Russian in *Soviet Physics — Solid State*, v. 3, no. 1, pp. 215–220, July 1961)

Studies on electrets of organic (wax) as well as polycrystalline ceramic dielectrics are reviewed. The electrets are grouped according to their preparation: (1) thermoelectrets, prepared by heating and cooling in an electric field; (2) photoelectrets, prepared in illumination but not heated; and (3) certain ceramic and phosphor electrets prepared in an electric field. The field within the electret, E_i, is derived for the organic short-circuited case and the inorganic partially short-circuited case. Methods of charging and the measurements of surface charge are discussed in detail. The phenomenological theory is verified quantitatively for various electrets. (*SSA*, #12,442)

1,426. EFFECTS OF RADIATION ON PROPERTIES OF ROCHELLE SALT CRYSTALS (IN WEAK ELECTRIC FIELDS)

Peshikov, E. V., Starodubtsev, S. V.
***Fizika Tverdogo Tela*, v. 4, no. 1, pp. 239–245, January 1962**
(Translated from the Russian in *Soviet Physics — Solid State*, v. 4, no. 1, pp. 170–174, July 1962)

Gamma irradiation reduced the domain contributions to the permittivity, dielectric losses, resonance frequency, Q-factor, and electromechanical coupling factor of rochelle salt in weak electric fields. (*PA*, 1962, #12,565)

1,427. ON THE PROBLEM OF THE PHYSICAL NATURE OF THE ELECTRET EFFECT IN CARNAUBA WAX

Gubkin, A. N., Matsonashvili, B. N.
***Fizika Tverdogo Tela*, v. 4, no. 5, pp. 1196–1205, May 1962**
(Translated from the Russian in *Soviet Physics — Solid State*, v. 4, no. 5, pp. 878–884, November 1962)

A study is reported of the electret properties of carnauba wax, in particular its persistent polarization and relaxation of charge. It is concluded that the nature of the electret state is the same in a wide range of dielectrics. (*PA*, 1962, #18,782)

1,428. DIELECTRIC CONSTANT AND DIPOLE MOMENT: CHROMONES, FLAVONES, AND BENZYLIDENECOUMARONES

Jatkar, S. K. K., Deshpande, C. M.
***Indian Chemical Society, Journal of the*, v. 37, pp. 69–79, 1960**

Experimental data for the dielectric constants and densities measured over a range of temperatures at various concentrations are tabulated. All measurements were made in benzene solutions. The dipole moments were calculated by a new equation for 2-methyl-5-hydroxychromone, 2-methyl-7-methoxychromone, 4′-methoxyflavone, 6-methyl-4′-methoxyflavone, 4′-benzyloxyflavone, 6-benzoyl-4′-methoxyflavone, 4′-methoxybenzylidenecoumaranone, and 4′-methoxy-5-methylbenzylidenecoumaranone.

1,429. THE DIELECTRIC PROPERTIES OF ROSIN-MALEIC ANHYDRIDE RESIN

Sen, A. K., Bhattacharya, G. N.
***Indian Journal of Physics and Proceedings of the Indian Association for the Cultivation of Science*, v. 35, pp. 509–516, 1961**

The dielectric properties of rosin-maleic anhydride resin were measured over the temperature range of 25 to 170°C and the frequency range of 1 to 500 kc. The characteristics of a polar resin exhibited in most of this temperature-frequency range are pointed out. The anomalous behavior of dielectric constant at high temperature, however, is also noted. An attempt has been made to explain this peculiarity on the basis of the estimated rotor dimension and infrared absorption spectrogram. OH groups attached to the molecule appear to be the probable rotating units.

1,430. DIELECTRIC PROPERTIES OF SOME MONO-SUBSTITUTED PHENOLS

Sarma, V. S. K., Dasgupta, S.
***Indian Journal of Pure and Applied Physics*, v. 1, no. 6, pp. 235–237, June 1963**

By using a permittivity bridge below 160 kc and a Q-meter beyond 200 kc, the dielectric loss factor, ε'', of *o*-nitrophenol, catechol, salicylic acid, *p*-nitrophenol, hydroquinone, and *p*-hydroxybenzaldehyde was measured at frequencies between 5 cps and 50 Mc. Higher losses, especially at the lower frequencies, were observed for para-substituted compounds.

Hydroquinone showed very high losses when measured at $\leqq 100°C$, e.g., at 100°C ε'' was almost 0.4 at ~10 cps. This may be attributed to the loss arising from conductivity.

1,431. EFFECTS OF GAMMA-RAY IRRADIATION ON ROCHELLE SALT

Toyoda, K., Kawabata, A., Tanaka, T.
***Institute for Chemical Research, Kyoto University, Bulletin of the*, v. 39, no. 2, pp. 189–194, March 1961**

It was found that the ferroelectric region became narrower as a result of irradiation, and that ferroelectricity disappeared after prolonged irradiation. The most striking change appears in the ferroelectric hysteresis loop, i.e., a double loop pattern in the irradiated crystal. It was also found that the piezoelectricity was affected as a result of irradiation. (*PA*, 1961, #14,554)

1,432. THE EFFECTS OF RADIATION ON MATERIALS. PART 3. RADIATION DAMAGE MECHANISMS: INSULATING MATERIALS

Linnenbom, V. J.
***Insulation*, v. 6, no. 3, p. 11–15, March 1960**

Behavior of electrical insulation in a radiation field was considered from two viewpoints: (1) temporary phenomena observed during irradiation, which depend largely on dose rate, and (2) permanent effects that persist after removal from the field, which usually depend on total dose. Both organic- and ceramic-type materials showed increased conductivity and current leakage when exposed to radiation. Most of the induced conductivity disappeared within a short time after the irradiation ceased. With organic insulators, the permanent radiation damage was usually more of a problem than the transient effects. Inorganic insulation materials suffered far less permanent damage than the organic materials. The following materials are listed in order of decreasing radiation stability: ceramics, mica, glass, polystyrene, mylar, polyethylene, lucite, silicone rubber, nylon, and teflon. The effects of temperature, humidity, and the presence of surrounding gases during irradiation are discussed.

1,433. IMPULSE BREAKDOWN OF SOLID DIELECTRICS

Vorobev, A. A., Vorobev, G. A.
***Izvestiya Tomskogo Politekhnicheskogo Instituta imeni S. M. Kirova*, no. 95, pp. 3–15, 1958**

The effects of volume charges and heat separation on the magnitude of the electric strength of dielectrics can be eliminated by impulse applications of very small duration, and advantage can be taken of the positive effects of lag in discharge and discharge propagation. However, in some cases the increase in electric strength of dielectrics with decrease in the impulse duration may be caused by thermal and polarization surface effects. Analysis is presented of experimental work on dielectrics concerning the effect of time of discharge, rate of discharge propagation, and polarity at breakdown.

1,434 EFFECT OF THE COMPOSITION AND STRUCTURE OF THE MOLECULES OF SOME ORGANOSILICON LIQUIDS ON THEIR ELECTRICAL PROPERTIES

Dolgov, B. N., Khadobin, Yu. I., Kharitonov, N. P., Renne, V. T., Bondarenko, P. N., Soya, G. P.
***Izvestiya Vysshikh Uchebnykh Zavedenii, Energetika*, v. 5, no. 6, pp. 31–36, 1962**

The electrical properties of bis(trialkylsiloxy)benzenes (1,2; 1,3; 1,4), and 1,3,5-tris(trialkylsiloxy)benzene of the type $C_6H_4[OSi(R'')(R')R'']_2$ and $C_6H_3[OSi(R'')(R')R'']_3$, where R′ = Me or Et and R″ = Pr, iso-Pr, Bu, or isoamyl, were investigated. Variations in substitution placement are shown to have noticeable effects on dielectric properties. An increase in molecular weight is also shown to affect ε, dielectric loss, specific resistance, and viscosity of meta and para compounds and, in some cases, ortho.

1,435. ACTION OF γ-RADIATION ON THE DIELECTRIC PROPERTIES OF "VINYLPLAST"

Nesterov, V. M., Toropova, V. N.
***Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika*, v. 1961, no. 6, pp 141–144, 1961**

Evolution of HCl and substantial changes in mechanical, optical, and electrical properties are observed with dosage of 10^7 r.

1,436. DIELECTRIC PROPERTIES OF INSULATING MATERIALS AFTER γ-IRRADIATION. II. POLYETHYLENE

Vorozhtsov, B. I., Nesterov, V. M., Olshanskaya, N. I.
***Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika*, v. 1962, no. 5, pp. 34–37, 1962**

Changes in dielectric constant, loss angle, dielectric permittivity, and electric conductivity of polyethylene with irradiation by γ-rays from Co^{60} were studied in the range of $40–10^{10}$ cps and 20–70°C. Polyethylene is stable up to 3000 rad/min. In general, after irradiation the loss angle tangent is proportional to $\tan \delta$ before irradiation multiplied by the 0.05–0.02 power of the irradiation dose. The dielectric strength seems to decrease when crystallinity decreases (above 40°C).

Methods of measurement of dielectric characteristics during irradiation are detailed in Part I (ibid., v. 1962, no. 4, pp. 163–170, 1962).

1,437. THE CHANGE IN DIELECTRIC LOSS IN CRYSTALLIZING POLYMERS UNDER THE ACTION OF IONIZING RADIATION

Olshanskaya, N. I., Vorozhtsov, B. I.
***Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika*, v. 1962, no. 5, pp. 150–155, 1962**

Changes in dielectric loss of crystallizing polyethylene, polyamide-68, Fluorplast-3, and Lavsan with ultraviolet, X-, and γ-ray irradiation were studied at frequencies of $40–10^5$ cps. The dielectric loss angle increases with increase in the irradiation intensity and with the degree of crystallinity of the sample. The changes are reversible. In the irradiated zone the crystal also shows increased electrical conductivity and a change of polarization.

1,438. EFFECT OF IONIZING RADIATION ON ELECTRICAL INSULATING MATERIALS
Adamec, V.
***Jaderna Energie*, v. 8, pp. 288–289, 1962**

The changes in conductivity, dielectric constant, loss coefficient, and electric strength during X-ray irradiation, and in mechanical properties after irradiation, were determined in samples of polyethylene, natural rubber, polystyrene, nylon, Capron, PhOH-HCHO resin, poly(Me methacrylate), poly(ethylene terephthalate), polycarbonate, poly(tetrafluoroethylene), poly(trifluorochloroethylene), and poly(vinyl chloride).

1,439. PIEZOELECTRIC PROPERTIES OF TRIGYLCINE-SULPHATE
Ikeda, T., Tanaka, Y., Toyoda, H.
***Japanese Journal of Applied Physics*, v. 1, no. 1, pp. 13–21, July 1962**

Since crystalline triglycine sulphate is centrosymmetric above the Curie point, the piezoelectricity in the ferroelectric phase is expected to be an "induced" one as in the case of barium titanate, distinct from an "intrinsic" piezoelectricity of rochelle salt. Temperature dependences of piezoelectric constants were measured by using various cuts of crystal, and some experiments on the electrostrictive effect above the Curie point were performed. Electrostrictive constants were obtained, and the above expectation was confirmed in several points. The phase transition was not found to be accompanied by any elastic change. Some effects of irradiation by X-rays and γ-rays on the piezoelectric constants were examined, and it is shown that irradiation prevents a diminution of piezoelectricity resulting from growth of anti-parallel domains, especially near the Curie point. (*PA*, 1962, #23,508)

1,440. PIEZOELECTRIC PROPERTIES OF TRIGLYCINE SULPHATE
Ikeda, T., Tanaka, V., Toyoda, H.
***Japanese Journal of Applied Physics*, v. 2, no. 3, p. 199, March 1963**

The matrix of electrostrictive constants was treated as a symmetrical one in the previous paper (preceding abstract), but this is incorrect. It is not like that of elastic coefficients, but is similar to that of photoelastic constants. The matrix (Q_{ij}) is not symmetrical, and the subsequent relational equations must be changed.

Only the components in the second, fourth and sixth columns of the matrix, which are related to P_2, can be determined. Discussion on the depolarization in the 45-deg *x*-bar should be omitted. The correct values of electrostrictive constants are:
$Q_{12} = 1.5$, $Q_{22} = 2.5$, $Q_{32} = -4.4$, $Q_{52} = -0.4$, $Q_{44} = -4.3$, $Q_{64} = 4.2$, $Q_{46} = 0.6$, and $Q_{66} = 2.2$, in 10^{-11} c.g.s. units.

1,441. DOMAIN WALL CAUGHT IN DISLOCATIONS IN FERROELECTRIC GLYCINE SULFATE CRYSTALS
Nakamura, T., Nakamura, H.
***Japanese Journal of Applied Physics*, v. 1, no. 5, pp. 253–259, November 1962**

Simultaneous observation of both dislocation etch pits and ferroelectric domain walls was made on the *b*-face of ferroelectric glycine sulfate crystals by the etching technique with water. The negative end of the domain is pebbled, while the positive end is smooth. The dislocation etch pits are well discernible from the "pebbles" on the etched face. It was revealed that under application of a dc electric field of about 30 v/cm, a domain wall is caught in dislocations during the domain wall motion, resulting in zigzag shape. Evidences were obtained that also in as-grown crystals, domain walls were caught in dislocations. It is assumed that dislocations in which a domain wall is caught are edge dislocations emerging out of the *b*-face.

1,442. DIELECTRICS FOR SATELLITES AND SPACE VEHICLES
Frisco, L. J.
March 30, 1962
Johns Hopkins University, Dielectrics Lab., Baltimore, Md.
R-3, Final Report for March 1, 1959 to February 28, 1962,
DA-36-039-sc-78321
AD-276,867

The effect of simulated space environment on the electrical properties of solid insulating materials are reported. Equipment and techniques are described for the measurement of loss properties, flashover strength, and electric strength during X-ray and ultraviolet irradiation at pressures in the 10^{-6} Torr range. Twenty-one organic and inorganic materials are included in the investigation. High-vacuum sparkover (uniform field) and flashover measurements at dc and 60 cps show that (1) electrode surface roughness is the controlling factor; (2) the dielectric properties of the material do not influence flashover voltage; and (3) X-ray and ultraviolet radiation has no effect on flashover voltage. At 2 and 18 Mc, high current densities at electrode edges or high losses in the solid material compromise flashover strength.

Electric strengths of low-loss polymers are not affected by X-ray irradiation in high vacuum. High-frequency electric strength is compromised by unfavorable thermal conditions in high vacuum. X-ray-induced ac losses are exhibited by several materials during and after irradiation. Transient effects during irradiation cause induced 60-cps dissipation factors as high as 0.40 in some tetrafluoroethylene polymers; detailed exposure and recovery data show the effects of oxygen and absorbed dose. X-ray-induced dc polarization, absorption and conduction currents are exhibited by most materials. In some cases, recovery is not complete after several months. Instantaneous and short-time effects of ultraviolet radiation on ac loss properties are not large enough to be of practical importance. The dc behavior is dominated by photoelectric effects. Materials that are subject to moisture absorption exhibit improved electrical properties after short periods in high vacuum. 34 references.

1,443. DIELECTRIC ABSORPTION OF SOME ALCOHOLS

Kamiyoshi, K., Fujimura, T.
***Journal de Physique et le Radium*, v. 23, no. 5, pp. 311–314, May 1962**

The dielectric absorption in 14 different alcohols (MeOH, EtOH, PrOH, iso-PrOH, BuOH, iso-BuOH, AmOH, iso-AmOH, *n*-hexyl alcohol, allyl alcohol, cyclohexanol, geraniol, propylene glycol, and glycerol) in a supercooled state was studied as a function of temperature at low frequency (0.5–300 kc). From these results it is proposed that the dielectric absorption of alcohol is due to the OH group.

1,444. MICROWAVE ABSORPTION OF A MIXTURE OF TWO POLAR LIQUIDS

Kamiyoshi, K., Fujimura, T.
***Journal de Physique et le Radium*, v. 23, no. 6, pp. 337–340, June 1962**

The dielectric behaviors of a number of mixtures of two polar liquids were studied as a function of concentration. The results show that in a mixture of two associated liquids the dielectric absorptions of each liquid join to be one common absorption at any concentration (*n*-propanol + cyclohexanol, ethanol + cyclohexanol), but in a mixture of associated and nonassociated liquids the absorptions only approach each other more or less (isoamyl bromide + geraniol, isoamyl bromide + cyclohexanol). Results contrary to this rule were observed in a mixture of glycerol and *n*-propanol (two absorptions). It is suggested that the amount of displacement of dielectric absorption in a mixture may be an indication of the degree of mixture. (*PA*, 1962, #19,576)

1,445. ELECTRICAL SURFACE PROPERTIES OF POLYMERS CONTAINING BOUND ANIONIC GROUPS

Holmes, F. H., Perkins, P. G.
***Journal of Applied Chemistry*, v. 12, pp. 150–156, April 1962**

Polystyrene cross-linked with divinylbenzene has been prepared, free from catalyst, in sheet form and has been sulphonated in the surface regions. Sheets incorporating carboxyl groups in various proportions have been prepared by copolymerizing styrene, divinylbenzene, and methacrylic acid. The electrical conductances of the polymer surfaces, with sodium as mobile cation, have been measured in air at various relative humidities. The observed increase of conductance with relative humidity is consistent with an increase in dielectric constant of the polymer.

1,446. ELECTRIC BREAKDOWN STRENGTHS OF SINGLE AND LAMINATED FILMS OF VINYL CHLORIDE-ACETATE

Greenler, R. G., Kay, R. M.
***Journal of Applied Physics*, v. 32, no. 7, pp. 1252–1255, July 1961**

The electric breakdown strengths of thin, unsupported vinyl chloride-acetate films in the thickness range of 1200 to 50,000 Å were measured. No dependence of breakdown strength on thickness is found in this region. Composite films composed of alternate layers of plastic film and thin conducting layers of silver show essentially the same breakdown strength as do single films. Five- and six-layer laminates which do not contain metal layers show a breakdown strength greater by a factor of 2 than that of single films of the same total thickness. (*PA*, 1961, #13,682)

1,447. DIELECTRIC LOSS IN POLY-(HEXAMETHYLENE ADIPAMIDE) AND POLY-(HEXAMETHYLENE SEBACAMIDE) AT LOW TEMPERATURES

Stein, M. N., Lauttman, R. C., Sauer, J. A., Woodward, A. E.
***Journal of Applied Physics*, v. 32, no. 11, pp. 2352–2357, November 1961**

The dielectric behavior of nylons 6.6 and 6.10 was studied in the temperature region −160 to +60°C at frequencies of 0.1 to 100 kc. The effects of thermal history, electron irradiation, and post-irradiation annealing on the two dielectric loss peaks found in this frequency-temperature range were explored. Electron irradiation of nylon 6,6 and 6,10 and thermal quenching of nylon 6,6 lower the γ peak (−70°C at 1 kc for nylon 6,6) and raise the β peak (+15°C for nylon 6,6 at 1 kc). Post-irradiation annealing of nylon 6,6 or 6,10 irradiated to low doses (25–100 mrad) removes the effect of the irradiation on the dielectric behavior, but on irradiation to high dosages (900–1000 mrad) the dielectric loss values in the region of the β maximum at 0.1 and 1.0 kc are greatly reduced. The frequency shifts of the dielectric-loss maxima for all samples give activation energies, in kcal/mole, which fall in the 8–15 range for the β maximum and 9–19 for the γ maximum. These absorption peaks and the effect of various variables on them are discussed in terms of the molecular structure and possible molecular motions responsible for their occurrence. (*PA*, 1961, #17,822)

1,448. INCREASE IN DIELECTRIC CONSTANT DURING SWITCHING IN BARIUM TITANATE AND TRIGLYCINE SULFATE

Fatuzzo, E.
***Journal of Applied Physics*, v. 33, no. 8, pp. 2588–2596, August 1962**

The increase in dielectric constant and losses during switching was measured in barium titanate and triglycine sulphate (TGS) at frequencies up to 2 Gc. These measurements revealed the presence of two relaxations: one at low frequencies (described by Landauer, Young, and Drougard), and a new one at higher frequencies. The relaxation frequency of this new relaxation is 100 Mc in the case of triglycine sulphate, and higher than 2 Gc in the case of $BaTiO_3$. The value of $\Delta\epsilon'$ at the relaxation frequency is 2 for triglycine sulphate and 1.2 for $BaTiO_3$. A model which explains the experimental facts is given. The increase in dielectric constant and losses is attributed to oscillations of the "side" walls of the ferroelectric domains in the case of the high-frequency relaxation. The low-frequency relaxation is believed to be due to oscillations of "front" walls of the newly formed domains. (*PA*, 1962, #16,783)

1,449. RADIATION DAMAGE AND THE FERROELECTRIC EFFECT IN ROCHELLE SALT

Krueger, H. H. A., Cook, W. R., Jr., Sartain, C. C., Yockey, H. P.
***Journal of Applied Physics*, v. 34, no. 1, pp. 218–224, January 1963**

Rochelle salt 45° X-cut square plates were exposed to Co^{60} radiation of 8.6×10^3 to 2.6×10^7 r and reactor radiation up to 2.4×10^6 r gamma plus 3.5×10^{15} neutrons/cm². Measurements were made over a temperature range including both Curie points (−30 to +30°C) of dielectric constant and loss, elastic stiffness coefficients c_{44}^E and c_{44}^D, and mechanical Q. In addition, double-crystal X-ray rocking curves were made above the upper Curie point to check line broadening. All the data indicate an initial improvement in crystal perfection (Curie points are sharper, linewidths narrower) up to 8.6×10^4 r, with subsequent degradation (Curie point and linewidth broadening: finally coalescence of Curie points) including elimination of the ferroelectric phase after 2.6×10^6 r Co^{60} radiation or 2.4×10^6 r gamma plus 3.5×10^{15} neutrons/cm² reactor radiation. The Q rose with radiation dosage as the ferroelectric phase disappeared, dropping only at the highest dosage. Destruction of the ferroelectric phase by radiation is compared to similar effects due to substitution of NH_4 for K in the rochelle salt lattice. (*PA*, 1963, #10,883)

1,450. A POLYVINYL CHLORIDE ELECTRET

van Beek, L. K. H., Schwarzl, F. R.
***Journal of Applied Polymer Science*, v. 6, pp. S61–S63, 1962**

It is expected that plastics with polar groups, which have been cooled in a strong electric field from the rubbery state to well below the transition temperature T_g, should be stable electrets. In order to obtain data on a plastic with short side-groups, polyvinyl chloride (PVC) electrets were prepared and studied. The preparation of the electret was similar to that described by Wieder and Kaufman. The thermal treatment and the current during formation are shown by curves.

It has become customary to characterize electrets by two quantities. The first is the total charge displaced during formation, $Q = \int_0^\infty i_t dt$, where i_t is the transient current obtained after correction for the steady-state conduction current. For PVC it is found, from integration of the curve mentioned above, that $Q = 10^{-2}$ coulomb, which is in the same order of magnitude as that for PMMA. The second quantity is the effective surface charge σ which is determined by the method of electrostatic induction. By measuring the voltage, the effective charge density is found from $\sigma = 0.022 \times 10^{-4} V/A$ coulomb/cm² where A is the surface area of the electret. For PVC σ was found to be 5×10^{-10} coulomb/cm². This was a heterocharge, which remained constant for 40 days and showed no indications of sign reversal. The significance of the quantities Q and σ is evaluated.

1,451. DIELECTRIC PROPERTIES OF POLYAMIDES

Curtis, A. J.
***Journal of Chemical Physics*, v. 34, no. 5, pp. 1849–1850, May 1961**

Dielectric relaxation measurements are reported over the frequency range 50 cps to 10 Mc at temperatures from −100 to +175°C on poly(hexamethylene adipamide)—nylon 6,6—and poly(hexamethylene sebacamide)—nylon 6,10. Four phenomena are identified: above 80°C a dipolar relaxation, sensitive to thermal history; an ionic process at very low frequencies above 60°C; a room temperature process at 10 kc (the β-peak found in mechanical measurements); and a low temperature peak corresponding to the mechanical γ-peak, which has not been previously reported. (*PA*, 1961, #12,305)

1,452. DIELECTRIC SATURATION IN ALIPHATIC ALCOHOLS

Malecki, J.
***Journal of Chemical Physics*, v. 36, no. 8, pp. 2144–2145, April 15, 1962**

The dielectric saturation in solutions of butanol-1, pentanol-1, and hexanol-1 in benzene and hexane was measured. The values of the permittivity variations as measured in solutions of alcohols point to the presence of a new type of dielectric saturation effect, which is shared in common by all the systems investigated. Because of the considerable electric conductivity of the liquids investigated, a pulse method was used. (*PA*, 1962, #13,349)

1,453. DIELECTRIC RELAXATION IN LIQUID ALCOHOLS AND DIOLS

Sagal, M. W.
***Journal of Chemical Physics*, v. 36, no. 9, pp. 2437–2442, May 1, 1962**

The temperature dependence of the dielectric relaxation time was investigated from −5 to +50°C for ethanol-cyclohexane solutions from 1.0 to 0.25 mole fraction ethanol. The previously observed maximum in the relaxation time around equimolar composition is explained by a hydrogen-bonded switching mechanism. Measurements of dielectric relaxation from 5 to 50°C were carried out on three isomeric butanediols which differ in the separation of the two OH groups along the carbon skeleton. The differences in relaxation times among the three isomers can be explained by the switching mechanism suggested by the results for the ethanol-cyclohexane solutions. The dielectric relaxation times of n-butanol from 5 to 50°C were also determined. The chain-length dependence of the dielectric relaxation time of the normal aliphatic alcohols is discussed in terms of the proposed mechanism. (*PA*, 1962, #13,351)

1,454. DIELECTRIC STUDIES OF THE POLYMER POLYVINYL ACETATE IN THE MOLTEN STATE

Hartt J. K., Carr, E. F.
***Journal of Chemical Physics*, v. 36, no. 9, p. 2523.**
May 1, 1962

The frequency dependence of the dielectric constant and dielectric loss at a temperature of 205°C for a frequency range of 70 to 24,000 Mc was investigated. The techniques were similar to those described by Roberts and von Hippel, and by Surber.

An absorption maximum was obtained at 250 Mc and the results are discussed. These results do not agree with those observed by Mead and Fuoss, or with the Debye theory using a single relaxation time. The measure of the deviation from a single relaxation time was obtained by using a Cole–Cole plot.

1,455. EFFECT OF ABSORBED WATER UPON THE DIELECTRIC PROPERTIES OF CERTAIN ACRYLIC ESTER POLYMERS

Scheiber, D. J., Mead, D. J.
***Journal of Chemical Physics*, v. 37, no. 1, pp. 81–84,**
July 1, 1962

The effect of absorbed water upon the dielectric properties of polymethylmethacrylate, polyethylmethacrylate, and polyethylacrylate was investigated experimentally over a temperature range from 70 to −195°C and at frequencies between 100 cps and 200 kc. It was found in each case that the absorbed water gave rise to a discernible loss index peak in the low-temperature region (0 to −100°C). The 2.1% water absorbed in a specimen of polyethylacrylate acts as a plasticizer, apparently lowering the glass transition by 5°C. The fact that the apparent activation energy and the temperature location of water-induced peak change with variations in the polymeric structure indicates that the induced loss peak is not to be identified with the loss peak found in ice, and, furthermore, suggests that the dielectric method can be employed to learn more about the water-polymer complex formed when water is absorbed into a polymer.

1,456. DIELECTRIC LOSS IN THE LIQUID CRYSTAL *p*-AZOXYANISOLE

Carr, E. F.
***Journal of Chemical Physics*, v. 37, no. 1, pp. 104–106,**
July 1, 1962

The real and imaginary parts of the complex dielectric constant of the normal liquid phase of *p*-azoxyanisole were measured at a temperature of 140°C for a frequency range from 0.5 to 24 kMc. A plot of the complex dielectric constant in the complex plane satisfies the requirements for a Cole–Cole representation reasonably well. The temperature dependence of the dielectric loss at a frequency of 6 kMc shows an absorption maximum in the neighborhood of the clearing point (135°C) for both the anisotropic and normal liquid phases. Measurements of the dielectric loss at frequencies 500 and 900 Mc indicate an increase in the dielectric loss as the sample changes from the anisotropic to the normal liquid phase. This change could not be established for measurements at other frequencies reported in this paper. (*PA*, 1962, #17,477)

1,457. DIELECTRIC PROPERTIES OF GLYCEROL–WATER MIXTURES

McDuffie, G. E., Jr., Quinn, R. G., Litovitz, T. A.
***Journal of Chemical Physics*, v. 37, no. 2, pp. 239–242,**
July 15, 1962

The frequency dependence of the complex dielectric constant of glycerol–water mixtures was measured in the megacycle frequency range at −7.5, −15.3, and −19.5°C for various concentrations between nearly pure glycerol and an equal molar mixture. Cole–Cole plots of the data indicate a single main relaxation with an asymmetric distribution of relaxation times of the Davidson–Cole form. The limiting dielectric relaxation time of the Davidson–Cole distribution was found to be strongly dependent on the water content and to vary exponentially with the molar concentration of water. The width of the distribution of relaxation times is independent of the concentration over the range studied and only slightly temperature dependent. The average dielectric relaxation times of the mixtures were extrapolated to 100% water. The dielectric relaxation time of water obtained by this extrapolation agrees satisfactorily with the measured value, indicating a smooth transition between the average relaxation time of pure glycerol and pure water, as well as indicating a change in the distribution of times from that of the Davidson–Cole form to a single time. These experimental findings can be explained in terms of the "group" concept of Schallamach in which it is assumed that in mixtures of associated–associated liquids, such as glycerol and water, dielectric orientation occurs through a cooperative effect in groups of molecules, these groups containing molecules of both kinds. The concentration dependence of the dielectric relaxation time is also compared to that of viscosity. The comparison indicates that the variation of dielectric times with water content is similar to, but not exactly the same as, the variation of viscosity. (*PA*, 1962, #19,574)

1,458. DIELECTRIC CONSTANT OF ETHANOL IN THE NEIGHBORHOOD OF THE CRITICAL TEMPERATURE

Newton, P., Copeland, C. S., Benson, S. W.
***Journal of Chemical Physics*, v. 37, no. 2, pp. 339–346,**
July 15, 1962

The dielectric constant of ethanol was measured in the neighborhood of its critical temperature at different densities in the range 0.185 to 0.519 g/cc. Small amounts (2–5%) of added water produce only a very small increase in the dielectric constant of ethanol at 245°C but a 10- to 20-fold increase in the specific conductance. There is a slow but unimportant decomposition of the ethanol into $H_2 + CH_3CHO$ which is catalyzed by the Pt metal of the conductance cell. Comparisons of the data for ethanol are made with the Clausius–Mosotti–Debye equation and also with the Kirkwood equation for the molar polarization as a function of density. Comparisons of the data are also made with that for NH_3 and H_2O where a comparable temperature and density range has been covered. (*PA*, 1962, #19.575)

1,459. POLARIZATION OF THE ELECTRET

Gross, B., de Moraes, R. J.
***Journal of Chemical Physics*, v. 37, no. 4, pp. 710–713,**
August 15, 1962

The internal charge distribution of the carnauba wax electret was determined by a sectioning method. After polarization and cooling, samples are cut into sections of different thickness. These are reheated and the ensuing discharge currents are measured. The total released charge, as determined by numerical integration of the corresponding current-time curve, gives the polarization of each section. A macroscopic space charge polarization would give charge values which, with decreasing thickness of sections, go to zero; a uniform volume polarization would give values which are independent of thickness. Measurements gave constant values and therefore prove the existence of a uniform volume polarization of the electret. (*PA*, 1962, #18,781)

1,460. DIELECTRIC RELAXATION IN ASSOCIATED LIQUIDS

McDuffie, G. E., Jr., Litovitz, T. A.
***Journal of Chemical Physics*, v. 37, no. 8, pp. 1699–1705,**
October 15, 1962

The dielectric properties of the associated liquids butanediol-1,3, 2-methyl pentanediol-2,4, glycerol, and hexanetriol-1,2,6 were measured over the temperature range −20 to +10°C, and over a frequency range of 0.01 to 1200 Mc. Dielectric relaxation times and their distributions were determined and indicate the following: (1) All four liquids exhibit an asymmetric distribution of relaxation times of the Davidson–Cole form. (2) With the exception of hexanetriol-1,2,6, the distribution of relaxation times becomes narrower with increasing temperature. It is proposed that groups (regions of appreciable order) exist in these liquids, and that dielectric orientation is closely related to the structural breakup of these groups, this breakup being a necessary condition for dipole reorientation. It is further proposed that the structural breakup is a cooperative process which does not proceed exponentially, therefore giving rise to a nonexponential decay of dielectric polarization. This concept offers an explanation for the observed distribution of relaxation times. The temperature dependence of the width of the distribution is explained by assuming that the group-size decreases with increasing temperature, and that as the groups become smaller, the structural-decay process becomes more exponential. (*PA*, 1963, #1704)

1,461. DISPERSION AT MILLIMETER WAVELENGTHS IN METHYL AND ETHYL ALCOHOLS

Saxton, J. A., Bond, R. A., Coats, G. T., Dickinson, R. M.
***Journal of Chemical Physics*, v. 37, no. 9, pp. 2132–2138,**
November 1, 1962

A description is given of measurements, made by a free-wave technique, of the dielectric properties of methyl and ethyl alcohols at wavelengths of 3.11, 4.30, and 9.04 mm. The observations are analyzed in relation to the theory of dispersion and, in conjunction with previously existing measurements at adjacent wavelengths, provide evidence of a second dispersion region at radio frequencies in each liquid in addition to the main one normally associated with Debye-type dipole-rotation phenomena. (*PA*, 1963, #1706)

1,462. DIELECTRIC CONSTANT OF HYDROGEN-BONDED LIQUIDS. I. CYANOACETYLENE

Dannhauser, W., Flueckinger, A. F.
***Journal of Chemical Physics*, v. 38, no. 1, pp. 69–72,**
January 1, 1963

The dielectric constant of cyanoacetylene was determined over the normal liquid range: $\epsilon(T) = (71{,}000/T)\text{-}170$. Analysis of the data in terms of a hydrogen-bonded linear polymer yields: $\Delta H = -2.80$ kcal; $\Delta S = -15.8$ eu per mole of hydrogen bond. The vapor pressure of solid and liquid HCCCN was measured. Molar enthalpies and entropies of fusion and vaporization are: 3.38 and 6.72 kcal, 12.1 and 21.3 eu, respectively. Hydrogen bonding in this and similar systems is discussed. (*PA*, 1963, #7216)

1,463. DIELECTRIC PROPERTIES OF SOME POWDERED ORGANIC SEMICONDUCTORS

Huggins, C. M., Sharbaugh, A. H.
***Journal of Chemical Physics*, v. 38, no. 2, pp. 393–397,**
January 15, 1963

The use of electrical conductivity measurements to characterize the charge density and/or mobility parameters of a material is discussed. The common practice of using simple, pressed electrodes with dc measurements is felt to be grossly inferior to four-probe techniques. Even this refinement, however, is subject to considerable error for powdered samples. Many workers have used fairly simple ac techniques to eliminate interparticle contact resistances in organic semiconductors; this approach is shown to have been misapplied. It is possible, however, to measure what appears to be a specific conductivity (independent of packing pressure or filling factor) by more elaborate ac analysis. Measurements of the effective parallel resistance and capacitance are given for anthracene (powder and single-crystal), metal-free β-phthalocyanine, and a β-carotene tri-iodide complex for a frequency range of 0.05 cps to 300 Mc.

1,464. INFLUENCE OF ELECTRIC AND MAGNETIC FIELDS ON THE DIELECTRIC CONSTANT AND LOSS OF THE LIQUID CRYSTAL ANISALDAZINE

Carr, E. F.
***Journal of Chemical Physics*, v. 38, no. 7, pp. 1536–1540,**
April 1, 1963

The real and imaginary parts of the complex dielectric constant of the normal liquid phase of anisaldazine were measured at a temperature of 185°C for a frequency range from 900 Mc to 24 kMc. A plot of the complex dielectric constant in the complex plane satisfies the requirements for the Cole–Cole representation reasonably well. The temperature dependence of the dielectric loss at frequencies 6, 15, and 24 kMc indicates that any changes in the dielectric loss for a random orientation are very small as anisaldazine passes from its anisotropic to normal liquid phase. This implies that a plot of the complex dielectric constant in the complex plane for the anisotropic phase would probably satisfy the requirements for a Cole–Cole plot. Measurements of the dielectric loss in the presence of an external electrostatic field show that an ordering exists with the long axes of the molecules parallel to the external electric field.

1,465. EFFECT OF PENETRATING RADIATION ON THE PRODUCTION OF PERSISTENT INTERNAL POLARIZATION IN ELECTRET-FORMING MATERIALS

Murphy, P. V., Ribeiro, S. C., Milanez, F., de Moraes, R. J.
***Journal of Chemical Physics*, v. 38, no. 10, pp. 2400–2404, May 15, 1963**

The electret state was produced in teflon and carnauba wax by simultaneous action of penetrating radiation and an electric field. Polymethylmethacrylate, polyvinylacetate, polystyrene, polyethylene, and nylon did not form electrets under these conditions. The shapes of isothermal decay curves and thermal depolarization "glow curves" were used to calculate activation energies for the depolarization process in teflon. The average activation energy as calculated from the "initial rise" of thermodepolarization curves was 0.93 ev. The persistent heterocharge of carnauba wax and of certain polymers may be caused by the orientation of dipolar units composed of a positive molecular ion and a partially solvated electron.

1,466. DIELECTRIC RELAXATION OF SOME AROMATIC MOLECULES CONTAINING METHOXY GROUPS

Vaughan, W. E., Roeder, S. B. W., Provder, T.
***Journal of Chemical Physics*, v. 39, no. 3, pp. 701–704, August 1, 1963**

The dielectric constants and losses of a series of aromatic molecules containing methoxy groups have been measured at 2.2-mm wavelength in the liquid state at various temperatures between 20 and 80°C. The results, together with existing lower-frequency data, are used for an expansion of the complex reduced dielectric constant in a series of terms of the Debye type. The effect of temperature and molecular and liquid structure on the parameters obtained is discussed.

1,467. DIELECTRIC RELAXATION OF AQUEOUS GLYCINE SOLUTIONS AT 3.2-CENTIMETER WAVELENGTH

Sandus, O., Lubitz, B B.
***Journal of Physical Chemistry*, v. 65, no. 5, pp. 881–885, May 1961**

The dielectric constants and the dielectric loss factors of water and 0.25 to 1 M aqueous glycine solutions were measured at temperatures of 20 to 50°C at 3.2-cm wavelength. At this frequency the appreciable dispersions allow more precise characterizations of the dispersion regions than those obtained with the use of lower frequency data alone. The critical wavelengths and the "high frequency" dielectric constants were calculated, assuming Debye behavior, from the data and the static dielectric constants found in the literature. It is shown that Debye behavior is consistent with the lower frequency data reported in the literature. It is also shown that the Oncley equation for the "high frequency" dielectric constants of proteins, assumed valid for glycine solutions, is not consistent with the results of this work or the lower frequency data. The values for the critical wavelengths are in best agreement with that of Bateman and Potapenko obtained at the highest frequency used heretofore ($\lambda = 25.5$ cm). The high values for the "high frequency" dielectric constants indicate further dispersion regions. The thermodynamic functions of activation were calculated from the critical wavelengths.

1,468. DIELECTRIC POLARIZATION AND HYDROGEN BONDING OF ADSORBATE: METHANOL AND ISOBUTANE ON POROUS VYCOR GLASS

Fiat, D., Folman, M., Garbatski, U.
***Journal of Physical Chemistry*, v. 65, no. 11, pp. 2018–2023, November 1961**

Dielectric properties of MeOH and isobutane adsorbed on porous Vycor glass were investigated at low surface coverages. A high-precision capacitance meter was used to measure changes in capacity to within 2×10^{-4} $\mu\mu$f. The adsorbate–adsorbent system is treated as a solution. Molar polarization P_m and molar differential polarizations P_{diff} of the adsorbate as a function of V (the amount adsorbed) were calculated by Onsager's equation and are presented as curves. The results obtained are explained by interaction between the adsorbate and the OH groups of the adsorbent.

1,469. DIELECTRIC BEHAVIOR OF VAPORS ADSORBED ON POROUS SOLIDS

Thorp, J. M.
***Journal of Physical Chemistry*, v. 66, no. 6, pp. 1086–1092, June 1962**

An investigation has been made of the dielectric behavior (at a frequency of 0.5 Mc) of water adsorbed on alumina, and of benzene adsorbed on both alumina and silica gel, at 25°C. Isosteric heats of sorption, and data relating to pore size distribution, were obtained from the determination of sorption isothermals. For water adsorbed on alumina, the plot of capacitance increment against the amount adsorbed was found to be reversible for both adsorption and desorption throughout the entire sorption range. The absence of dielectric hysteresis was considered to be due to strong adsorbate–adsorbate interaction. Evidence was obtained for the physical adsorption of a layer of orientated water molecules onto an alumina surface modified by initial chemisorption. The evaluated dielectric constant, ϵ_2, for benzene adsorbed entirely in the capillary condensed state, on both alumina and silica gel, compared well with ϵ_{liq}, the literature value for the normal liquid. In an adsorbed benzene monolayer, ϵ_1 was lower than ϵ_{liq} on silica gel, but higher (and equal to ϵ_{solid}) on alumina. The former was considered to be due to the interaction of the π-electrons in the benzene monolayer with the silica hydroxyl groups. It was assumed that this interaction was absent with alumina, the higher value of ϵ_1 observed with the latter being due to close-packing of the benzene molecules on the surface. Dielectric hysteresis was observed for benzene on alumina, but not on silica gel. An explanation has been given in terms of the uneven electron density in the benzene molecule, together with the different polarizing influences of the two adsorbent surfaces.

1,470. MICROWAVE ABSORPTION AND MOLECULAR STRUCTURE IN LIQUIDS. XLVII. THE DIELECTRIC RELAXATION OF QUINOLINE, ISOQUINOLINE, AND SEVERAL MONO-SUBSTITUTED BIPHENYLS IN A VERY VISCOUS SOLVENT

Di Carlo, E. N., Smyth, C. P.
***Journal of Physical Chemistry*, v. 66, no. 6, pp. 1105–1108, June 1962**

The dielectric constants and losses at wavelengths of 1.25, 3.22, 10, 25, and 50 cm have been measured for isoquinoline and quinoline in Nujol solution at 20, 40, and 60°C. Measurements also have been made at wavelengths of 10, 25, and 50 cm on Nujol solutions of 4-iodobiphenyl, 2-iodobiphenyl, 2-bromobiphenyl, and 2-methoxybiphenyl at the above temperatures. Measurements of dielectric constant alone have been made at a wavelength of 575 m, and refractive indices were determined for the sodium D line. The Cole–Cole arc plots have been used to calculate the most probable dielectric relaxation times and the distribution parameters for the solutions. The free energies and heats of activation for the dielectric relaxation processes also have been calculated. The effect of difference in dipole location is too small to detect in quinoline and isoquinoline. The effect is very large in the biphenyls, 4-iodobiphenyl having relaxation times about six times those of 2-iodobiphenyl. The relaxation times show that the relaxation of 4-iodobiphenyl occurs by rotation of the molecule around its two short axes, while relaxation of the 2-substituted biphenyls occurs predominantly by rotation around the long axis. No separation of relaxation times could be effected for any of the molecules. In the case of 2-methoxybiphenyl, this shows that rotation of the methoxy group is prevented by steric hindrance. The large difference between the slope of the optical dielectric constant and that of the square of the refractive index for this molecule points to libration of the methoxy group. The energies of activation are consistent with the observed relaxation times. The observed distribution parameters were large for all the molecules indicating that they were determined, for the most part, by the nature of the solvent used.

1,471. STEREOSPECIFICITY AND DIELECTRIC PROPERTIES OF POLAR POLYMERS

Pohl, H. A., Zabusky, H. H.
***Journal of Physical Chemistry*, v. 66, no. 8, pp. 1390–1396, August 1962**

A method of determining stereoregularity in polar high polymers by dilute solution dielectric measurements is investigated on polyvinyl isobutyl ethers, polyethyl acrylates, and poly-*p*-chlorostyrenes of differing steric forms. In all cases no significant differences were found in the dielectric constants or dipole moments of the different steric forms of the same polymer. This was generally true of the relaxation times and distribution of relaxation times of the polymers also. The results are compared to those on polymethyl methacrylates where differences were found, and it is concluded that the degree of hindrance to rotation about the carbon–carbon bonds of the main chain and the degree of steric repulsion to positioning of side groups are the determining factors as to whether differences in dielectric properties will be observed. A simple and approximate method of predicting relative polarizations and dipole moments of stereospecific vinyl polymers based on dipole–dipole and repulsion energies is presented. It is concluded that the method of determining stereoregularity in polar polymers by dilute solution dielectric measurements is not generally applicable, but the method is a valuable tool for gaining insight into the flexibility of polar polymer chains.

1,472. FERROELECTRIC DOMAIN DELINEATION IN TRIGLYCINE SULPHATE AND DOMAIN ARRAYS PRODUCED BY THERMAL SHOCKS

Chynoweth, A. G., Feldmann, W. L.
***Journal of Physics and Chemistry of Solids*, v. 15, no. 3–4, pp. 225–233, October 1960**

The ferroelectric domains in single crystals of triglycine sulphate can be delineated with high resolution simply by etching the crystal in a water bath for a few seconds at room temperature. Both the ends and sides of domains can be revealed where they intersect planes perpendicular and parallel to the ferroelectric axis, respectively. With these techniques many totally internal cigar-shaped domains, with their long axes parallel to the ferroelectric axis, have been discovered. It has also been shown that a very regular array of domains is introduced into the crystal when it is subjected to a thermal shock. A cooling shock gives rise to many small spike-shaped nuclei extending into the crystal from the surfaces. A warming shock results in a regular array of considerably larger domains. It seems that in both cases the driving force that creates these new domains is the field arising from the polarization discontinuities which, in turn, are caused by the transient thermal gradients set up in the crystal when subjected to the thermal shock. The shapes of the spike-shaped domains introduced by the cooling shock agree with those predicted by a, necessarily, idealized model. (*PA*, 1961, #17,834)

1,473. THE FORMATION AND DISCHARGE OF CARNAUBA WAX ELECTRETS IN NUCLEAR RADIATION FIELDS

Murphy, P. V.
***Journal of Physics and Chemistry of Solids*, v. 24, no. 2,**
pp. 329–330, February 1963

It is reported that a 4-Mrad dose of Co^{60} gamma rays reduced the heterocharge of a thermoelectret by a factor of eight and the density of unpaired electrons by a factor of eighteen. "Radioelectrets" were formed by the simultaneous action of an electric field and β-rays from Sr^{90}. The isothermal decay currents for radioelectrets and thermoelectrets varied with time according to $i = kt^{-n}$. The residual volume polarizations were determined and compared: that of the radioelectret was proportional to the total radiation dose. (*PA*, 1963, #13,126)

1,474. DIELECTRIC PROPERTIES OF POLYMETHACRYLIC ESTERS IN DILUTE SOLUTIONS

Mandel, M.
***Journal of Polymer Science, Part B: Polymer Letters*,**
v. 1, no. 5, pp. 265–267, 1963

The dielectric properties of Me, Et, and Bu methacrylic esters in C_6H_6, dioxane, CCl_4 and toluene were investigated at 50 to −30°C. It was found that both the dielectric constant ε and the square of the refractive index n^2 varied linearly with the mass fraction of the solute x, so $(\partial\varepsilon/\partial x)_0$ and $(\partial n_\infty^2/\partial x)_0$ are equal to the slopes a and b of the straight lines $\varepsilon - \varepsilon_s = ax$ and $n_\infty^2 - (n_\infty^2)_s = bx$. For a given polymer, a and b varied with the solvent but were independent of molecular weight. Furthermore, a did not change with temperature. For six out of eleven systems a slight decrease of b with increasing temperature was found.

It is pointed out that the experimental dielectric increment $\Delta\varepsilon = (\varepsilon - \varepsilon_s)$ should be interpreted in terms of the properties of a homogeneous suspension. The $\Delta\varepsilon$ will depend on the dielectric constant of the macromolecular regions, which are large compared to the dimensions of the solvent molecules and may be considered as very concentrated solutions of highly interacting polymer segments. From this point of view, it is easily understood why $\Delta\varepsilon$ will not be molecular weight dependent (as long as M is sufficiently large) and will not present a pronounced temperature variation.

1,475. DIELECTRIC PROPERTIES OF SEMICRYSTALLINE POLYCHLOROTRIFLUOROETHYLENE

Scott, A. H., Scheiber, D. J., Curtis, A. J., Lauritzen, J. I., Jr., Hoffman, J. D.
***Journal of Research of the National Bureau of Standards, Section A—Physics and Chemistry*, v. 66A, no. 4,**
pp. 269–305, July–August 1962

The dielectric properties of polychlorotrifluoroethylene (T_m = 224°C, T_g = 52°C) have been measured at temperatures between −50 and +250°C, and at frequencies between 0.1 cps and 8.6 kMc. Specimens of known crystallinities, ranging from $\chi = 0.80$ to $\chi = 0.00$ (pure liquid), were studied. Comprehensive tables of data are presented. The experimental techniques employed to measure the dielectric properties over these wide ranges of temperature, frequency, physical state, and sample type (disks, cylinders, and thin films) are discussed. The operation and calibration of the specimen holder, bridges, resonant circuits, and waveguide apparatus used are discussed in detail.

When the dielectric loss index, ε'', at 1 cps is plotted as a function of temperature for a highly crystalline specimen ($\chi = 0.80$), where the crystallinity consists largely of lamellar spherulites, three distinct loss peaks are readily apparent. These peaks occur at about −40°C (low-temperature process), 95°C (intermediate-temperature process), and 150°C (high-temperature process). The dielectric data are compared with the mechanical loss data obtained at 1 cps by McCrum. Mechanical loss peaks at temperatures virtually identical to those in the ε'' vs. T plot are found.

The high-temperature process is attributed to the presence of well-formed chain-folded lamellar spherulites. Some evidence points to the surfaces of the lamellae as the site of the loss mechanism. The high-temperature loss peak does not appear in resolved form in nonspherulitic specimens even when the crystallinity is high. The intermediate-temperature process originates in the normal supercooled amorphous phase, and is due to the complex dipole relaxation effects involving motions of large numbers of polymer chain segments that are associated with the onset of the glass transition at T_g = 52°C. As determined by $\overline{V} - T$ data, the glass transition temperature at T_g = 52°C that is associated with this relaxation effect does not shift appreciably with increasing crystallinity. The low-temperature dielectric loss process, which is active far below T_g, originates principally in the supercooled amorphous regions, and evidentally corresponds to a fairly simple motion involving a small number of chain segments. This process tends to exhibit anomalous behavior in highly crystalline specimens, particularly at low temperatures.

A large dipolar contribution of crystals to the static dielectric constant was observed. This contribution increased with increasing temperature and corresponded to a very rapid dipole reorientation process ($\tau \sim 10^{-11}$ sec at 23°C).

1,476. EFFECT OF THE STRETCHING ON DIELECTRIC PROPERTY OF POLYMETHYL METHACRYLATE

Murakami, I.
***Journal of Science of the Hiroshima University, Series A: Mathematics, Physics, Chemistry*, v. 25, no. 1, pp. 149–158,**
July 1961

The complex dielectric constants of polymethyl methacrylate plates (degree of polymerization: 15,000) were measured in the range from 30 to 2 × 10^8 cps, at temperatures between 40 and 110°C, for samples stretched to different degrees and for unstretched ones. An X-ray analysis was employed to discern the structural changes involved. From the measurements, the following values were obtained: (1) the relaxation frequency; (2) the activation energy, including the activation free energy and the activation entropy; and (3) the effective dipole moments for the monomer link. The results seem to indicate generally that the dielectric dispersion of the polymethyl methacrylate in its glassy state is that corresponding mainly to the relaxation in orientation polarization of the ester side-groups. Furthermore, whereas above 70°C the relaxation frequency is equal to that for the unstretched samples, below 70°C it shifts to a lower value with increase in stretch. In other words, below 70°C the dielectric movement of an ester side group presupposes a cooperation, in small degrees, of the molecular backbone. (*PA*, 1962, #8461)

1,477. DIELECTRIC BEHAVIOR OF A TERTIARY LIQUID MIXTURE OF ETHYL ALCOHOL, o-CRESOL, AND α-BROMONAPHTHALENE

Sarojini, V.
***Journal of Scientific and Industrial Research*, India, v. 19B, p. 115, 1960**

When measuring ε' and ε'', mixtures of 1:1:1 and 2:2:1 were used at 30°C with frequencies of 500–2500 Mc; at 1800 Mc measurements were made over the range 20–80°C with both mixtures. For each mixture the curves show three maxima in the frequency and temperature variation.

1,478. RELAXATION TIMES OF SOME ORGANIC POLAR MOLECULES AT 3 cm

Srivastava, H. N.
***Journal of Scientific and Industrial Research*, India, v. 19B, pp. 449–451, 1960**

Dielectric relaxation times of benzylamine, EtCOBu, and dibenzyl ketone in benzene, of Bu_2NH and iso-Bu_2NH in CCl_4, and of MeCOEt and MeCOPr in decalin were determined. The effect of the molecular structure on relaxation time is pointed out.

1,479. DIELECTRIC PROPERTIES OF PHENYLETHYL ALCOHOL

Gurunadham, G.
***Journal of Scientific and Industrial Research*, India, v. 20B, p. 408, 1961**

For the frequencies (in megacycles) 1, 450, 1000, 2000, and 9200, the dielectric constants and loss factors, respectively, were determined to be: 12.80,—; 10.83, 1.87; 7.11, 3.44; 5.05, 2.30; and 3.31, 1.25. The relaxation time was 22.91 × 10^{-11} sec, the distribution parameter was 0.23, and the high-frequency dielectric constant was 2.7

1,480. DIELECTRIC DISPERSION IN CERTAIN ESTERS: BUTYL STEARATE, BENZYL PROPIONATE, AND BENZYL ACETATE

Rao, V. M.
***Journal of Scientific and Industrial Research*, India, v. 21B, no. 2, pp. 65–67, 1962**

The variations of dielectric constant and dielectric loss are measured as functions of frequency at six values in the range 1 to 9200 Mc for the three esters. Graphical determination of the distribution parameters and the relaxation time is shown to agree well with previous values. The dipole moment, the molar polarization, and the molar refraction are also measured. Some interpretation is included.

1,481. DIELECTRIC MEASUREMENTS AT 1 kMc

Dasgupta, S.
***Journal of Scientific and Industrial Research*, India, v. 21B, no. 2, pp. 68–69, 1962**

Equations are derived for the calculation of dielectric loss and relative permittivity for measurements at 10^8 to 10^{11} cps, and corrections are presented for losses in the waveguide wall and "end." Use of a quarter wavelength polythene sample to accurately adjust the sample length may enhance the sensitivity of the measurement. The dielectric loss and relative permittivity were measured on samples of Et palmitate and Et stearate, both with and without the polythene spacer, and reasonable agreement was shown.

1,482. MICROWAVE INVESTIGATIONS OF RELAXATION TIMES IN DILUTE SOLUTIONS

Srivastava, H. N.
***Journal of Scientific and Industrial Research*, India, v. 21B, no. 8, pp. 366–369, 1962**

The relaxation times (τ) of some simple alkylamines, aliphatic ketones, and disubstituted benzenes in dilute solutions were determined by the microwave technique. The validity of three different equations (proposed by Debye, Wirtz and co-workers, and Murty) for calculating τ from known molecular parameters (molecular size, molecular weight, molar refraction and polarizability of the solute and the solvent) is examined by comparing the calculated values with the experimentally observed values. Exceptions where the proportionality between τ and the molecular parameters does not hold are pointed out. (*PA*, 1963, #1707)

1,483. DIELECTRIC CONSTANT AND DIPOLE MOMENT OF NITRO COMPOUNDS. I. DIELECTRIC CONSTANT AND DIPOLE MOMENT OF NITROBENZENE

Jatkar, S. K. K., Phansalkar, V. K.
***Journal of the University of Poona, Science and Technology*, no. 22, pp. 49–56, 1962**

The dielectric constant of $PhNO_2$ was measured at various temperatures between 30 and 120°C and in solutions in benzene and dioxane at various concentrations. Moments were calculated from new and previously published data. Effects of temperature and concentration are noted. The results are interpreted.

1,484. DIELECTRIC CONSTANT AND DIPOLE MOMENT OF NITRO COMPOUNDS. II. DIELECTRIC CONSTANT AND DIPOLE MOMENT OF *o*-, *m*-, AND *p*-NITROTOLUENE

Jatkar, S. K. K., Phansalkar, V. K.
***Journal of the University of Poona, Science and Technology,* no. 22, pp. 57–64, 1962**

Dielectric constants of the three compounds were measured in the pure form and in solutions in benzene and dioxane. However, the constant of molten *p*-nitrotoluene could not be determined because it is conducting. The dipole moments were calculated by the new equation and Onsager's equation, and the effects of concentration and temperature noted.

1,485. DIELECTRIC CONSTANT AND DIPOLE MOMENT OF NITRO COMPOUNDS. III. DIELECTRIC CONSTANT AND DIPOLE MOMENT OF α-NITRONAPHTHALENE

Jatkar, S. K. K., Phansalkar, V. K.
***Journal of the University of Poona, Science and Technology,* no. 22, pp. 65–68, 1962**

The dielectric constant was determined in the molten state at various temperatures, and in benzene and dioxane at various concentrations. The moments were calculated, and the difference between the moment of α-nitronaphthalene and that of $PhNO_2$ was attributed to intramolecular H-bonding in the former.

1,486. DIELECTRIC CONSTANT AND DIPOLE MOMENT OF ACETOPHENONE AND ITS HYDROXY DERIVATIVES

Phansalkar, V. K.
***Journal of the University of Poona, Science and Technology,* no. 22, pp. 69–78, 1962**

The dielectric constants of PhAc and o-HOC_6H_4Ac were measured in the liquid state at various temperatures, and in solutions in benzene and dioxane at various concentrations and temperatures. Those of solutions of p-HOC_6H_4Ac and 2,4,1-, 2,5,1-, and 2,6,1-$(HO)_2C_6H_3Ac$ were determined in dioxane at different temperatures and concentrations. Dipole moments were determined, that of PhAc being independent of temperature but increasing with concentration, and those of the derivatives being independent of temperature and concentration. The results are interpreted in relation to structure.

1,487. DIELECTRIC PROPERTIES OF CELLULOSE NITRATE SOLUTIONS

Higashide, F.
***Kogyo Kagaku Zasshi,* v. 64, pp. 1269–1272, 1961**

The dielectric loss of cellulose nitrate solutions was measured at 25°C, both with and without the addition of a polar plasticizer. The measurement results support the author's previously expressed belief that a microcoagulum is formed by interaction of cellulose nitrate and plasticizer.

1,488. STUDIES ON DIELECTRIC BEHAVIORS IN A SERIES OF POLYALKYL-METHACRYLATES

Ishida, Y., Yamafuji, K.
***Kolloid-Zeitschrift,* v. 177, no. 2, pp. 97–116, August 1961**
(in English)

The frequency dependences of ε' and ε'' at various fixed temperatures for polymethyl methacrylate (PMMA), polyethyl methacrylate (PEMA), polybutyl methacrylate (PBMA), polyisobutyl methacrylate (PIBMA), polycyclohexyl methacrylate (PCMA), and polynonyl methacrylate (PNMA) were measured over wide frequency and temperature ranges.

The α- and β-absorptions were observed in the cases of PMMA and PEMA; the α-, β-, γ-absorptions were observed in the case of PCMA; and only one absorption was observed in each of PBMA, PIBMA, and PNMA. The absorptions in PBMA, PIBMA, and PNMA are inferred to be the α-absorptions in which the small β-absorptions hide themselves.

The shapes of the α- and the β-absorptions become sharper with increasing temperature. Comparison of α-absorptions of these polymers shows that of PNMA, with the most flexible long dipoles, to be the most sharp; differences between the shapes of the β-absorptions of PMMA and PEMA were not so remarkable.

The mean values of the apparent activation energies for the α-absorptions are compared; PNMA which shows the most loose molecular packing has the smallest value among the above polymethacrylates. This is in marked contrast to the case of the β-absorption, since no great difference was observed among the apparent activation energies of the β-absorption as long as the side group is methyl- or ethyl-ester group.

The values of the magnitudes of the β-absorptions in PMMA and PEMA increase with increasing temperature. Since the magnitude of the α-absorption cannot be determined independently, the temperature dependence of this magnitude can be disregarded. However, the sum of the magnitudes of the two absorptions can be determined, which seem to increase with increasing temperatures, take their maxima at certain temperatures, respectively, and then decrease. Actually, such a tendency was observed in the case of PEMA. Only the increasing part was observed in PMMA, and only the decreasing part in the other polyalkyl methacrylates, owing to the limitation of the range of the measurement. When the values at a fixed temperature are compared, the polymer with the largest dipole concentration shows the largest value.

The theory of the α- and β-absorptions of these polymers was developed by using a so-called "site model," and the behaviors of the absorptions in these polymers were discussed qualitatively as well as semi-quantitatively with the aid of this theory. The temperature dependences of the magnitudes of the absorptions near T_g were explained theoretically, and the qualitative agreements between the theory and the observations seem to be satisfactory. The activation energy for the β-absorption was also calculated theoretically and led to the value 10 ~ 25 kcal/mole which is in good agreement with the observed values.

1,489. DIELECTRIC BEHAVIOR OF POLYETHYLENE-OXIDE (POLYOX)

Ishida, Y., Matsuo, M., Togami, S., Yamafuji, K., Takayanagi, M.
***Kolloid-Zeitschrift*, v. 183, no. 1, pp. 74–75, May 1962**
(in English)

In previous dielectric investigation of polyoxymethylene (POM), two kinds of dielectric absorption resulting from the amorphous part were observed. The high temperature absorption has been called the α, and the low temperature has been called the β. The α-absorption of POM is so small and broad that it is difficult to identify. Such a characteristic of the α-absorption of POM seems to be ascribed to its high crystallinity and it is thought that this absorption will be more distinctly observed in a polyether with lower crystallinity. For instance, crystallinity of polyethyleneoxide (PEO) is lower than that of POM and, hence, the absorption of PEO should be more pronounced than that of POM.

The dielectric behavior of PEO is measured and the α-absorption is found to be more distinct than that of POM as expected. The apparent activation energy of the α-absorption is about 9 kcal/mole and that of the α-absorption is estimated at the order of 50 kcal/mole. Ionic conduction is indicated at higher temperatures.

1,490. TEMPERATURE DEPENDENCE OF DIELECTRIC RELAXATION BEHAVIOR FOR VARIOUS POLYMER SYSTEMS

Saito, S.
***Kolloid-Zeitschrift*, v. 189, no. 2, pp. 116–125, June 1963**
(in English)

In order to make clear the temperature dependence of dielectric relaxation behavior, dielectric constants and losses were measured over wide ranges of frequency and temperature for several polymer systems. The dielectric measurements were carried out over the frequency range of 10^{-4} or 10^{-1} to 10^6 cps at various temperatures above glass transition temperature T_g. The values of T_g and thermal expansion coefficient were determined by volume expansion measurements for the same specimen as that used for the dielectric measurements. The temperature dependences of the dielectric relaxation time τ are not described by the Arrhenius equation but by the Williams–Landel–Ferry equation. Choosing the reference temperature of T_g, the parameters in WLF equation are determined. The parameters are independent of degree of polymerization $\bar{P}$. For polyvinyl chloride, polyvinyl acetate and polymethyl methacrylate, the value of τ increases with increase of $\bar{P}$. It is confirmed that this behavior is brought about from increase in value of T_g with increase of $\bar{P}$. The effects of plasticizer or crystallinity or side-chain length on the parameters are studied for polyvinyl chloride and di-(2-ethylhexyl) phthalate systems or polyethylene terephthalates of polyalkyl methacrylates. These effects are discussed in terms of free volume concept. To study the relationship between the relaxation behavior and the free volume, Cohen and Turnbull's theory concerning self-diffusion in simple liquids is applied to the dielectric relaxation data of polymer systems. Using the WLF equation and Cohen-Turnbull's theory, fractional free volume at T_g and volume of critical void for segmental motion are estimated on the assumption that thermal expansion of free volume is equal to the difference between the thermal expansion coefficients above and below T_g. For polyvinyl chloride, the dielectric relaxation behaviors are compared with the mechanical relaxation behaviors. The temperature dependence of τ is similar to that of mechanical relaxation time. Variations of the distribution of τ with temperature are examined for several polymer systems. It is confirmed that the reduced variable method is valid for polyvinyl acetate but cannot be applied to partly crystallized polymers and polymer plasticizer systems.

1,491. ON THE POSSIBILITY OF STRUCTURAL STUDIES OF CARBON BLACK FILLED VULCANIZATES BY MEASUREMENTS OF THE DIELECTRIC CONSTANTS AND DIELECTRICAL LOSSES

Lukomskaya, A. I., Dogadkin, B. A.
***Kolloidnyi Zhurnal*, v. 22, no. 5, pp. 576–586, February 1960**

An analysis of the temperature–frequency relations of the dielectrical properties of black-filled vulcanizates shows that these properties can be subjected to quantitative treatment. In this way, characteristics are obtained on the basis of which the structure of the filled vulcanizates may be determined. The degree of development of carbon black chain and net structures is estimated by the "shape factor" computed on separating the experimental dielectric constant into its individual components. Since the "shape factor" changes with the change in "structural" dielectrical losses ε''_{str}, the development of carbon black structures may be assessed by this component of the experimental coefficient of dielectrical losses ε''. At high frequencies and low temperatures ε''_{str} coincides with ε''. At low frequencies and high temperatures (as in the case of direct current) the measure of development of carbon black structures is the loss in electrical conductivity. Further information on the changes in structure of filled vulcanizates is given by direct measurement of ε' and ε'' in the process of vulcanization.

1,492. EXPERIMENTAL INVESTIGATIONS IN THE SEARCH FOR NEW PIEZOELECTRIC SUBSTANCES

Rez, I. S., Sonin, A. S., Tsepelevich, E. E., Filimonov, A. A.
***Kristallografiya*, v. 4, no. 1, pp. 65–68, February–March 1959**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 4, no. 1, pp. 59–62, January–February 1960)

Experimental data on the detection of piezoelectric activity in various substances tested in 1956–1957 are assembled. The choice of substances for the tests was made approximately in accordance with the requirements of the genetic principle of this search, as formulated by one of the authors of this paper. Inorganic, complex, and organic substances are included. The tests were carried out with a PT-2 piezo tester, somewhat modified by A. A. Filimonov. Increase in the sensitivity of the apparatus and development of a new model of the piezo tester (PT-3) make it possible, in the cases where this is necessary, to improve the differentiation of piezo activity from the masking effects by observations on the changes in the readings of the instruments during the measurements as the load on the sample changes. In particular, the tribo-EMF increases with reduction in load, whereas the emission of electrons in the breakdown of the crystals of a substance that does not possess piezoelectric activity begins to be appreciable only when a certain threshold pressure on the sample is exceeded. The test for tribo-EMF is more precise at a high dispersity of the sample; the test for autoelectronic emission is unequivocal when the test is carried out on a single monocrystal.

As a result of the tests, the substances were placed in three groups: (1) substances with marked piezoelectric activity, greater than or equal to the activity of the quartz standard, tested under the same conditions; (2) substances with only slight activity, less than that of the quartz standard; and (3) substances not showing the piezo effect. The probability of incorrectly diagnosing the presence of a positive effect is at a maximum in group 2, in which a slight piezo-EMF can be readily masked by spurious effects. The probability of nondetection of piezoelectric activity by a tester working by the excitation of direct piezo moduli is reduced by the use in the determination, not of a single grain, but of a mixture of grains of the powder, in which it is possible to establish the effect for the part oriented in an optimum way. For the detection of piezoelectric activity in a substance found to be centrosymmetrical from X-ray data, it is necessary to take into account possible overestimation of the symmetry in structural investigations of low accuracy; the unequivocal establishment of the piezo effect in such cases will involve a correction for the space group.

1,493. STUDY OF PROCESSES OF THE PIEZOELECTRIC POLARIZATION OF ROCHELLE SALT CRYSTALS BY OBSERVATION OF THEIR DOMAIN STRUCTURE

Zheludov, I. S., Romanyuk, N. A.
***Kristallografiya*, v. 4, no. 5, pp. 710–717, September–October 1959**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 4, no. 5, pp. 670–678, May–June 1960)

By observation of the domain structure of rochelle salt crystals, with the use of optical methods, a study has been made of the processes of piezoelectric polarization of these crystals in the direction of the ferroelectric axis X.

1,494. SOME PECULIARITIES OF THE ELECTRICAL CONDUCTIVITY OF GUANIDINE ALUMINUM SULFATE HEXAHYDRATE (GASH)

Gurevich, V. M., Zheludev, I. S., Rez, I. S.
***Kristallografiya*, v. 4, no. 5, pp. 718–722, September–October 1959**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 4, no. 5, pp. 679–682, May–June 1960)

A method of measuring the electrical conductivity of single crystals of GASH for direct current is described and the results of measurements are given. The existence of transitional conductivity processes and an anomaly in the region of +50°C has been found.

1,495. ELECTRICAL CONDUCTIVITY OF A SINGLE CRYSTAL OF TRIGLYCINE SULFATE

Gurevich, V. M., Zheludev, I. S., Rez, I. S.
***Kristallografiya*, v. 5, no. 1, pp. 142–145, January–February 1960**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 5, no. 1, pp. 133–135, July–August 1960)

Triglycine sulfate (TGS) has previously been found to have a small coercive force and a highly rectangular hysteresis loop, which features have caused it to be examined very carefully. The electrical conductivity is the sole fundamental physical parameter dealt with in the literature, and that parameter forms the subject of the present work. The dc resistance of a TGS single crystal was measured, and the dielectric constant ε was found from simultaneous capacitance measurements. The measurements were made at fixed temperatures in the range from 70–78°C downward (phase transition occurring at 49°C) along the crystallographic axes X, Y, and Z. The crystal shows its ferroelectric behavior along Y. The Y-cut plates showed symmetrical rectangular hysteresis loops; the spontaneous polarization P_s at 50 cps and 24°C was 2.4 $\mu C/cm^2$; the coercive field E_c was about 240 v/cm. No loops with X- and Z-cut plates were found. Curves are presented for: conduction transients in a Y-cut TGS crystal in various fields; specific resistivity of a Y-cut TGS crystal as a function of temperature; log σ_v and ε as functions of $1/T$ for Y-cut TGS; log σ_v and ε as functions of $1/T$ for an X-cut TGS crystal; and log σ_v and ε as functions of $1/T$ for a Z-cut TGS crystal. The previously expressed view that transients are caused by ferroelectric behavior is confirmed.

1,496. RELATION BETWEEN THICKNESS AND DIELECTRIC PARAMETERS FOR PLATES OF TRIGLYCINE SULFATE

Sonin, A. S., Gladkii, V. V.
***Kristallografiya*, v. 5, no. 1, pp. 145–147, January–February 1960**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 5, no. 1, pp. 136–137, July–August 1960)

Triglycine sulfate is at present being studied intensively (1) in order to elucidate the polarization processes, and (2) because the substance may have important practical uses. The values given by various workers for the coercive force, spontaneous polarization, etc., tend to differ considerably. Those differences may be caused either by great differences in the methods used to grow the crystals, or by differences between parts of a given crystal, or by variations in the electrical parameters with the geometrical parameters (especially the thickness) of the plates. Merz has shown that $BaTiO_3$ shows this last type of variation, for example. This type of variation for triglycine sulfate crystals is considered here. Spontaneous polarization, coercive force, polarization-reversal time and current, and calculated activation field are investigated and found to vary greatly with thickness. Methods of cutting and metallization are also thought to affect the parameters.

1,497. THE EFFECTS OF ULTRAVIOLET LIGHT ON FERROELECTRIC TRIGLYCINE SULFATE

Silvestrova, I. M., Romanyuk, N. A.
***Kristallografiya*, v. 5, no. 1, pp. 147–150, January–February 1960**
(Translated from the Russian in *Soviet Physics—Doklady*, v. 5, no. 1, pp. 138–141, July–August 1960)

The effects of ultraviolet light on the behavior of ferroelectric triglycine sulfate (TGS) are considered. TGS plates were used whose thicknesses ranged from 0.5 to 3.5 mm and which had been cleaved along the cleavage planes normal to the polar axis. The plates were irradiated along that axis or at right angles to it. The most obvious effect (as with X-rays) is that the shape of the hysteresis loop changes. Three types of distortion are shown. Rough measurements of the absorption coefficient of TGS crystals, which were made by means of an SF-4 quartz spectrophotometer, are reported. An attempt was made to determine whether the effects were caused by surface or bulk damage. Spontaneous polarization, temperature effects on ε, dielectric constant, and piezoelectric modulus were investigated.

1,498. THE ASYMMETRY OF PULSED POLARIZATION REVERSAL IN TRIGLYCINE SULFATE FOR DIFFERENT INTERVALS BETWEEN PULSES OF OPPOSITE POLARITY

Shuvalov, L. A.
***Kristallografiya*, v. 5, no. 2, pp. 282–287, March–April 1960**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 5, no. 2, pp. 262–267, September–October 1960)

Experimental data on the current and time asymmetry of polarization reversal in plates of triglycine sulfate, to which unequally spaced voltage pulses are applied, are presented as a function of field, temperature, and the spacing between pulses of opposite polarity.

1,499. PULSED POLARIZATION REVERSAL IN CRYSTALS OF HEAVY WATER TRIGLYCINE SULFATE

Shuvalov, L. A.
***Kristallografiya*, v. 5, no. 3, pp. 409–414, May–June 1960**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 5, no. 3, pp. 385–389, November–December 1960)

Experimental data are presented on polarization reversal in heavy water triglycine sulfate by periodical, bipolar voltage pulses, and on the dependence of current and time of polarization on the amplitude of the pulses, temperature, and frequency. The pulsed characteristics of ordinary and heavy water triglycine sulfate are compared.

1,500. [FERROELECTRIC] BEHAVIOR OF TRIGLYCINE SULPHATE CRYSTALS AT VERY LOW FREQUENCIES [0.01–50 c/s]

Gurevich, V. M., Zheludev, I. S., Rez, I. S.
***Kristallografiya*, v. 5, no. 5, pp. 802–805, September–October 1960**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 5, no. 5, pp. 763–766, March–April 1961)

1,501. POLARIZATION OF ROCHELLE SALT UNDER THE ACTION OF SINGLE SQUARE ELECTRICAL PULSES

Romanyuk, N. A., Zheludev, I. S.
***Kristallografiya*, v. 5, no. 6, pp. 904–911, November–December 1960**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 5, no. 6, pp. 861–867, May–June 1961)

The method proposed by Abe for recording the state of polarization of rochelle salt crystals has been improved. The rapid processes of polarization of rochelle salt under the action of single square electrical pulses were studied, as well as the processes of the spontaneous decay of the polarized state of the specimen. (*PA*, 1961, #17,836)

1,502. A STUDY OF THE PHASE TRANSITION OF A TRIGLYCINE SULPHATE MONOCRYSTAL AT THE CURIE POINT BY MEASURING THE ELECTRICAL CONDUCTIVITY

Gurevich, V. M., Zheludev, I. S.
***Kristallografiya*, v. 6, no. 1, pp. 135–137, January–February 1961**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 6, no. 1, pp. 110–112, July–August 1961)

Disks (19 × 19 × 1.5 mm) were cut from a triglycine sulphate monocrystal. Measuring electrodes (7 × 7 mm) and a high-voltage electrode (16 × 16 mm) were applied, and the disks then placed in a thermostated holder. The Curie point was found to be 48.8°C for increasing temperature and 48.5°C for decreasing temperature. The dc conductivity was measured at intervals of 0.2–0.3°C around the Curie point. The curve of specific resistance vs. temperature showed a discontinuity and hysteresis at the Curie temperature, indicating a first-order phase transition. (*PA*, 1962, #6521)

1,503. THE EFFECT OF UNIPOLARITY OF ROCHELLE SALT ON ITS ELECTRICAL PROPERTIES

Karmen, K. N.
***Kristallografiya*, v. 6, no. 3, pp. 426–431, May–June 1961**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 6, no. 3, pp. 336–340, November–December 1961)

The method for studying the unipolarity of rochelle salt has been improved. It has been found that the prolonged action of a field causes a change in the unipolarity. The time needed to change the unipolarity considerably exceeds the time for rearranging the domain structure under the same conditions. The stability of the state achieved depends on the history of the specimen and the value and sign of the intensity of the constant electrical field. (*PA*, 1961, #19,922)

1,504. ELECTROSTRICTION IN ROCHELLE SALT SINGLE CRYSTALS

Fotchenkov, A. A., Zheludev, I. S., Zaitseva, M. P.
***Kristallografiya*, v. 6, no. 4, pp. 576–581, July–August 1961**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 6, no. 4, pp. 461–465, January–February 1962)

The dependence of electrostriction properties on the strength of the alternating electric field, and the degree of polarization of the specimen by a constant field were studied for an *X*-cut rochelle salt crystal in the vicinity of the upper Curie point. The character of the relationships found is explained by the behavior of the domain structure in electric fields. (*PA*, 1963, #13,121)

1,505. DIELECTRIC PARAMETERS OF DEUTERATED TRIGLYCINE SULPHATE

Silvestrova, I. M.
***Kristallografiya*, v. 6, no. 4, pp. 582–590, July–August 1961**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 6, no. 4, pp. 466–471, January–February 1962)

Results are given from measurements on deuterated triglycine sulphate; these are compared with those of ordinary triglycine sulphate, and deductions are drawn from the thermodynamic theory of ferroelectricity. (*PA*, 1963, #13,122)

1,506. EFFECTS OF γ-RAYS ON THE FERROELECTRIC PARAMETERS OF CRYSTALS OF GUANIDINIUM ALUMINUM SULFATE

Yurin, V. A., Baberkin, A. S., Zheludev, I. S.
***Kristallografiya*, v. 7, no. 1, pp. 147–150, January–February 1962**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 7, no. 1, pp. 121–123, July–August 1962)

The effects of γ-rays on guanidinium aluminum sulfate (GAS), $C(NH_2)_3Al(SO_4)_2 \cdot 6H_2O$, are reported. Special attention is paid to the possibility of producing a stable monodomain state.

These GAS specimens gave the following results:

1. The ordinary loop gradually became double if the specimen was irradiated unpolarized; the critical field E_c was proportional to the integral dose (coefficient of proportionality about 300 v/cm-Mr at room temperature). This rise in E_c was accompanied by one in the coercive field E_{c0} for both halves of the loop, which was observed by applying the alternating field briefly every 40–60 min during the irradiation and also during pauses between parts of a dose.

2. A steady field $E_=$ exceeding the saturation field E_s caused the loop to become unipolar after the crystal had received a certain dose in the monodomain state (with $E_=$ applied). The bias field E_b was also proportional to dose; there was a corresponding rise in E_{c0}. The sense of the bias field was opposed to that of $E_=$; the sign of the bias field fixed in the specimen by the irradiation was the same as that of $E_=$.

3. There was no appreciable change in the saturation polarization P_s, at least up to 80 Mr. The measurements could not be extended to higher doses because the voltages required exceed the breakdown voltage.

4. If the specimen was irradiated while subject to an alternating field $E_\sim > E_s$, the loop did not become double even at very high doses, although E_{c0} increased. The loop soon became double, however, if $E_\sim$ was removed when the irradiation had finished. The rate at which this occurred was a covariant function of temperature.

5. The domain structure in the static state can be observed by virtue of the electroluminescence if the hysteresis loop is double, although dc and ac fields must be applied simultaneously. The first such structure to be recorded for irradiated GAS is shown (a structure not detectable by optical methods). The domain boundaries lie parallel or normal to the faces of the hexagonal prism in the growth pyramids of those faces. The irradiation appears to have no appreciable effect on the shapes and sizes of the domains.

6. GAS remains colorless after irradiation.

The conclusion is reached that γ-rays produce in GAS either a stable polydomain state (double loop) or a stable monodomain state (displaced loop); in both cases, the state is that maintained during the irradiation. Production of a stable monodomain state in a third ferroelectric confirms the prediction that such a state can be produced in many ferroelectrics by impurities or by radiation. The effect may make it possible to use the piezoelectric and pyroelectric effects in ferroelectric crystals in order to convert energy from one form to another.

1,507. THE FERROELECTRIC PROPERTIES OF TRIGLYCINE SULFATE CRYSTALS IRRADIATED WITH γ-QUANTA

Yurin, V. A., Silvestrova, I. M., Zheludev, I. S.
***Kristallografiya*, v. 7, no. 3, pp. 394–402, May–June 1962**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 7, no. 3, pp. 312–318, November–December 1962)

An experimental study is reported of the effect of γ-radiation on the shape and parameters of the hysteresis loop, the effect of static electric fields and temperature on the hysteresis loop of irradiated crystals, and the effect of γ-radiation on the dielectric properties of triglycine sulfate crystals. The results are compared with similar data for rochelle salt containing copper ions.

1,508. THE DIELECTRIC AND NONLINEAR PROPERTIES OF SEIGNETTE'S SALT AT ULTRA-HIGH FREQUENCIES

Petrov, V. M.
***Kristallografiya*, v. 7, no. 3, pp. 403–407, May–June 1962**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 7, no. 3, pp. 319–322, November–December 1962)

Results are given of an investigation into reverse characteristics ϵ and tan δ of rochelle salt at frequencies of 1000 and 3000 Mc, and nonlinearity at 200 Mc, between 18 and 36°C.

1,509. THE INVERSE PIEZOELECTRIC EFFECT IN Z-CUT CRYSTALS OF GUANIDINIUM ALUMINUM SULFATE (GAS)

Zheludev, I. S., Lelekov, V. S.
***Kristallografiya*, v. 7, no. 3, pp. 463–465, May–June 1962**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 7, no. 3, pp. 369–370, November–December 1962)

The method of modulation interferometry (developed by Gorelick and Bershtein) and an apparatus designed by Fotchenkov to measure the piezoelectric effect were used to measure d_{33} for guanidine aluminum sulfate (GAS) as a function of a polarizing field on Z-cut specimens. The constant and alternating fields were applied along the Z-axis. Resulting data are graphed. The curves give an indication of the type of polarization in GAS. There is a linear relation of d_{33} to field for high field strengths, which provides a means of estimating the spontaneous polarization, P_s. Calculation of P_s from the data gives a value of 0.3×10^{-6} coulomb/cm², which agrees well with the value found from the hysteresis loop.

1,510. FERROELECTRIC BEHAVIOR OF TRIGLYCINE SULFATE AT HIGH HYDROSTATIC PRESSURES

Zheludev, I. S., Tikhomirova, N. A., Fridkin, V. M.
***Kristallografiya*, v. 7, no. 5, pp. 795–797, September–October 1962**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 7, no. 5, pp. 643–644, March–April 1963)

The conductivity and dielectric parameters of triglycine sulfate are reported for hydrostatic pressures up to 25,000 atm. The conductivity at these pressures has been measured in terms of (1) the forward current and (2) the reverse current when the electrodes are short-circuited. The initial reverse current is graphed as a function of field for two pressures; the current increases with the pressure, and saturation sets in at lower voltages. This result is explained by the decrease in the part of the polarization associated with ferroelectric absorption; the part associated with electron or ion conduction increases with the pressure. The effects of pressure on the loop point to the same conclusion. The dielectric constant was measured at 800 cps; as the pressure increased, ϵ was found to fall monotonically, but the fall was not more than 50% of the initial ϵ, as for other materials.

The results generally indicate that it is difficult for the domains to change their orientation at high pressures, whereupon adsorption tends to be replaced by ion or electron conduction.

1,511. ELECTRETS OF ELASTIC POLYMERS

Gul, V. E., Lushcheikin, G. A., Fridkin, V. M.
***Kristallografiya*, v. 7, no. 5, pp. 797–799, September–October 1962**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 7, no. 5, pp. 645–646, March–April 1963)

The literature carries no information on electrets whose orientation (produced by a field) has been fixed by cross-linking (vulcanization). This method is of substantial interest, for it should make possible production of new and highly stable polar textures. Moreover, the properties of such electrets should cast fresh light on orientation and polarization processes in mechanically deformed polymers.

Elastic insulators have been used based on natural rubber treated with the usual amounts of vulcanizing agents but free from fillers. The mixture was prepared by rolling, and was vulcanized in a press at 70 kg/cm² between sheets of aluminum foil. The surface charge density was measured.

Strong fields give rise to a homocharge on one surface and a heterocharge on the other, the latter eventually becoming a homocharge. Charges of the same sign sometimes occur on both surfaces for fields between 5 and 10 kv/cm; both charges eventually become heterocharges. An empirical formula is given for the surface charge.

The piezoelectric modulus was measured along the polarization direction by static methods. This modulus was shown to be a function of the heterocharge density, the one being proportional to the other, at least up to 10^{-7} esu.

These results all relate to electrets made by vulcanization in an electric field applied for the first two minutes (total vulcanization time 30 min at 142°C). The charge density was much less if the field was applied somewhat later (after the vulcanization had been in progress for ten minutes). It did not seem possible to make electrets from materials already vulcanized.

1,512. THE INVERSE PIEZOELECTRIC EFFECT IN TRIGLYCINE SULFATE

Fotchenkov, A. A., Zaitseva, M. F.
***Kristallografiya*, v. 7, no. 6, pp. 934–937, November–December 1962**
(Translated from the Russian in *Soviet Physics—Crystallography*, v. 7, no. 6, pp. 756–758, May–June 1963)

Y-cut crystals of triglycine sulfate have been used to measure d_{22} as a function of alternating field and temperature (for various polarizing fields) and as a function of polarizing field during polarization reversal. The principal features are explained in terms of the domain structure of TGS.

1,513. DIELECTRIC MEASUREMENTS FOR THE EXAMINATION OF PLASTICS

Langbein, G.
***Kunststoffe*, v. 51, pp. 503–508, 1961**

Dielectric methods may be used for the determination of moisture; since dielectric properties of a polymer vary with crystalline and amorphous modifications, the stereospecificity of polymers may be determined by this method.

1,514. THE ELECTRIC PROPERTIES OF CURED EPOXIDE RESINS

Jellinek, K.
***Kuntstoff Rundschau*, v. 9, pp. 549–554, 1962**

Dependence of the electrical properties of commercial bisphenol A–epichlorohydrin epoxide resins on the hardeners used is considered. The dielectric properties investigated over a wide range of temperatures and frequencies are volume and surface resistivity, dielectric strength, leakage-current resistance, dielectric constant, and dissipation factor. The hardeners are of aliphatic and aromatic amine, polyamidoamine, and acid anhydride type. The electrical properties at high temperatures are discussed for epoxide resins with increased flexibility or with increased glass temperature.

1,515. DIELECTRIC PROPERTIES OF TRANS-1,4-POLYBUTADIENE

Pegoraro, M., Mitoraj, K.
***Makromolekulare Chemie*, v. 61, pp. 132–138, 1963**
(in English)

Measurements were made of the dielectric constant and of tan δ of *trans*-1,4-polybutadiene with a steric purity higher than 99% at a constant frequency of 50 cps and at variable temperatures between −50 and +170°C.

The behavior of the dielectric constants points out a first-order transition at 76°C, corresponding to the known variation of conformation of the crystalline chain. and another first-order transition at 146°C, corresponding to the complete melting.

The values of tan δ are of the order of 10^{-3} up to the first transition, and then increase considerably due to the increase in electric conductivity.

1,516. MOLECULAR STRUCTURE AND STATISTICAL THEORY OF ELECTRIC MOMENTS OF LINEAR POLYMERS. II. ELECTRIC DIPOLE MOMENTS OF POLY(ETHYLENE OXIDE) GLYCOL IN BENZENE SOLUTION

Magnasco, V., Dellepiane, C., Rossi, C.
***Makromolekulare Chemie*, v. 64, pp. 16–25, 1963**
(in English)

In Part I (*Il Nuovo Cimento*, v. 18, p. 554, 1960), Magnasco has proposed a method for calculating the mean square electric dipole moment of poly(ethylene oxide) glycol (POEG) based on the rotation matrices method, for three different molecular structures, assuming the internal flexibility of the macromolecule in solution and the statistical independence of rotations.

In this work the experimental determination is reported of the polar moment of a POEG series with molecular weight ranging from 194 to 7770, in benzene solution at 25°C. The experimental results are briefly discussed.

1,517. DIPOLE MOMENTS AND MOLECULAR STRUCTURE OF COPOLYMERS. II. DIPOLE MOMENT OF METHYL ACRYLATE-STYRENE COPOLYMERS

Shima, M., Kotera, A.
***Makromolekulare Chemie*, v. 65, pp. 172–180, 1963**
(in English)

In Part I (*Journal of Polymer Science*, v. 56, pp. 213–223, 1962), a method was described for evaluating the dipole moment of copolymers in relation to the distribution of polar monomer unit sequences; the use of the method was illustrated with the experimental results of methyl methacrylate-styrene copolymers. In this paper the measurements of the dipole moments of methyl acrylate-styrene copolymers are described, and the results are compared with those obtained for methyl methacrylate-styrene copolymers.

1,518. SOME DIELECTRIC PROPERTIES OF TRIGLYCINE SULFATE, GUANIDINE ALUMINUM SULFATE HEXAHYDRATE, AND TRIGLYCINE TELLURATE

Kaczmarek, F.
June 1961
Massachusetts Institute of Technology, Laboratory for Insulation Research, Cambridge
TR 163, Nonr-184110, AF 19(604)-6155
AD-259,984

The dielectric constants of triglycine sulfate and guanidine Al sulfate hexahydrate were measured as a function of frequency up to about 23 kMc. The constants of tryglycine sulfate were also measured as a function of temperature. The dielectric constant of triglycine tellurate, recently synthesized, was measured in the low frequency region. 18 references.

1,519. DIELECTRIC BREAKDOWN OF POLY(TETRAFLUOROETHYLENE). V. EFFECT OF MOLECULAR WEIGHT. 2. DIELECTRIC BREAKDOWN TESTS

Iida, S.
***Nagoya Kogyo Gijutsu Shikensho Hokoku*, v. 7, pp. 178–184, 1958**

The relation between the molecular weight and breakdown voltage of poly(tetrafluoroethylene) was observed in samples obtained by polymerization under various conditions or by degradation from γ-irradiation. Behavior is compared in samples compacted by a free baking method and by a hot-compressior method. In general, in the low-molecular-weight range, breakdown voltage increases with molecular weight, while in a high-molecular-weight range, there is a tendency to decrease.

1,520. THE ELECTRIC STRENGTHS OF HEXANE VAPOR AND LIQUID IN THE CRITICAL REGION

Watson, P. K., Sharbaugh, A. H.
1961
National Academy of Sciences. National Research Council, Washington, D.C.
Publication 973, pp. 95–96

The electric breakdown field strengths of hexane vapor extrapolated to pressure giving density corresponding to the liquid state are higher than those actually observed for the liquid. Probably because of field emission, observed breakdown strengths above the critical temperature, for density more than 0.01 g/cc, are less than the extrapolated curve. New measurements show that the values of breakdown strength for liquid and vapor converge as the critical point is approached. Formation of vapor bubbles may account for the lower strengths in liquids.

1,521. LONG-TIME EFFECTS OF HUMIDITY CHANGE ON THE DIELECTRIC PROPERTIES OF CERTAIN POLYMERS

Scott, A. H., Harris, W. P.
1963
National Academy of Sciences, National Research Council, Washington, D.C.
Publication 1080, pp. 41–44

The dielectric constants and dissipation factors of polyethylene, polystyrene, and polycarbonate were measured over time intervals ranging from 100 days to three years after transfer from (1) 52% relative humidity to dry conditions, and (2) dry conditions to 52% relative humidity. In general, dielectric constants and dissipation factors decrease under the first conditions and increase under the second conditions. The three polymers are compared for stability.

1,522. PIEZORESISTANCE EFFECTS IN CRYSTALLINE AND AMORPHOUS MOLECULAR SOLIDS [ABSTRACT]

Pohl, H. A., Henry, A. W.
In "Program and Abstracts: Organic Crystal Symposium, October 10-12, 1962," p. 203
National Research Council, Ottawa, Canada, 1962

It is shown that certain crystalline and amorphous molecular solids exhibit large and reversible piezoresistance coefficients. Over a pressure range in which most metals double in conductivity (about 40,000 atm), these solids increase up to about 1000-fold in conductivity. Part of the change is due to changes in activation energy, and part to changes in the mobility. A simple theoretical treatment of the effect is presented, based upon an absolute reaction rate formalism treating the pressure effects on the intermolecular overlap of electron orbitals. The equations appear to fit the experimental observations up to the critical pressure at which metalloid behavior appears.

1,523. DIELECTRIC CHARACTERISTICS OF CHLOROBIPHENYL AND CHLOROBIPHENYL-IMPREGNATED PAPER. I. DIELECTRIC CHARACTERISTICS OF CHLOROBIPHENYL

Tomago, A., Yamauchi, I.
***National Technical Report*, Matsushita Electric Industrial Co., Osaka, Japan, v. 8, pp. 526–532, 1962**

Temperature and frequency characteristics of electrical conductivity, dielectric constant, and dielectric loss tangent of commercial trichloro- and pentachlorobiphenyl (TD and PD) after being refined were measured. Electrical conductivity of TD was higher than that of PD at the same temperature, both increasing exponentially with temperature.

1,524. TRANSITION IN THE DIELECTRIC PROPERTIES OF SOLID SECONDARY ALCOHOLS

Dryden, J. S., Welsh, H. K.
***Nature*, v. 192, no. 4799, pp. 255–256, October 21, 1961**

The only previously concluded fact about the mechanism of the large dielectric absorption in aliphatic secondary alcohols is that the presence of some lattice defect or arrangement of defects is required for this large absorption.

In the belief that further progress can be made only from measurements on single crystals grown from pure material, attempts have been made to grow single crystals from the melt. Although the crystals have been below standard, measurements made on the oriented polycrystalline material obtained have revealed a sharp transition in the dielectric properties of certain alcohols at a temperature about −4°C. The transition was not apparent in samples pressed from powders, although a suggestion of its presence was noted in samples annealed for long periods.

Dielectric absorption is plotted as a function of frequency for a sample of 9-heptadecanol. Also plotted are the relative permittivity at 4.8 cps as a function of temperature, and the estimated permittivity below the absorption region as a function of temperature. Work is also reported on 8-pentadecanol and 10-nonadecanol.

1,525. INTRINSIC ELECTRIC STRENGTH OF POLYTHENE

Cooper, R., Rowson, C. H., Watson, D. B.
***Nature*, v. 197, no. 4868, pp. 663–664, February 16, 1963**

Statistical analysis of new and earlier data indicates that the intrinsic electric strength E_1 of polythene decreases with specimen thickness. For Alkathene 7, $E_1 = 12.8 - 3 \log_{10} t$ Mv/in. at 20°C for thickness t of 1 to 18×10^{-3} in. With evaporated Al electrodes the mean E_1 was 11.2 Mv/in. compared with 12.4 Mv/in. with graphite electrodes. Tests with 1-μsec front impulses also gave lower mean values than tests with slowly increasing direct voltage. (*PA*, 1963, #13,125)

1,526. DIELECTRIC PROPERTIES OF CROSS-LINKED POLYSTYRENE FILM FORMED IN THE GLOW DISCHARGE

Stuart, M.
***Nature*, v. 198, no. 4888, pp. 59–60, July 6, 1963**

Irradiation of a monomer vapor frequently causes polymerization leading to the formation of a solid deposit on any convenient surface. Electrons, ultraviolet, X- or γ-radiation, or an electrical discharge can be used.

In the work recorded here, a glow discharge at 180 kc is used to form uniform 1-μ polystyrene film. The discharge is maintained between parallel cylindrical aluminum electrodes in several millimeters of mercury pressure of styrene vapor contained in a pre-evacuated chamber. Aluminum foil, in contact with one electrode, serves as the substrate for the film. This electrode rotates uniformly during polymerization. Aluminum is afterwards evaporated onto the surface of the polymer film to provide a second electrode. Power factor and capacitance vs. temperature at several frequencies are shown as graphs. The wide distribution of relaxation times results from the complex structure of the film. ESR measurements made at room temperature *in vacuo* show the presence of free radicals which presumably peroxidize on exposure to air. An interesting feature of the films is their insolubility, indicating a high degree of cross-linking.

1,527. ORIENTATION OF CETYL ALCOHOL IN A HIGH D.C. FIELD IN RELATION TO GROSS'S THEORY OF THE ELECTRET

Chandy, K. C.
***Naturwissenschaften*, v. 49, no. 5, p. 102, March 1962**
(in English)

An X-ray study of cetyl alcohol solidified in a dc field is reported; the intent is to explain the absence of homocharges on this material. It is concluded that this is due to inhomogeneity because of the presence of a number of polymorphic forms. (*PA*, 1962, #14,644)

1,528. DIELECTRIC DISPERSION OF DILUTE SOLUTIONS OF ETHYL CELLULOSE

Imamura, Y.
***Nippon Kagaku Zasshi*, v. 82, pp. 984–987, 1961**

The bridge method was used for measuring critical frequency ν_c of dielectric dispersion of ethyl cellulose in Tetralin at 20 to 100°C. An equation relating ν_c and intrinsic viscosity at 30°C is given, and the activation energy of dielectric relaxation is considered.

The results are explained by considering the rigidity of the molecules in comparison with that of vinyl polymers.

1,529. DIELECTRIC LOSS AND VOLUME RESISTIVITY OF UNSATURATED POLYESTER RESINS

Shito, N.
***Nippon Kagaku Zasshi*, v. 82, pp. 1449–1456, 1961**

Dielectric constant and dielectric loss angle at 60 cps, as well as dc volume resistivity, were measured for an unsaturated polyester resin prepared from maleic acid, adipic acid, propylene glycol, and styrene. The polyester in the resin acted as a plasticizer as well as a cross-linking agent. Data are presented and interpreted.

1,530. DIELECTRIC PROPERTIES OF THIOPHENE AND FURAN

Matsumoto, M., Kondo, S.
***Nippon Kagaku Zasshi*, v. 83, pp. 261–263, 1962**

The dielectric properties of thiophene and furan were investigated at 68–300°K and 1–300 kc. The observed triple points and transition points of these compounds agreed quite well with those obtained from thermal studies by Waddington. The dielectric behavior in four phases is explained in terms of molecular orientation.

1,531. DIELECTRIC PROPERTIES OF UNSATURATED POLYESTER RESINS CONTAINING THE ISOPHTHALATE STRUCTURE

Shito, N.
***Nippon Kagaku Zasshi*, v. 83, pp. 542–548, 1962**

The dielectric constant and the loss factor of several unsaturated polyester resins formed from poly(propylene maleate adipate isophthalate) and styrene monomers were measured at 20–160°C in the frequency range 120–30,000 cps. Resulting data are presented. Degree of polymerization and the extent to which the isophthalate structure is contained both influence the activation energy of relaxation. These effects are discussed.

1,532. DIELECTRIC POLARIZATION OF ORGANIC CRYSTALS CONTAINING HYDROGEN BONDS

Yabumoto, S.
***Nippon Kagaku Zasshi*, v. 84, pp. 547–552, 1963**

1,533. DIELECTRIC PROPERTIES OF ION-EXCHANGE RESINS

Takeshita, S.
***Nippon Kagaku Zasshi*, v. 84, pp. 569–576, 1963**

1,534. DIELEKTRISCHE POLARISATION UND DIE WECHSELWIRKUNG DER CARBONSÄUREN UND AMINE (DIELECTRIC POLARIZATION OF COMPLEXES COMPOSED OF CARBOXYLIC ACIDS AND AMINES)

Sobczyk, L.
In "Hydrogen Bonding," Papers presented at the Symposium on Hydrogen Bonding, Ljubljana, Yugoslavia,
July 29–August 3, 1957, pp. 323–329
Hadži, D., Editor
Pergamon Press, Inc., New York, N.Y., 1959

In connection with previous papers, some investigations of dielectric polarization of complexes composed of carboxylic acids and amines were carried out in order to establish a relationship between their polarity and p*K* value of acidic component.

The measurements have indicated a linear relation between *P* (or ΔP) and p*K*. The following components were used: C_6H_5COOH, CH_2ICOOH, $CH_2ClCOOH$, $CHCl_2COOH$, CCl_3COOH, *N*-methylpyperidine, diethylamine, and ethylamine. The majority of systems contained benzene as solvent, and in two cases dioxan solution was used in order to test the stability of complexes with hydrogen bond and to confirm the absence of their additional association. The role of the so-called polar hydrogen bond in acid-base interactions was stressed.

1,535. THE PERMITTIVITY OF HYDROSTATICALLY STRESSED DIELECTRICS

Gibbs, D. F., Jarman, M.
***Philosophical Magazine*, v. 7, no. 76, pp. 663–670, April 1962**

Experiments were carried out to determine the change of permittivity of some well-known solid dielectrics with pressure. The dielectrics, in the form of slabs of the order of 0.1 mm thick and 1 cm² in area were submitted to hydrostatic pressures up to 3000 kg/cm² in oil, and the fractional change in capacity was observed. Dielectrics investigated included alkali halides, polystyrene, polyethylene, rutile, and ammonium iodide. (*PA*, 1962, #23,494)

1,536. THICKNESS DEPENDENCE OF THE NUCLEATION FIELD OF TRIGLYCINE SULPHATE

Kay, H. F., Dunn, J. W.
***Philosophical Magazine*, v. 7, no. 84, pp. 2027–2034, December 1962**

The applied electric field at the onset of polarization reversal during switching of a triglycine sulphate single crystal with a sinusoidal applied field was measured as a function of crystal thickness. In contrast to the sinusoidal coercive field measurements of Pulvari and Kuebler, this field is frequency independent and thickness dependent according to the relation $E_n \propto (\text{thickness})_{-2/3}$. The results are discussed as a nucleation phenomenon on the basis of a simple model and lead to an estimate of the domain wall surface energy of triglycine sulphate as being of the order of 1 erg/cm². Finally, a criticism of the theory is discussed. (*PA*, 1963, #6619)

1,537. ON THE EFFECTS OF X-RAY IRRADIATION ON TRANSIENT PHENOMENA IN ROCHELLE SALT

Rewaj, T.
***Physica Status Solidi*, v. 2, no. 9, pp. 1151–1157, 1962**
(in English)

Transient variations of the permittivity ε subsequent to application or removal of a dc electric field are measured in pure rochelle salt before and after X-ray irradiations with doses up to 5.82×10^6 r. Irradiation is found to affect the form of the transient phenomena considerably. The maximum of the variations observed during the measurements shifts toward higher polarizing field strengths as irradiation dose increases. The variations diminish after sufficiently high irradiation doses. It is proposed that the defects produced by irradiation at first only slow down the reorientational motion of the domains; however, as defects accumulate, they entirely immobilize an increasingly large proportion of the domains, thus preventing them from participating in the polarization of the sample.

1,538. THE ELECTRET EFFECT IN PARAFFIN WAX

Gorzkiewicz, J.
***Physica Status Solidi*, v. 3, no. 2, pp. 276–282, 1963**
(in English)

Electrets were prepared from pure paraffin wax by irradiation with β-rays followed by formation in a constant electric field. The charge of the electrets was measured by means of the inductive method and with a Faraday cylinder. The dependence of the electret charge on intensity of forming field, forming time, irradiation time, and storage time after irradiation was investigated, as was the permanence of the charge. Electrets prepared in this way have charges of the same order of magnitude as thermic electrets made from carnauba wax and formed in similar forming fields.

1,539. NEW FERROELECTRICS OF THE TETRAMETHYL-AMMONIUM-TRIHALO-MERCURATE FAMILY

Fatuzzo, E., Nitsche, R., Roetschi, H., Zingg, S.
***Physical Review*, v. 125, no. 2, pp. 514–516, January 15, 1962**

Three new ferroelectrics belonging to a family of the general formula $[X(CH_3)_4]HgY_3$ (where $X = N, P$; $Y = Cl, Br, I$) were discovered. They are: $[N(CH_3)_4]HgBr_3$, $[N(CH_3)_4]HgI_3$, and $[P(CH_3)_4]HgBr_3$. The preparation of single crystals of these compounds (monoclinic, space group $P2_1$) is described. The dielectric constants are of the order of 10, the spontaneous polarizations between 1 and 3 μcoulomb/cm². Curie points could not be observed because of thermal decomposition of the compounds around 170°C. The switching time varies with the seventh power of the applied field *E*.

1,540. GAMMA IRRADIATION EFFECTS ON ELECTRETS

Gross, B., de Moraes, R. J.
***Physical Review*, v. 126, no. 3, pp. 930–932, May 1, 1962**

Carnauba wax electrets were irradiated with γ-rays from a Co^{60} source. Doses varied between 0 and 5 Mr. After irradiation, the polarization of the electrets was determined by reheating them in short circuit and measuring the released charge. This charge was found to decrease roughly exponentially with dose, with a decay constant of the order of 1 Mr. A background effect due to Compton polarization is described. (*PA*, 1962, #12,573)

1,541. CRITICAL FLUCTUATIONS IN TRIGLYCENE SULFATE

Brophy, J. J., Webb, S. L.
***Physical Review*, v. 128, no. 2, pp. 584–588, October 15, 1962**

Critical-point polarization fluctuations in ferroelectric triglycene sulphate were observed at the Curie temperature by measuring the random noise voltages appearing between electrodes applied to the crystal. These noise voltages are interpreted in terms of the Nyquist noise associated with the crystal conductance and, therefore, can be used to determine the true crystal impedance at and near the transition temperature where the crystal is highly nonlinear. The polarization noise density at the Curie point has a simple relaxation spectrum with a time constant of 5.3×10^{-3} sec, which, furthermore, is relatively independent of temperature near the Curie temperature. A thermal Barkhausen noise observed in barium titanate as the crystal is passed slowly through the transition temperature appears to be associated with the inherent domain structure of the sample. (*PA*, 1963, #893)

1,542. POLARIZATION RELAXATION IN TRIGLYCINE SULFATE ABOVE THE CURIE TEMPERATURE

Hill, R. M., Ichiki, S. K.
***Physical Review*, v. 128, no. 3, pp. 1140–1145,**
November 1, 1962

Measurements of the complex dielectric constant for normal and deuterated triglycine sulphate are reported. These measurements cover a range of 20°C above the Curie temperature and frequencies up to 7.7×10^{10} cps. A frequency- and temperature-dependent relaxation of the dielectric constant was observed which first sets in around 5×10^{7} cps. It was found that all the observations of ε^* could be expressed as

$$\varepsilon^* = \frac{C}{T - T_c}\,[f(\nu\tau_0) + i\,g(\nu\tau_0)]$$

where C and T_c are the Curie constant and temperature; and τ_0 is inversely proportional to $(T - T_c)$. Expressions for $f\,(\nu\tau_0)$ and $g\,(\nu\tau_0)$ which give a good fit to the data were derived by assuming that each dipole has a Debye relaxation characteristic and that there is a Gaussian distribution of relaxation times, with τ_0 being the measure of the width of the distribution. (*PA*, 1963, #2961)

1,543. ON THE ANOMALOUS INCREASE OF THE PERMITTIVITY DURING SLOW SWITCHING PROCESSES ON TRIGLYCINE SULPHATE

Fousek, J., Málek, Z., Salim, A. J., Al Ali, N. S.
***Physical Society, Proceedings of the*, v. 80, pt. 5,**
pp. 1199–1200, November 1962

An investigation is reported of the increase in permittivity in extremely slow switching processes characterized by maximum switching currents in the range 4×10^{-5} amp m^{-2} to 3×10^{-3} amp m^{-2}, the electric field across the crystal varying at a rate between 1 v cm^{-1} min^{-1} and 100 v cm^{-1} min^{-1}. The increase in permittivity, measured at 1 kc, may be as large as 700%. Typical graphs of permittivity and switching current vs. the instantaneous field strength, and of the increase in permittivity vs. the switching current show that the maximum increase in permittivity is not proportional to the maximum switching current and does not occur at the same field strength. (*PA*, 1963, #2960)

1,544. SOME PROPERTIES OF X-RAY DAMAGED ROCHELLE SALT

Okada, K.
***Physical Society of Japan, Journal of the*, v. 15, no. 2,**
pp. 363–364, February 1960

Measurements were made of the properties of a-cut rochelle salt crystals damaged by exposure to 50-kv X-rays. Biased hysteresis loops were observed in poled crystals, and symmetric double hysteresis loops were observed in completely unpolarized specimens. The domain clamping responsible for these effects was observed directly by optical methods on crystals damaged in a selected region. Permittivity measurements on crystals which exhibited a symmetric double hysteresis loop showed a shift of upper and lower Curie temperature with moderate biasing field, in the opposite direction to that observed in undamaged crystals, i.e., similar to the change in an antiferroelectric. In strong fields, the damaged crystals behaved in the same manner as virgin specimens. (*PA*, 1961, #10,077)

1,545. FERROELECTRIC PROPERTIES OF X-RAY DAMAGED ROCHELLE SALT

Okada, K.
***Physical Society of Japan, Journal of the*, v. 16, no. 3,**
pp. 414–423, March 1961

Radiation damage effects by X-rays in rochelle salt were studied experimentally and theoretically. A double hysteresis loop is explained as a superposition of two biased single loops. Each biased single loop corresponds to one of the two oppositely polarized domains of which the crystal is composed. When damaged, single domain crystals show biased single loops, and the internal bias induced can be compensated by an external dc biasing field; however, the Curie point of the damaged crystals compensated by this suitable external field is lower than that of the virgin by ΔT, which depends upon the X-ray dosage. In this respect the effect of damage differs from that of the stress. It is assumed that the irradiation gives rise to polar anisotropy centers which produce effective bias fields in undamaged ferroelectric regions. Irradiation time dependences of the spontaneous polarization, the coercive field, and the internal bias are studied. A phenomenological theory is developed to explain the various phenomena. The polarization within the polar anisotropy center is estimated to be of the order of 100 esu near the shifted Curie point. (*PA*, 1961, #14,555)

1,546. THE FERROELECTRIC PHASE TRANSITION IN $(GLYCINE)_3 \cdot H_2SO_4$ AND CRITICAL X-RAY SCATTERING

Shibuya, I., Mitsui, T.
***Physical Society of Japan, Journal of the*, v. 16, no. 3,**
pp. 479–489, March 1961

On the assumption that the ferroelectric phase transition in $(\text{glycine})_3 \cdot H_2SO_4$ is of the order-disorder type, expressions for Bragg reflections and critical scattering of X-rays are given in terms of a long-range order parameter and pair correlation functions. Temperature dependence of the critical scattering is discussed on the basis of the Bragg–Williams approximation and of a modified Fröhlich theory. Experimental observations agree with theoretical predictions and prove that the phase transition is of the order-disorder type. The observed critical scattering exhibits a pronounced peak at the Curie point, suggesting that the local field theory is not a good approximation. The shape of the peak appears to be quite different from that in the ferromagnetic case. It has been found that the S atoms do not shift appreciably when the glycine groups rotate. A method for evaluating the pair correlation function is proposed. (*PA*, 1961, #14,556)

1,547. DIELECTRIC α- AND β-DISPERSIONS IN POLYVINYL BUTYRAL (PVB)

Takahashi, Y.
***Physical Society of Japan, Journal of the*, v. 16, no. 5,**
p. 1024, May 1961

The dielectric loss ε'' in a sample of PVB, which was heat-treated at 200°C for 30 min, was measured in the temperature range -70 to $+120$°C and the frequency range 0.3 to 10^6 cps. The higher temperature dispersion labeled as α and the lower temperature dispersion labeled as β were observed. The plot of log f_m vs. $1/T$ (where f_m is the frequency at which ε'' is maximum) is a curve for the α-dispersion but a straight line for the β-dispersion. The dielectric activation energies for the former are 93, 66, 53, 42, and 34 kcal/mole at 80, 92, 102, 110 and 120°C, respectively. For the β-dispersion, the energy is 12 kcal/mole and is independent of temperature. (*PA*, 1961, #19,921)

1,548. DIELECTRIC α-, β- AND γ-DISPERSIONS IN THE THERMOSETTING PHENOLIC RESINS

Takahashi, Y.
***Physical Society of Japan, Journal of the*, v. 16, no. 5,**
pp. 1028–1029, May 1961

The frequency dependence of the dielectric permittivity ε' and dielectric loss ε'' was measured over the frequency range 0.3 cps to 1 Mc and the temperature range -60 to $+170$°C for a phenolic resin (synthesized from phenol, *o*-cresol and formaldehyde under aqueous ammonia catalyst), and was cured at 200°C. The α-dispersion at low frequencies and high temperatures is attributed to the motions of macromolecules of phenolic resin. A β-dispersion at 0.3 to 10^3 cps (depending on temperature) is interpreted as due to the motions of unreacted methylol and amino groups. A γ-dispersion at high frequencies and low temperatures is also found. Comparison is made with results in the literature. (*PA*, 1961, #17,824)

1,549. PIEZOELECTRIC PROPERTIES OF TRIGLYCINE SULPHATE

Ikeda, T., Tanaka, Y., Toyoda, H.
***Physical Society of Japan, Journal of the*, v. 16, no. 12,**
pp. 2593–2594, December 1961

Triglycine sulphate has the crystal class C_{2h}–$2/m$ in the paraelectric state above its Curie point at 47.5°C; below this temperature it transforms to a ferroelectric state of class C_2–2. The constants d_{21}, d_{23}, and d_{25} were measured on *y*-cut bars having angles 90, 0 and ± 45 deg between their long axes and the *z*(*c*) axis; d_{22} was measured on a *y*-long bar. Specimens were prepoled under a field of 900 v/cm, and a dc bias of 90 v/cm was applied during measurement. The temperature dependences of d_{23}, $s_{33}E$, and $s_{33}D$ are shown. It is shown that the piezoelectricity is due to electrostriction. The effects on the constants of Cu X-radiation during poling were examined. (*PA*, 1962, #6531)

1,550. HYSTERESIS AND THERMAL STUDIES ON FERROELECTRIC TRANSITIONS IN THIOUREA

Futama, H.
***Physical Society of Japan, Journal of the*, v. 17, no. 3,**
pp. 434–441, March 1962

The hysteresis loop, the specific heat, and the thermal expansion of $CS(NH_2)_2$ were studied, with particular reference to its ferroelectric transitions. With a variation of temperature, the hysteresis loop in the intermediate phase III is transformed into a double loop. The field dependence of the transition temperature is given by $dTc/dE = +$ and $-$ 0.5°C: cm/kv for the upper and lower sides of phase III, respectively. Below phase III, a decrease of the critical field was observed by applying a stress on the [100] or [001] face. A new ferroelectric loop was also observed at -102°C with the spontaneous polarization of 2×10^{-4} μcoulomb/cm². The specific heat anomaly was found at -106°C with the latent heat of 6.6 ± 0.01 cal/mole. In [100] and [001] directions, expansion anomalies were found; a jump of 0.9×10^{-3} was observed especially in the [100] direction at -105°C. The results are examined according to the phenomenological theory. The dipole moment of the molecule in the crystal is discussed and a molecular model of the transition is also introduced. (*PA*, 1962, #12,566)

1,551. MEASUREMENT OF MICROWAVE DIELECTRIC CONSTANTS OF FERROELECTRICS.

II. DIELECTRIC CONSTANTS AND DIELECTRIC LOSSES OF $NaNO_2$ AND $(GLYCINE)_3 \cdot H_2SO_4$

Nakamura, E.
***Physical Society of Japan, Journal of the*, v. 17, no. 6,**
pp. 961–966, June 1962

Dielectric constants and loss tangents of $NaNO_2$ and $(glycine)_3 \cdot H_2SO_4$ (TGS) single crystals were measured at 3.3 kMc by the resonant cavity method from room temperature to 200°C for $NaNO_2$ and to 80°C for TGS. Dielectric constants measured along the *b*-axes of both crystals at 3.3 kMc are smaller than those at 1 Mc. No dielectric dispersion was observed along the *a*- and *c*-axes of $NaNO_2$. Dielectric constants along these axes increased monotonically with temperature. The mechanisms of the dielectric dispersion of both the crystals are discussed in connection with their spectroscopic properties and crystal structures. (*PA*, 1962, #16,768)

1,552. DOMAIN WALLS CAUGHT IN SUDARÉS IN ROCHELLE SALT CRYSTAL

Ohi, K., Nakamura, T.
***Physical Society of Japan, Journal of the*, v. 17, no. 7, p. 1195, July 1962**

Sudarés and ferroelectric domains were observed simultaneously, and evidence of strong interaction between the domain walls and the sudarés was found. (*PA*, 1963, #2959)

1,553. DIELECTRIC EVIDENCE OF MOLECULAR ROTATION IN SOLIDS

Smyth, C. P.
***Physics and Chemistry of Solids*, v. 18, no. 1, pp. 40–45. January 1961**
(Paper presented at the Plastic Crystals Symposium, Oxford University, England, April 5–6, 1960)

Measurements of dielectric constant as a function of temperature give clear evidence of molecular rotation in many crystalline phases, comparable to the rotation in liquids and in a few organic glasses which have been studied. The effect of molecular shape upon rotation is examined, showing that spheroidal and cylindrical molecules may rotate. The rotation may usually be presumed to consist of rotational jumps between potential energy minima. Rotational freedom depends upon the closeness of the approach to one of the ratios of the molecular radii in different directions, but is influenced by the closeness of the molecular packing. Many solids which show a rotational transition point are soft, waxy, and translucent in this rotator phase between the transition point and the melting point, and brittle below the transition point. A number of solids which show anomalous dielectric dispersion like that found in liquids and organic glasses, but no rotational transition, are brittle. It appears that plasticity may result from the increase in volume per molecule occurring when slightly unsymmetrical molecules begin to rotate at a transition point. Dielectric relaxation measurements show that the internal friction resisting molecular rotation in the crystal is, in some cases, about the same as in the liquid state, and, in other cases, much less. (*PA*, 1962, #8456)

1,554. DIELECTRIC PROPERTIES OF PHENOL-FORMALDEHYDE RESINS AT DIFFERENT STAGES OF HARDENING

Kanavets, I. F., Grigoreva, L. F.
***Plasticheskie Massy*, v. 1961, no. 3, pp. 15–20, March 1961**
(Translated from the Russian in *Soviet Plastics*, v. 1961, no. 3, pp. 14–19, March 1961)

Phenol-formaldehyde resins of the novolak and resol type are often used as binders in the manufacture of dielectric materials. However, the literature contains little information on the electrical insulating properties of A-, B-, and C-stage resins. Although resins are widely used in the manufacture of electrical insulating articles, their [illegible]al properties have been insufficiently studied. The degree to which these properties vary with the type of resin, the stage of hardening, the mix formula, and other factors which depend on manufacturing methods and service conditions is not clear.

P. A. Kremlevskii considers that the electrical properties of phenol and cresol resins are of particular interest and that factories should introduce an electrical method of controlling the hardening process. S. Ya. Yamanov has attempted to give a theoretical basis to the study of dielectric loss and to explain this phenomenon from a structural model of the resins. I. A. Maigeldinov and P. N. Shcherbak have studied the dependence of the electric strength of phenolic plastics on the thickness of the article and the time kept under voltage.

In order to establish laws enabling the electrical insulating properties of products to be improved both during manufacture and under working conditions, the electrical properties of the following three main types of phenol-formaldehyde resins at the A-, B-, and C-stages are studied: (1) novolak 18, (2) resol 21-s, and (3) aniline-phenol-formaldehyde resol 211.

Phenol-formaldehyde resins were chosen since they are the most widely used, their method of manufacture is well known, and laws applicable to them are also characteristic of other resins.

Bulk resistivity, the loss factor (tan δ) at 50 cps, the dielectric constant ε, and the breakdown potential were measured at 20–160°C and at various degrees of hardening.

1,555. DEPENDENCE OF THE DIELECTRIC PROPERTIES OF EPOXY INSULATION ON THE TYPE OF FILLER

Dobrer, E. K.
***Plasticheskie Massy*, v. 1962, no. 3, pp. 32–37, March 1962**
(Translated from the Russian in *Soviet Plastics*, v. 1962, no. 3, pp. 28–32. March 1962)

Dielectric properties of epoxy resin ED-6 were determined for different fillers. The temperature dependence of the loss tangent and of volume resistivity was measured and the dielectric permittivity was calculated. Results are presented in graph form.

The following conclusions were drawn:

1. The dielectric properties (ε', tan δ, ρ_v) of epoxy insulation depend to a considerable degree on the type of filler and its chemical composition. Epoxy insulation containing calcined powdered quartz has the best dielectric properties (tan δ and ρ_v as functions of temperature). Compounds containing calcined marshalite and alumina have similar properties, while those containing uncalcined powdered quartz and marshalite and ground ceramic waste have considerably poorer dielectric properties.

2. The addition of certain fillers (barium titanate, titanium dioxide, etc.) enables epoxy resin dielectrics to be produced with high dielectric permittivity and controllable temperature coefficient of permittivity.

3. The water-absorption of epoxy insulation depends on the type of filler. Insulation based on a compound made with kaolin has the greatest water absorption.

4. The structure of the insulation depends largely on the type of filler and the shape of its particles.

5. Technical Specifications or State Standards must be developed for fillers for epoxy insulation, stipulating the permissible amount of impurities (particularly bivalent iron) and the shape of the filler particles.

1,556. THE DIELECTRIC AND DYNAMIC MECHANICAL PROPERTIES OF POLYOXYMETHYLENE (DELRIN)

Read, B. E., Williams, G.
***Polymer*, v. 2, no. 3, pp. 239–255, September 1961**

The dielectric and dynamic mechanical properties of polyoxymethylene (Delrin) have been measured in order to investigate molecular motions in this polymer. The dynamic shear modulus and loss factor have been determined in the frequency range from 0.05 to 1 cps, from −190°C up to the melting point (180°C). Two loss maxima have been observed at about −77 and +87°C, respectively. The dielectric properties have been investigated over the frequency range 120 cps to 9 kMc and the temperature range −80 to +150°C. A single broad relaxation absorption was observed which correlates with the low temperature mechanical relaxation. The effect on these relaxations of swelling the polymer with dioxan is consistent with motions occurring in the amorphous regions of the polymer only.

1,557. LOW FREQUENCY DIELECTRIC RELAXATION OF POLYOXYMETHYLENE (DELRIN) USING A DIRECT CURRENT TECHNIQUE

Williams, G.
***Polymer*, v. 4, no. 1, pp. 27–34, March 1963**

The dielectric measurements on polyoxymethylene previously reported have been extended to the low frequency range 10^{-2} to 10^{-4} cps, using a direct current method. Measurements have been made over the temperature range 20 to −110°C. Two regions of absorption are observed and discussed in relation to the dielectric and dynamic mechanical results obtained at higher frequencies.

1,558. THE DIELECTRIC BEHAVIOUR OF OXIDIZED HIGH-PRESSURE POLYETHYLENE. I.

Tuijnman, C. A. F.
***Polymer*, v. 4, no. 2, pp. 259–268, June 1963**

Dielectric measurements on oxidized high-pressure polyethylene and mixtures of model substances in high-pressure polyethylene can be explained by assuming that the low-frequency (α) dispersion is due to chain movement in the crystallites and that the high-frequency (γ) dispersion is related to movements in the amorphous phase.

1,559. TEMPERATURE DEPENDENCE OF DIELECTRIC RELAXATION BEHAVIOR FOR VARIOUS POLYMER SYSTEMS

Saito, S.
***Reports on Progress in Polymer Physics in Japan*, v. 6, pp. 227–228, 1963 (in English)**
(Available through Kobayasi Institute of Physical Research, Kokubunji, Tokyo, Japan)

The dielectric relaxation times (τ) for various polymers have been measured over a wide range of temperature. It has been proved that the dependency of τ on temperature does not take the Arrhenius form but is ruled by the WLF equation in a variety of polymer systems. The WLF equation has been applied on the experimental data in the following form:

$$\log_{10}\frac{\tau(T)}{\tau(T_g)} = -\frac{C_1(T - T_g)}{C_2 + T - T_g}$$

where T_g is glass transition temperature and C_1 and C_2 are constants. From the volume (V)–temperature (T) curve, T_g has been determined for the same sample as that used in dielectric measurements. Values of C_1, C_2, and $\tau(T_g)$ have been obtained for various polymer systems.

When the relation of τ to the degree of polymerization ($\overline{P}$) is examined, the value of τ increases with the increase of $\overline{P}$ at any constant temperature. This variation of τ with $\overline{P}$ is observed for polyvinyl chloride, polyvinyl acetate, and polymethyl methacrylate. The effects of plasticizers, crystallinity, and side-chain length on the temperature dependence of τ are also examined.

Dielectric relaxation data for polyvinyl chloride have been compared with mechanical relaxation data by Sommer. There is a little difference in relaxation times, but a good similarity exists between the temperature dependences of both processes.

1,560. DIELECTRIC PROPERTIES OF CYANOETHYLATED CELLULOSE

Saito, S.
***Reports on Progress in Polymer Physics in Japan*, v. 6, pp. 229–232, 1963 (in English)**
(Available through Kobayasi Institute of Physical Research, Kokubunji, Tokyo, Japan)

The relationship between dielectric dispersion and degree of cyanoethyl substitution is reported.

Four samples of different degrees of substitution were used for the dielectric measurements. The values of the degree of substitution (of the three available hydroxyl groups per a glucosidic unit) are 2.06, 2.40, 2.56, and 2.70. The dielectric measurements were carried out over the frequency range of 1 to 10^6 cps at various temperatures below room temperature.

1,561. DIELECTRIC PROPERTIES OF OXIDIZED POLYPROPYLENE

Kishi, N., Uchida, M.
***Reports on Progress in Polymer Physics in Japan*, v. 6, pp. 233–234, 1963 (in English)**

(Available through Kobayasi Institute of Physical Research, Kokubunji, Toyko, Japan)

The temperature dependence of dielectric properties of polypropylene modified by oxidation was measured by an inductive-ratio arm bridge. The oxidized samples were prepared by exposure to ultraviolet radiation for 100 hr at 40°C. Data are given on temperature dependence of the dielectric loss factor at various frequencies. A graph shows that for oxidized polypropylene two loss peaks can be clearly observed in high temperature and room temperature range. These two peaks correspond to the α_c and α_a peak in the dynamic mechanical properties of polypropylene. As the exposure time increases, the maximum heights of these peaks increase. The peak positions and heights depend upon crystallinity, tacticity, etc.

The temperature dependence of the dielectric loss factor at 1 kc for slow cooled and quenched samples is shown, and some characteristics for these samples are tabulated.

The positions of α_a and α_c peak temperature at 1 kc and the apparent activation energy are plotted as a function of *n*-heptane extracted residue content.

1,562. DIELECTRIC MEASUREMENTS OF STEREOSPECIFIC POLYMETHYL METHACRYLATES

Nagata, N., Hikichi, K., Kaneko, M., Furuichi, J.
***Reports on Progress in Polymer Physics in Japan*, v. 6, pp. 235–236, 1963 (in English)**
(Available through Kobayasi Institute of Physical Research, Kokubunji, Tokyo, Japan)

Dielectric properties of stereospecific polymethyl methacrylates (PMMA), atactic and isotactic, were measured in the frequency range from 1 to 3 × 10^5 cps and temperature range from −30 to +120°C. Primarily, this work investigates the relations between stereospecificity and molecular relaxation below glass transition temperature. Dielectric constants ε' and loss factors ε'' are plotted for the atactic and isotactic PMMA, respectively.

The apparent activation energies for the β-dispersion of the atactic and isotactic PMMA are 19 and 8 kcal/mole, respectively, the latter less certain because of the very weak β-absorption peak. Further experiments are needed for the precise interpretation of the β-dispersion in polymethyl methacrylates. Syndiotactic PMMA is being investigated.

1,563. EFFECTS OF CROSS-LINKING AND BLENDING ON THE RELAXATION TIME SPECTRUM OF THE DIELECTRIC α_a-ABSORPTION IN THE LINEAR HIGH POLYMER

Ishida, Y., Shimada, K., Takayanagi, M., Yamafuji, K.
***Reports on Progress in Polymer Physics in Japan*, v. 6, pp. 237–240, 1963 (in English)**
(Available through Kobayasi Institute of Physical Research, Kokubunji, Tokyo, Japan)

With the increase of degree of crystallinity of the linear high polymer, the relaxation time spectrum of the dielectric α_a-absorption becomes remarkably broader than that of the usual amorphous high polymer. In the visco-elastic measurements, the same phenomenon is also observed. The main cause of this phenomenon has been sought by experiment, and the search is reported in the present paper.

The characteristic features of the molecular chains in the amorphous part of the semicrystalline polymer may be the cause. Two possibilities are considered: the first is the network-like structure of the molecular chains in the amorphous part of the semicrystalline polymer due to the existence of small crystallites, the second is the alteration of the values of the frictional coefficients and the force constants of the molecular chains in the amorphous part owing to the effects of the crystalline part. In order to test the first possibility, the molecular chains of polychloroprene were cross-linked by γ-ray irradiation to produce a network-like structure. As a method for testing the second possibility, the effect of blending was investigated. Polychloroprene and polyvinyl chloride were adopted as the testing sample and the blending polymer, respectively.

It was concluded that the first possibility seems to be less effective for broadening the shape of the dielectric α_a-absorption curve. The second possibility remains as a proper model for explaining this phenomenon. However, further investigations are necessary in order to obtain a more detailed and well-defined model for an explanation.

1,564. GROWTH AND ELECTRICAL PROPERTIES OF FERROELECTRIC GLYCINE SULFATE SINGLE CRYSTALS

Toyoda, H., Tanaka, Y., Shiokawa, W.
***Review of the Electrical Communication Laboratory*, Nippon Telegraph and Telephone Public Corporation, Tokyo, v. 9, no. 7-8, pp. 485–496, July–August 1961**

The crystal growth, distribution of dislocation lines, electrical conductivity, and dielectric constant were investigated. The effects of crystal imperfection on these properties are particularly interesting. Addition of Cr^{3+}, Sn^{2+}, and OH^- to the mother solution brings about some appreciable changes in the crystal habit. Most of the dislocation lines rise from the pores near the seed crystal, and the distribution of lines seems to be related to the domain structure. The dc conduction of the crystal obeys Ohm's law; the resistivity along the *b*-axis is 2 × 10^{14} ohm/cm at room temperature. The resistivity shows a temperature dependence of $\exp(\Delta E/kt)$ where ΔE is 1.5 ev in the ferroelectric phase and 0.7 ev in the paraelectric phase. Irradiation with X-rays decreases the resistivity by one order of magnitude and causes a slight increase of ΔE in the paraelectric phase. The dielectric constant of a normal crystal below the Curie point increases with signal amplitude and shows a low-frequency dispersion. Impurity addition and irradiation diminish or remove these dependencies and cause some anomalies between 52 and 56°C. Heavy irradiation lowers the peak value at the Curie point. Crystal imperfections affect the ferroelectric properties through the increase of short-range order. (*PA*, 1962, #6520)

1,565. PERSISTENT INTERNAL POLARIZATION

Freeman, J. R., Kallmann, H. P., Silver, M.
***Reviews of Modern Physics*, v. 33, no. 4, pp. 553–573, October 1961**

Trapping of carriers in photoconductors gives rise to a persistent internal polarization. Studies are made on ZnS–CdS phosphors and on anthracene in particular, but the effect is found in various organic and inorganic materials. Experiments distinguish two effects: barrier polarization due to high resistance layers at photoconductor–electrode boundaries, and bulk polarization due to retention of the less mobile carriers in the volume of the specimen. A charge layer model of polarization is developed. Experimental techniques are described, together with experiments on buildup and release of the charge (thermally and by optical irradiation) in both types of polarization. Finally, experiments on the effects in single crystals of sulphides and anthracene are reported. (*PA*, 1962, #4089)

1,566. DIELECTRIC PROPERTIES OF MIXTURES OF NATURAL RUBBER AND REINFORCING FILLERS

Chasset, R., Thirion, P., Nguyen-Phuc, V.-B.
***Revue Generale du Caoutchouc*, v. 36, pp. 857–862, 1959**

Pure natural rubber gum stock and mixtures of natural rubber with C black and with colloidal silica were studied and the dielectric constant and absorption were measured. The effects of temperature, imposed frequency, and quantity of filler are discussed.

1,567. A STATISTICAL INTERPRETATION OF THE ELECTRICAL BREAKDOWN OF LIQUID DIELECTRICS

Lewis, T. J., Ward, B. W.
***Royal Society of London, Proceedings of the, Series A—Mathematical and Physical Sciences*, v. 269, no. 1337, pp. 233–248, September 11, 1962**

Previous investigators, when measuring the electric strength of hydrocarbon liquids with short-duration rectangular pulses, have assumed that the statistical component of the breakdown time was insignificant compared with the formative time. In the present investigation, however, the time to breakdown was measured directly by the use of step-function pulses, and clear evidence for a statistical time lag was found. The formative time was $\sim$ 0.1 μsec, which was less than that given by previous estimates. A statistical interpretation of short-pulse measurements is presented which provides a consistent explanation of the results of other workers. Furthermore, by using an experimentally derived equation for the variation of the mean rate of breakdown $f(E)$ with applied stress E, it has been shown that the form of the relationship between strength and pulse duration obtained by other workers agrees with that obtained by a statistical analysis. Experiments on air-saturated *n*-hexane with both short-duration and step-function pulses support the statistical ideas presented and indicate that electrode conditions are extremely important. It was found that strength and time to breakdown were affected by the number of breakdown measurements on a sample. Experiments with gas-free *n*-hexane and nonuniform fields have demonstrated the importance of air content when long duration pulses are used. It was found that, although the statistical time lag was insignificant, formative time lags as long as 10 μsec occurred with a point-cathode, sphere-anode configuration.

1,568. DIELECTRIC DISPERSION OF ROCHELLE SALT CRYSTALS AT LOW FREQUENCIES

Ida, M., Kawada, S.
***Science Reports of the Kanazawa University*, v. 7, no. 2, pp. 55–59, 1961**

The Cole–Cole plot is semicircular above the Curie point for frequencies above 3 cps; the plot deviates below 10 cps at high humidity or below the Curie point. Low-frequency dispersion is reduced permanently by X-ray irradiation.

1,569. DIELECTRIC DISPERSION OF TRIGLYCINE SULFATE AT LOW FREQUENCIES

Ida, M., Kawada, S.
***Science Reports of the Kanazawa University*, v. 8, no. 1, pp. 39–44, 1962**

By using [010] and [001] plates about 2 cm thick at temperatures both below and above the Curie point, dielectric measurements were made on triglycine sulfate crystals at frequencies between 1 kc and 1 cps. The effects of polarization and of X-ray damage were also studied.

1,570. DIELECTRIC PROPERTIES OF SOLID POLYMERS

Curtis, A. J.
***SPE (Society of Plastics Engineers) Transactions*, v. 2, no. 1, pp. 82–85, January 1962**

Basically, the study of dielectric relaxation, by the measurement of dielectric constant and loss index over a temperature and frequency range, can give information about motions in polymers involving orientation of polar segments. Insofar as motion of polymers studied by other methods involves motion of polar segments, the results and interpretations should agree with those from dielectric relaxation data. Non-crystalline polar polymers have previously been shown, in a large number of cases, to exhibit dielectric relaxation associated with molecular motions above the glass transformation temperature. Dielectric relaxation has also been observed in many amorphous polymers well below the glass transformation temperature, indicative of molecular motions. These low temperature relaxation phenomena have generally been attributed to the orientation of rotatable side groups on the backbone of the polymer molecules. There exist, however, some examples of dielectric and mechanical relaxation processes below the glass temperatures in polymers where no rotatable side groups are known to exist.

An examination of the available data on polystyrene suggested the presence of such low temperature relaxation in this material. In this structure there is no rotatable dipole in any side group, but study of the problem is complicated by the extremely low dipole moment of the repeat unit, about 0.3 Debyes. The problem could be made more accessible, experimentally, by increasing the dipole moment. This was accomplished by studying poly(*p*-chlorostyrene). Thus the dipole moment per repeat unit was raised to ~ 1.5 Debyes while retaining a structure in which the dipole was rigidly attached to the main polymer chain. In order to provide a further variation on the same basic structure, poly(*m*-chlorostyrene) was also prepared. In this case the rotation of the phenyl group would be expected to produce dielectric relaxation below the glass temperature. Disk-shaped samples were prepared and dielectric measurements were carried out from −178 to +145°C over a frequency range from 0.01 cps to 10 Mc. Representative data for poly(*p*-chlorostyrene) are tabulated; these measurements were carried out by D. J. Scheiber with the low frequency dielectric apparatus described by him previously. Data on poly(*m*-chlorostyrene) are also tabulated, and a plot of the dielectric loss index as a function of frequency at various temperatures is given. The results are interpreted and their pertinence to crystalline polymer behavior is discussed.

1,571. DIELECTRIC PROPERTIES OF DIMETHYL SULFOXIDE-BENZENE MIXTURES

Lindberg, J. J., Kenttamaa, J., Nissema, A.
***Suomen Kemistilehti*, v. 34, pp. 156–160, 1961**

Dimethyl sulfoxide forms chain polymers in benzene solution and there is a π-electron interaction. Data are presented for various concentrations.

1,572. VISCOSITY AND ELECTRICAL PROPERTIES OF PLASTICIZERS OF POLY(VINYL CHLORIDE)

Van-Gaut, Yu. N.
***Trudy Kharkovskogo Politekhnicheskogo Instituta imeni V. I. Lenina*, v. 27, pp. 111–122, 1959**
(See also *Referativnyi Zhurnal. Khimiya*, 1960, #94,623)

Variation with temperature of viscosity (η) and dielectric properties was studied for dioctyl phthalate, tritolyl phosphate, dioctyl sebacate, and dibutyl sebacate from 0 to 100°C. The frequency variation of tan δ and ϵ was also investigated in the range 5×10^4 to 2×10^7 cps. For the latter two compounds, log η and log of specific volumetric resistance (e_v) in the temperature range 0–100°C showed a linear character. For the former two compounds, the relation of log e_v had a broken form, consisting of two straight lines. The empirical relation of η and e_v to temperature was found, and from it the basis for computing the energy of activation. The relation of tan δ to temperature was a characteristic curve for polar solvents, with a strongly expressed maximum, which shifted with frequency variation. In general, ϵ decreased linearly with increase in temperature; e_v decreased with added moisture; and tan δ increased with moisture.

1,573. ELECTRICAL STABILITY OF POLY(VINYL CHLORIDE) INSULATION

Van-Gaut, Yu. N.
***Trudy Kharkovskogo Politekhnicheskogo Instituta imeni V. I. Lenina*, v. 27, pp. 123–128, 1959**
(See also *Referativnyi Zhurnal, Khimiya*, 1960, 94,624)

The electrical stability of poly(vinyl chloride) was studied by using alternating, pulsating, and direct current. In a heterogeneous electric field, the electric stability sharply decreases with increasing dielectric thickness. The disruptive voltage increases extremely slowly for large dielectric thicknesses. In a homogeneous electric field, the electrical stability is 1.5–1.6 times as high as that in ac and 2.7–3.0 times as high as that in pulsating current. Comparisons are drawn between the stability of the polymer used for insulation and that for other use.

1,574. RELATION BETWEEN THE ELECTRICAL PROPERTIES OF THE ORGANO-SILICON COMPOUNDS AND THEIR COMPOSITION AND STRUCTURE

Golubkov, G. E.
In "Khimiia i Prakticheskoe Primenenie Kremneorganicheskikh Soedinenii, Trudy Konferentsii, Leningrad, September 25–27, 1958," no. 6, pp. 286–288
Tsentralnoe Biuro Tekhnicheskoi Informatsii, Leningrad, USSR, 1961

Electrical conductivity, ϵ, and loss factor, tan δ, as well as associated properties, were investigated for different polysiloxanes with Me, Et, Ph, ClC_6H_4, or $PhNHCH_2$ side groups at frequencies of 200 to 1.5×10^4 cps and at temperature >180°C. Effects of temperature variation and cross-linking were studied.

1,575. DETERMINATION OF THE DIPOLE MOMENTS AND RELAXATION TIME OF OLEIC ACID FROM SOLUTIONS IN DIOXANE AND CARBON TETRACHLORIDE IN CONNECTION WITH G. V. POTAPENKO'S THEORY

Pugacheva, A. I.
***Uchenye Zapiski Moskovskogo Oblastnogo Pedagogicheskogo Instituta*, v. 92, pp. 43–48, 1960**
(See also *Referativnyi Zhurnal, Fizika*, 1961, #6V70)

Measurements were made at 20°C on the dielectric constant and absorption coefficient of solutions of oleic acid in dioxane and CCl_4. Dipole moments and relaxation times were then calculated, and from known data on the relaxation time, the volume of oleic acid molecules was calculated to be 4×10^{-22} m^3.

1.576. DIELECTRIC AND ABSORPTION COEFFICIENTS OF OLEIC ACID, DETERMINED IN A FIELD OF 3-CENTIMETER ELECTROMAGNETIC WAVES

Klygo, K. I., Bogdanov, L. I.
***Uchenye Zapiski Moskovskogo Oblastnogo Pedagogicheskogo Instituta*, v. 92, pp. 171–178, 1960**
(See also *Referativnyi Zhurnal, Khimiya*, 1961, #21B122)

The variation of the intrinsic component of dielectric permittivity and the absorption coefficient of oleic acid with temperature is determined from −20 to +100°C in the centimeter range, and results are given. Total, atomic, and orientational polarization is calculated from the obtained data. The relaxation times for various wavelengths are presented.

1,577. THE HYDROGEN BOND AND THE STATIC DIELECTRIC CONSTANT OF ORGANIC LIQUIDS

Lutskii, A. E., Mikhailenko, S. A.
***Ukrainskii Fizichnii Zhurnal*, v. 7, pp. 812–816, 1962**

Measurements were made for more than 40 organic compounds, comprising various alcohols, phenols, ethers, amides, and acids, from 16 to 190°C, for the purpose of calculating the correlation factor, *g*. Graphs of *g* vs. *T* are presented for ten of the compounds. It is shown that in the Kirkwood–Froelich theory four general types of curves may arise.

1,578. DIELECTRIC CONSTANTS OF BIOLOGICAL OBJECTS

Sedunov, B. I., Frank-Kamenetskii, D. A.
***Uspekhi Fizicheskikh Nauk*, v. 79, no. 4, pp. 617—639, April 1963**
(Translated from the Russian in *Soviet Physics—Uspekhi*, v. 6, no. 2, pp. 279–293, September–October 1963)

1,579. A STUDY OF MOLECULAR RELAXATION IN POLYMERS BY THE DIELECTRIC METHOD

Mikhailov, G. P., Borisova, T. I.
***Uspekhi Khimii*, v. 30, pp. 895–913, 1961**
(Translated from the Russian in *Russian Chemical Reviews*, v. 30, no. 7, pp. 386–396, July 1961)

A review of the dielectric method for determining molecular relaxation is presented. Styrene–methylacrylate copolymer, styrene–methylmethacrylate copolymer, polyesters, and other polymers are used for examples. 32 references.

1,580. EFFECTIVE DIPOLE MOMENTS OF α AND β - CHLOROSUBSTITUTED POLYALKYL-METHACRYLATES

Mikhailov, G. P., Borisova, T. I.
***Vysokomolekulyarnye Soedineniya*, v. 2, no. 12, pp. 1779–1785, 1960**

Based on the temperature and frequency relations of the generalized dielectric constant $\epsilon = \epsilon' - i\epsilon''$, an analysis has been made of the spectrum of relaxation times, and the effective dipole moments have been calculated for α and β chlorine derivatives of polyalkylmethacrylates. The results have been compared with analogous data for the homologous series of polyesters of methacrylic acid. The effect of the second polar group on the relaxation properties of the polymer, depending upon the position of the incorporated dipole, has been elucidated.

1,581. TEMPERATURE DEPENDENCE OF THE DIELECTRICAL LOSSES IN HOMOLOGUES OF METHYL ACRYLATE AND VINYL ACETATE POLYMERS

Mikhailov, G. P., Krasner, L. V.
***Vysokomolekulyarnye Soedineniya*, v. 4, no. 7, pp. 1071–1075, 1962**

The temperature dependence of tan δ and ε′ of some members of the homologous series of polymethylacrylates and polyvinylacetates as well as of their β-chlorosubstituted derivatives has been investigated at frequencies within the limits 0.2–100 kc. Measurements were made within the temperature range −170 to +80°C. It has been found that addition of a polar radical to the chain via the ester oxygen augments the relaxation time and activation energy of dipole-radical and dipole-elastic processes. A rise in relaxation time and activation energy has also been observed for the β-chlorosubstituted polymers of both series.

1,582. EFFECTIVE DIPOLE MOMENTS OF HOMOLOGUES OF METHYL ACRYLATE AND VINYL ACETATE POLYMERS

Mikhailov, G. P., Krasner, L. V.
***Vysokomolekulyarnye Soedineniya*, v. 4, no. 7, pp. 1076–1083, 1962**

Temperature-frequency expressions for tan δ and ε′ have been obtained for three members of the homologous series of polymethylacrylate and polyvinylacetate as well as of their β-chloro-substituted derivatives. Measurements were made at frequencies ranging from 0.2 to 100 kc and temperatures from −170 to +80°C. Calculations were made of the effective dipole moments for the glass and elastic states of the polymers, and the effect of isomerism of the side chain on the nature of molecular interaction in the polymers has been elucidated.

1,583. THERMO-MECHANICAL AND ELECTRICAL PROPERTIES OF COMPOSITE POLYMERS

Andrianov, K. A., Golubkov, G. Ye.
***Vysokomolekularnye Soedineniya*, v. 4, no. 9, pp. 1375–1379, 1962**

The results of investigations of epoxy-polysiloxane polymers of various composition have been presented. The existence of relaxational change in polarization in an electric field has been shown, and the effect of polysiloxanes and epoxy resins on the mechanical and thermo-mechanical properties has been described.

**1,584. SYNTHESIS AND STRUCTURAL STUDY OF
CATALYTIC POLY-*n*-BUTYLMETHACRYLATE.
III. ON THE POSSIBILITY OF EVALUATING THE
STEREOREGULARITY OF THE POLYMER FROM
DETERMINATIONS OF THE DIELECTRICAL
LOSSES AND POLARIZATION**
Borisova, T. I., Burshtein, L. L., Mikhailov, G. P.
***Vysokomolekularnye Soedineniya*, v. 4, no. 10,
pp. 1479–1485, 1962**

The temperature-frequency relation of $\tan\delta$ and ε' and the dipole moments of poly-*n*-butylmethacrylate of syndiotactic, isotactic, and atactic structure has been studied both in bulk and in solution. Measurements were made in the range of 20 cps–150 kc at temperatures varying from −60 to +100°C. The curves depicting this relation for the isotactic polymer differ from the corresponding curves for the atactic and syndiotactic products The dipole moments calculated per monomer unit for the polymer in solution and in the high elastic state are higher for the isotactic specimen. The effect of the stereoregularity of the structure on the dielectric properties of poly-*n*-butylmethacrylate is explained by changes in the intramolecular interactions in the polymer.

**1,585. TEMPERATURE AND FREQUENCY DEPENDENCIES
OF THE DIELECTRIC LOSSES OF STYRENE-
METHACRYLATE AND STYRENE-METHYL VINYL
KETONE COPOLYMERS**
Mikhailov, G. P., Krasner, L. V.
***Vysokomolekulyarnye Soedineniya*, v. 5, no. 7,
pp. 1085–1090, 1963**

**1,586. PRÄZISIONSMESSUNGEN DER DIELEKTRIZITÄTS-
KONSTANTEN VON FÜNF EICHSUBSTANZEN ZUR
DK- UND DIPOLMOMENTBESTIMMUNG.
III. MITTEILUNG: DIE MESSUNGEN BEI 100 kHz
(STATISCHE DK) (PRECISION MEASUREMENTS
OF THE DIELECTRIC CONSTANTS OF FIVE PURE
SUBSTANCES FOR DIELECTRIC COEFFICIENT
AND DIPOLE MOMENT DETERMINATION.
III. MEASUREMENTS AT 100 kc/s (STATISTICAL
DIELECTRIC CONSTANT))**
Mecke, R., Joeckle, R.
***Zeitschrift für Elektrochemie*, v. 66, no. 3,
pp. 255–260, March 1962**

(Part I of this series was concerned with purity tests; Part II was devoted to a description of equipment.) The dielectric constants of the five reference substances—cyclohexane, benzene, carbon tetrachloride, di-*n*-butylether and fluorobenzene —were redetermined with high precision at 100 kc, and the sources of errors (e.g., errors depending on the material, the equipment and the actual measurement) were examined and analyzed very closely. It was possible to demonstrate that the errors associated with the material, which in previous work had been examined by inadequate methods, have a much greater effect on the determination of the dielectric constant than the errors associated with the equipment or the actual measurement. The uncertainty interval of the dielectric constant caused by errors associated with the material was calculated or estimated, respectively. It was noted that, especially in the case of di-*n*-butylether, the precision measurement of the dielectric constant is limited at the fourth decimal by the chemical instability of the reference compounds. (*PA*, 1962, #17,771)

**1,587. PRÄZISIONSMESSUNGEN DER DIELEKTRIZITÄTS-
KONSTANTEN VON FÜNF EICHSUBSTANZEN ZUR
DK- UND DIPOLMOMENTBESTIMMUNG.
IV. MITTEILUNG: MESSUNG DER DK VON CYCLO-
HEXAN, BENZOL, TETRACHLORKOHLENSTOFF,
FLUORBENZOL UND DI-*n*-BUTYLÄTHER IM
MIKROWELLENBEREICH BEI 9000 MHz
(PRECISION MEASUREMENTS OF THE
DIELECTRIC CONSTANTS OF FIVE PURE
SUBSTANCES. IV. MEASUREMENTS OF THE
DIELECTRIC CONSTANTS OF CYCLOHEXANE,
BENZENE, CARBON TETRACHLORIDE, FLUORO-
BENZENE AND DI-*n*-BUTYLETHER IN THE
MICROWAVE REGION NEAR 9000 Mc/s)**
Mecke, R., Klingenberg, G., Mecke, W.
***Zeitschrift für Elektrochemie*, v. 66, no. 6,
pp. 514–519, June 1962**

The dielectric constants of cyclohexane, benzene, and carbon tetrachloride were measured with the aid of 3-cm resonance equipment, and the errors of the measurements were examined. The total error amounts to 0.12%. A further reduction of this error limit involves considerable effort. The dielectric constant of the polar compounds fluorobenzene and di-*n*-butylether was determined with 3-cm reflection equipment. At 9300 Mc both compounds possess high dielectric loss factors. The error of these measurements is comparatively large and amounts to about 5 and 10% for the real and imaginary parts of the dielectric constant respectively. (*PA*, 1962, #21,916)

**1,588. DIE HAUPTDIELEKTRIZITÄTSKONSTANTEN DER
HOMOGEN GEORDNETEN KRISTALLINFLÜSSIGEN
PHASE DES *p*-AZOXYANISOLS (THE PRINCIPAL
DIELECTRIC CONSTANTS OF HOMOGENEOUSLY
ORIENTED LIQUID-CRYSTAL PHASE OF
p,p'-AZOXYANISOLE)**
Maier, W., Meier, G.
***Zeitschrift für Naturforschung*, v. 16a, no. 5,
pp. 470–477, May 1961**

For highly purified 4,4'-di-methoxyazoxylbenzene (*p,p'*-azoxyanisole) in the nematic fluid-crystal phase, the principal dielectric constants ε_1 and ε_2 and the dielectric anistropy $\Delta\varepsilon$ were found at 0.10, 0.26, 0.65, and 1.60 Mc. The results were compared with the theory of former publications. Values of the principal molecular polarizabilities were calculated from the refractive index measurements of Chatelain, and by these data the dipole moment and orientation present in the molecule were determined.

1,589. ANISOTROPE DK-DISPERSION IM RADIOFREQUENZGEBIET BEI HOMOGEN GEORDNETEN KRISTALLINEN FLÜSSIGKEITEN (ANISOTROPIC DIELECTRIC DISPERSION OF HOMOGENEOUS LIQUID CRYSTALS AT RADIO FREQUENCIES)

Maier, W., Meier, G.
***Zeitschrift für Naturforschung*, v. 16a, no. 11, pp. 1200–1205, November 1961**

The dielectric constant of the normal liquid phase and those associated with the liquid crystalline phase were measured between 100 kc and 4 Mc for the following liquid crystals: 4,4-di-*n*-propyloxy-azoxybenzol, 4,4-di-*n*-butyloxy-azoxybenzol, 4,4-di-*n*-hexyloxy-azoxybenzol and 4,4-di-*n*-heptyloxy-azoxybenzol. In a homogeneous magnetic field of 2000 gauss, ε' shows a characteristic dispersion as does the appropriate dielectric loss. (*PA*, 1962, #7226)

1,590. ABSORPTIONSMESSUNGEN AN DIPHENYLVERBINDUNGEN IM MIKROWELLENBEREICH (ABSORPTION MEASUREMENTS IN THE MICROWAVE REGION ON DIPHENYL COMPOUNDS)

Hufnagel, F., Klages, G., Knobloch, P.
***Zeitschrift für Naturforschung*, v. 17a, no. 1, pp. 96–98, January 1962**

Results are given of new experimental observations of dielectric absorption ε'' at 0.7, 1.5, 10.1, and 60 cm wavelength on diphenyl compounds in dilute benzene solution at 20°C. Dipole moments, relaxation times (corresponding to the center of gravity of the distribution curve), and the flattening as compared to a Debye curve for a single relaxation time are given for 13 diphenyl compounds. Mechanisms to account for the observations are proposed. (*PA*, 1962, #11,382)

1,591. DIE PIEZOELEKTRIZITÄT UND ELEKTROSTRIKTION DES SEIGNETTESALZES (THE PIEZOELECTRICITY AND ELECTROSTRICTION OF ROCHELLE SALT)

Schmidt, G.
***Zeitschrift für Physik*, v. 161, no. 5, pp. 579–603, 1961**

The piezoelectric constants g and the electrostrictive constants Q were determined by polarization and displacement measurements. The temperature range covered the ferroelectric region and temperatures a little beyond this. A dc field was applied in the ferroelectric range to align the domains. The curve of g_{14} vs. temperature was found to be continuous through the ferroelectric region without any anomalies at the two Curie points. With certain reservations the same applied to Q_{11}. However, g_{12} and g_{13} were not proportional to polarization, and Q_{12} and Q_{13} in the ferroelectric regions showed anomalies on approaching the Curie points. It is concluded that the existence of the ferroelectric state in rochelle salt cannot be regarded simply as a consequence of the particular temperature variation of the electrical parameters of the crystal, but must be ascribed to a change in the structure of the crystal. (*PA*, 1961, #10,078)

1,592. UNTERSCHIEDLICHE FERROELEKTRISCHE EIGENSCHAFTEN IN VERSCHIEDENEN GEBIETEN VON SEIGNETTEKRISTALLEN (THE DIFFERENT FERROELECTRIC PROPERTIES IN DIFFERENT REGIONS OF ROCHELLE SALT CRYSTALS)

Müser, H. E., Unruh, H. G.
***Zeitschrift für Physik*, v. 162, no. 3, pp. 313–328, 1961**

Very accurate measurements of the Curie points have shown small systematic differences between different regions of the same crystal, the regions being related to the orientation of the original seed crystal. A small dependence on temperature of crystal growth was also found. While the nature of the impurities in the crystals was not known, experiments with purposely added ammonium tartrate pointed to a possible explanation in the preferential deposition of impurities in certain regions during growth. (*PA*, 1961, #10,079)

1,593. EINFLUSS MECHANISCHER SPANNUNGEN AUF DIE DIELEKTRISCHEN EIGENSCHAFTEN DES PARAELEKTRISCHEN SIEGNETTESALZES (THE INFLUENCE OF MECHANICAL STRESSES ON THE DIELECTRIC PROPERTIES OF PARAELECTRIC ROCHELLE SALT)

Schmidt, G., Neumann, K. H.
***Zeitschrift für Physik*, v. 166, no. 2, pp. 207–215, 1962**

The dependence of the reciprocal electrical susceptibility β as a function of mechanical tension T was determined for paraelectric rochelle salt crystals. Measurements were made at 9 Mc with the aid of an HF bridge. The slope of the β–T curves is proportional to the electrostriction constants Q_{112} (or Q_{113}) and generally depends on T. This implies a dependence of the true elastic constants S^P_{22} and S^P_{33} on the polarization. The piezoelectric constant g_{14} must be independent of T_2 and T_3 since S'^P_{22}, and hence the monoclinic constants S^P_{24} and S^P_{44}, do not change sign with the reversal of spontaneous polarization. Q_{112} and Q_{113} may however be influenced by shear stresses. (*PA*, 1962, #6532)

1,594. DIE ELEKTROSTRIKTION IN DIPOLFLÜSSIGKEITEN (ELECTROSTRICTION IN POLAR LIQUIDS)

Zahn, W.
***Zeitschrift für Physik*, v. 166, no. 3, pp. 275–288, 1962**

The coefficient of electrostriction (i.e., increment in pressure per unit of electric field strength) was measured for 12 organic liquids of widely varying dielectric constants and permanent electric moments. The experimental technique consisted of generating standing density waves by an alternating field; the pressure was transmitted to a quartz plate, giving rise to a piezoelectric voltage which was measured. Variation of density in the apparatus was adiabatic; the results were converted to correspond to isothermal electrostriction. By these experiments Debye's relation between the coefficient of electrostriction and the pressure effect on the dielectric constant is verified. On the other hand, the relation between dielectric constant and density as given by Onsager's theory is not in agreement with experiment. (*PA*, 1962, #7227)

,595. DIELECTRIC CONSTANT AND DIELECTRIC LOSS OF GLYCEROL

Tourky, A. R., Rizk, H. A., Elanwar, I. M.
***Zeitschrift für Physikalische Chemie*, Frankfurt, v. 30,**
pp. 116–122, 1961 (in English)

The mean values of ε' and ε'' for glycerol were found to decrease in the frequency band 10^5–10^7 cps at −19 to 0°C. The verage values of relaxation time at −19, −10, and 0°C are given, and activation entropy and enthalpy for dielectric reaxation within this temperature range are presented.

It is pointed out that at lower frequencies the loss due o the dc conductivity which is present at all temperatures predominates over the Debye loss at >20°C.

,596. MOLECULAR ROTATION IN ETHYLENE BROMIDE

Tourky, A. R., Rizk, H. A., Elanwar, I. M.
***Zeitschrift für Physikalische Chemie*, Frankfurt, v. 30,**
pp. 240–249, 1961 (in English)

The change with temperature of the dielectric constant of ethylene bromide from −35 to +50°C in the frequency band 10^5–10^7 cps shows an abrupt change at the melting point (10°C) and another slight change at a lower temperature, ndicating a change in rotational freedom of the *trans* molecules. Calculated values of the solution dipole moments are presented and discussed.

,597. SOUND ABSORPTION IN ROCHELLE SALT CLOSE TO ITS LOWER CURIE POINT

Shustin, O. A., Velichkina, T. S., Baranskii, K. N.,
Yakovlev, I. A.
***Zhurnal Eksperimentalnoi i Teoreticheskoi Fiziki*, v. 40,**
no. 3, pp. 979–980, March 1961
(Translated from the Russian in *Soviet Physics—JETP*,
v. 13, no. 3, pp. 683–684, September 1961)

A high absorption of 5-Mc waves is found at −18°C. Such absorption represents relaxation due to the reestablishment of equilibrium in a crystal undergoing a second-order phase transition. Excellent agreement with a theory of Landau is obtained.

,598. INVESTIGATION OF REORIENTATION OF THE GUANIDINIUM ION IN THE FERROELECTRIC $C(NH_2)_3 \cdot Al(SC_4)_2 \cdot 6H_2O$ BY THE NUCLEAR MAGNETIC RESONANCE METHOD

Lundin, A. G., Mikhailov, G. M., Habuda, S. P.
***Zhurnal Eksperimentalnoi i Teoreticheskoi Fiziki*, v. 40,**
no. 5, pp. 1282–1288, May 1961
(Translated from the Russian in *Soviet Physics—JETP*,
v. 13, no. 5, pp. 903–907, November 1961)

Reorientation of the $[C(NH_2)_3]^+$ ion has been detected in the ferroelectric $C(NH_2)_3 \cdot Al(SO_4)_2 \cdot 6H_2O$ at temperatures above 130°K by means of nuclear magnetic resonance. The temperature dependence of the second moment of the absorption line of a polycrystalline sample has been examined between 90 and 400°K. The height of the potential barrier for the reorientation of the $C(NH_2)_3$ group has been estimated, and some conclusions are drawn regarding the reorientation mechanism.

1,599. DIELECTRIC CONSTANTS OF SOME ORGANIC COMPOUNDS OVER A WIDE TEMPERATURE RANGE

Komandin, A. V., Bonetskaya, I. K.
***Zhurnal Fizicheskoi Khimii*, v. 34, no. 4, pp. 845–849,**
April 1960
(Translated from the Russian in *Russian Journal of Physical Chemistry*, v. 34, no. 4, pp. 402–403, April 1960)

A continuation of earlier papers by the authors on the relation between the dielectric properties and chemical structure of molecules of organic compounds in the liquid and supercooled states is presented. Dielectric constants were measured by a heterodyne method at 1.72 × 10^6 cps. Tables and graphs give (1) the dielectric constants and densities of *o*-methoxybenzoic acid methyl ester, acetylsalicylic acid, salipyrine (a compound of salicylic acid and antipyrine), and benzophenone; (2) the calculated values of the total and orientation polarizations for liquid and supercooled states; and (3) Kirkwood's coefficient *g* for intermolecular interaction. The dielectric constants of each substance given are the mean values of a series of three to five experiments. Other measurements and calculations are from prior works. The results are discussed.

1,600. REFLECTION OF CRYSTAL-PHASE TRANSITIONS IN THE TEMPERATURE DEPENDENCE OF THE DIELECTRIC PROPERTIES OF LIQUIDS AND SOLUTIONS

Urazovskii, S. S., Ezhik, I. I.
***Zhurnal Fizicheskoi Khimii*, v. 36, no. 1, pp. 156–160,**
January 1962
(Translated from the Russian in *Russian Journal of Physical Chemistry*, v. 36, no. 1, pp. 77–79, January 1962)

The dielectric constant (ε) and tangent of the loss angle (tan δ) were measured as a function of temperature for α-nitronaphthalene, 0.1, 1, and 3% solutions of *p*-dichlorobenzene in C_6H_6, pure *p*-dichlorobenzene, and a mixture of 3% solutions of diphenylamine, bibenzyl, and benzophenone in xylene. Crystal phase transitions show as abrupt changes in the dielectric-property curves.

1,601. DIELECTRIC PROPERTIES OF COMPOUNDS OF THE MAGNUS SALT TYPE

Baranova, L. I.
***Zhurnal Neorganicheskoi Khimii*, v. 6, no. 3, pp. 740–748,**
March 1961
(Translated from the Russian in *Russian Journal of Inorganic Chemistry*, v. 6, no. 3, pp. 380–381, March 1961)

The dielectric constants are given for $Pt(NH_3)_4 \cdot PtCl_4$ and for the salts formed by replacement of $(NH_3)_4$ by the amines: $(MeNH_2)_4$; $(NH_3)_2(EtNH_2)_2$; $(EtNH_2)_4$; $(en)(MeNH_2)_2$;

(en)$_2$; $(NH_3)_2CH_3CH(NH_2)CH(NH_2)CH_3$; and $[CH_3CH(NH_2)CH(NH_2)CH_3]_2$.

1,602. DIELECTRIC CONSTANT OF LIQUID BINARY SYSTEMS CONTAINING POLAR COMPONENTS

Osipov, O. A., Panina, M. A., Kashireninov, O. E., Nemirov, G. V., Shelomov, I. K.
***Zhurnal Obshchei Khimii*, v. 31, pp. 3153–3160, 1961**

Dielectric constant determinations on 26 liquid binary systems, made by the heterodyne method, showed that the dielectric isotherms fall into three forms: in the first group the mutually unreacting systems yield rectilinear isotherms which deviate from linearity in either positive or negative direction (e.g., Me_2CO–MeCOEt); the second group of systems shows a negative deviation from the linear isotherm caused by destruction of chain-type association through the hydrogen bond (primarily) (e.g., iso-BuOH–$PhNO_2$); and the third group of systems shows positive deviations from linearity (e.g., $PhNH_2$–Et_2O). Data on dipole moments of components and the binary systems are tabulated.

1,603. DIELECTRIC PROPERTIES OF ACETONE-BENZENE SOLUTIONS IN A SUPER-HIGH FREQUENCY FIELD AND CONCENTRATION FLUCTUATIONS

Akhadov, Ya. Yu., Shakhparonov, M. I., Kasimov, R. M., Kornilova, N. B.
***Zhurnal Strukturnoi Khimii*, v. 2, no. 2, pp. 131–139, March–April 1961**
(Translated from the Russian in *Journal of Structural Chemistry*, v. 2, no. 2, pp. 123–131, March–April 1961)

Results are presented of studies of the dielectric constant ε' and conductance ε'' of acetone solutions in benzene over a wide range of concentrations and temperatures at $\lambda = 3.21$ cm. Negative deviations of ε' and ε'' from additivity were found. The viewpoints attributing these deviations from additivity to formation of associated groups of polar molecules and to the influence of concentration fluctuations on ε' and ε'' are compared. It is shown that the hypothesis of associated complexes cannot account for all the experimental facts. The observed results are satisfactorily explained if the influence of concentration fluctuations on ε' and ε'' is taken into account.

SYNTHESIS AND APPLICATION

1,604. CONCERNING LIGHT DETECTORS UTILIZING THE PYROELECTRIC EFFECT

Silvestrova, I. M.
***Akademiya Nauk, SSSR, Izvestiya, Seriya Fizicheskaya*, v. 24, no. 10, pp. 1213–1215, 1960**
(Paper presented at the Ferroelectricity Conference—Entry #1,321; translated from the Russian in *Bulletin of the Academy of Sciences of the USSR, Physical Series*, v. 24, no. 10, pp. 1216–1218, 1960)

Triglycine sulphate was used as a light detector by amplifying the voltage developed by the pyroelectric effect. The sensitivity varies markedly with temperature, there being a pronounced maximum at 46–47°C. If a field is applied, however, the sensitivity increases continuously with temperature. The sensitivity increases with increasing field. The coercive field is ~ 400 cm^{-1}. There is some hysteresis associated with the polarizing field. (*PA*, 1962, #18,768)

1,605. RADIATION EFFECTS ON ELECTRICAL INSULATION

Brancato, E. L., Kallander, J. W.
***Electrical Manufacturing*, v. 66, no. 3, pp. 157–163, September 1960**

Plastic insulating materials are considered. The dependence of electrical characteristics on dose rate and on other radiation parameters is discussed.

1,606. ELECTRET EFFECT OF DIELECTRICS

Gubkin, A. N., Matsonashvili, B. M.
***Elektrichestvo*, no. 8, pp. 56–60, 1962**

A critical examination is made of theories which have been proposed to explain the electret effect in dielectrics. The properties of electrets are closely linked with residual polarization, and electrets can be prepared only from dielectrics (such as polar polymers, waxes, resins, and also some ceramic materials) possessing long-lasting residual polarization and a low conductivity. Practical applications for electrets are reviewed. 17 references.

1,607. THE EFFECT OF THE DIELECTRIC CONSTANT OF THE EMBEDDING MEDIA ON ELECTROLUMINESCENT LIGHT INTENSITY

Tanaka, J., Berg, D.
***Electrochemical Society, Journal of the*, v. 110, no. 6, pp. 580–582, June 1963**

The effect of the dielectric constant of solid embedding materials on the brightness of electroluminescent lamps is described for dielectric constants up to 65. The theory Roberts used for spheres embedded in a dielectric medium is applied and successfully accounts for the variation of light intensity with dielectric constant.

1,608. PERSPEX ELECTRETS

Bhatnagar, C. S.
***Indian Journal of Pure & Applied Physics*, Council of Scientific and Industrial Research, New Delhi, v. 1, no. 3, pp. 107–110, March 1963**

1,609. CHARACTERISTICS OF PLASTICS USED IN ELECTRICAL ENGINEERING

Hersping, A.
***Kunststoffe*, v. 52, pp. 73–77, 1963**

Plastics used in West Germany for electric purposes are surveyed. Moisture absorption, dielectric strength, and resistance to surface leakage are discussed as properties of importance for these uses.

1,610. INSULATING PAPERS FOR 310°F

Traut, G. R., Berry, R. C., Greenman, N. L.
***Materials in Design Engineering*, v. 55, no. 3, pp 12–13, March 1962**

Three epoxy-impregnated polyester (Dacron) fiber papers may now replace synthetic-fiber paper insulating materials. Physical and electrical properties are tabulated. Compared with insulating fabrics, papers generally offer (1) the economy inherent in the high production papermaking process, (2) availability in more thicknesses, (3) better processability and forming, and (4) greater neatness.

1,611. FERROPLASTICS BASED ON CARBONYL POWDERS; THEIR PRODUCTION AND ELECTROMAGNETIC PROPERTIES

Tolmasskii, I. S., Fridenberg, A. E.
***Plasticheskie Massy*, v. 1961, no. 12, pp. 15–19, December 1961**
(Translated from the Russian in *Soviet Plastics*, v. 1961, no. 12, pp. 14–18, December 1961)

The ferromagnetic base of such a plastic is carbonyl iron for which the separate loss coefficients are low. The dielectrics used are water glass for preliminary insulation of the iron particles, and a solution of phenolformaldehyde resol resin in ethyl alcohol as the binder. Properties of the new ferroplastic, measured at frequencies up to 100 kc, are considerably superior to those of the material in current use.

Pot-type and rod cores are used for frequencies up to 20 Mc. Two types of ferroplastic have been developed for them. One is based on carbonyl iron which has not been heat treated, and uses double insulation (water glass and PF resin solution in ethyl alcohol); the other is based on iron-nickel powder N-50, using double insulation (water glass and an organosilicon resin). For frequencies above 20 Mc, cores are mostly of the pot and rod types. The ferromagnetic base used is the fine fraction of carbonyl iron obtained by gas flotation. The composition of the insulation and the method of preparing the ferroplastic are the same as for cores working at frequencies up to 20 Mc Cores working at frequencies up to 1 Mc are mainly annular or of the rod type. Two types of ferroplastic have been developed for this frequency range. One is based on reduced carbonyl iron and a solution of PF resin in ethyl alcohol; the other is based on iron-nickel powder N-5 and a solution of PF resin in ethyl alcohol.

The ferromagnetic base of a ferroplastic for stable working at 150°C is ordinary carbonyl iron, the dielectric being water glass as the preliminary insulation and a solution of phenolformaldehyde resin in ethyl alcohol as the binder. To stabilize their electromagnetic properties the cores are subjected to special heat treatment.

1,612. MOST IMPORTANT TRENDS IN THE DEVELOPMENT OF SYNTHETIC DIELECTRICS

Andrianov, K. A.
***Trudy Vsesoyuznogo Elektrotekhnicheskogo Instituta imeni V. I. Lenina*, no. 3, pp. 3–24, 1959**
(See also *Referativnyi Zhurnal Khimiya*, 1961, #7P84)

Among the dielectrics considered are: organic polymer compounds (block and graft copolymers, polymers with C chain molecules containing Ph groups, linear polycondensation plastics, unsaturated polyesters), and organic-inorganic compounds. Methods of synthesis and mixing for dielectric materials are pointed out.

1,613. ELECTRIC RESISTANCE MADE OF ORGANIC BINDING MATERIAL

Galperin, B. S.
March 25, 1960 (application date)
U. S. Department of Commerce, Washington, D. C.
USSR Patent 140,474
(See also *Byulleten Izobretenii*, no. 16, p. 26, 1961)

From 4 to 12% of a thermoplastic resin is added to a thermosetting resin.

1,614. DIELECTRIC

Burshtein, V. Kh., Shteinpress, A. B.
January 27, 1962 (patent application, April 3, 1961)
U. S. Department of Commerce, Washington, D. C.
USSR Patent 144,016
(See also *Byulleten Izobretenii*, no. 1, p. 63, 1962)

A claim is made for the preparation of a dielectric material by combining, during rolling, 3 to 5% of butadiene-styrene nonpolar rubbers with a copolymer of styrene and α-methylstyrene.

1,615. DISPERSING CONDUCTIVE PARTICLES IN RESIN-BONDED ELECTRICAL RESISTORS

Pass, R. H.
October 2, 1962 (patent application, January 23, 1961)
U. S. Department of Commerce, Washington, D. C.
U. S. Patent 3,056,750 (assigned to Air Reduction Co., Inc.)

A claim is made for improved resistivity/weight ratio and stability at elevated temperature in resin-bonded electrical resistors by predispersing the conductive C or metal particles in a polymerizable resin solution, removing solvent, and polymerizing the resin. The solid conductor-resin mixture is then ground to the desired particle size, and the particles are dispersed in various partially polymerized resins to form a liquid or paste composition which can be processed to form solid resistors. Spacing of conductor particles is made more uniform by the predispersion. The process is especially useful for making resistors for printed circuits.

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