

THREE-YEAR COMPREHENSIVE REPORT

1989-1992

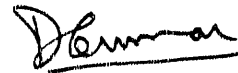
UNITED STATES DEPARTMENT OF ENERGY

DE-FG05-87ER60503

"A PHYSICO-CHEMICAL STUDY OF SOME AREAS
OF FUNDAMENTAL SIGNIFICANCE TO BIOPHYSICS"



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April 30, 1992

MASTER

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FOREWORD

In the last three years, we have submitted three annual reports and two proposals. In addition, we have published 32 papers, (some of which are in process of publication) most in journals of excellent repute. It is the sum of such entities which constitutes the gist of this Comprehensive Report.

We will make an attempt to summarize all of the above efforts in Section III. However, our attempt will fall quite short. Hence, we have no recourse but to suggest that a proper perspective will be gained only by readings from the list of Section II.A. In particular, our three Annual Reports will provide a much more complete account of accomplishments than this very terse summary.

I. STATEMENT OF OTHER SUPPORT

The work described in this Comprehensive Report (1989-1992) was also supported by the following agencies:

1.	Biomedical Research Support Grant awarded to L. Klasinc (4/1/89 - 3/31/92), Federal (PHS) Funds	\$8,290.
2.	LSU Foundation Grant awarded to D. Kumar to refurbish Luminescence Spectrometer (Aug. 1990), Private Funds	\$4,882.
3.	LSU Center for Energy Studies Equipment Grant awarded to D. Kumar (Fall, 1990), State Funds	\$16,500.
4.	Tektronix, Inc. Grant to D. Kumar towards purchase of Digital Scope (1/28/91), Private Funds	\$4,358.
5.	LSU Equipment Start-up Grant to S. P. McGlynn (Fall, 1990), State Funds	\$50,000.
	TOTAL OTHER SUPPORT	<u>\$84,030.</u>

II. LIST OF TITLES , SYMPOSIA AND PERSONNEL

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A. BIBLIOGRAPHY OF TITLES PUBLISHED

1989-1992

(serial numbers refer to the numbers allotted in previous reports)

242. W. S. Felps, K. Rupnik and S. P. McGlynn, "Intravalence Transitions of the Cyanogen Halides," This manuscript has been published with revised title, "Electronic Spectroscopy of the Cyanogen Halides," J. Phys. Chem. 95, 639 (1991).
316. U. Asaf, W. S. Felps and S. P. McGlynn, "Electron Scattering in Dense He-Ar Gas Mixtures: A Pressure Shift Study". Phys. Rev. A, 40, 5458 (1989).
317. Lj. Pasa-Tolic, B. Kovac, L. Klasinc, J. V. Knop, C. Kubli-Garfias and S. P. McGlynn, "Photoelectron Spectra, MNDO Calculations and Electronic Structure of Some Saturated Steroids," Croat. Chem. Acta 62, 813 (1989).
318. K. Rupnik, U. Asaf and S. P. McGlynn, "Electron Scattering in Dense Atomic and Molecular Gases: An Empirical Correlation of Polarizability and Electron Scattering Length," J. Chem. Phys., 92, 2303 (1990).
319. A. Alebic-Juretic, J. Cvitas and L. Klasinc, "Heterogeneous Polycyclic Aromatic Hydrocarbon Degradation with Ozone on Silica Gel Carrier," Environ. Sci. Technol. 24, 62 (1990).
320. K. Rupnik, "VUV and Laser Raman Studies in the Correlation Between Atomic and Molecular Polarizabilities and Number Density Shifts," Proceedings of International Conference on LASERS '89, D. B. Harris and T. M Shay, Eds., STS Press, 1990, p. 774.
321. D. Kumar and S. P. McGlynn, "Nature of Laser Optogalvanic Signals," Proceedings of International Conference on LASERS '89, D. B. Harris and T. M Shay, Eds., STS Press, 1990, p. 757.
322. D. Kumar and S. P. McGlynn, "Laser Optogalvanic Spectroscopy," Proceedings of International Conference on LASERS '89, D. B. Harris and T. M Shay, Eds. STS Press, 1990, p. p. 753.
323. S. P. McGlynn, K. Wittel and L. Klasinc, "The Orbital Concept as a Foundation for Photoelectron Spectroscopy," in Theoretical Models of Chemical Bonding, Part 3 of Molecular Spectroscopy, Electronic Structure and Intramolecular Interactions, ed. Z. B. Maksic, Springer Verlag, Berlin, 1991, p. 63
324. L. Klasinc, Lj. Pasa-Tolic, H. Spiegl, J. V. Knop and S. P. McGlynn, "Electronic Structures and Long-Range Interaction in Androstanes," Computers Chem., 14, 287 (1990).

325. Annual Report for 1989-1990. A Bibliography of Titles, Reports of Work in Progress and Work Completed (items 314-326 for the period of 1989-1990 of Research Grant Number DE-FG05-87ER60503).
326. D. Kumar and S. P. McGlynn, "Role of Photoacoustics in Optogalvanics," *J. Chem. Phys.* **93**, 3899 (1990).
327. Lj. Pasa-Tolic, L. Klasinc and S. P. McGlynn, "The He I PE Spectrum and Electronic Structure of Nitroethene," *Chem. Phys. Lett.* **170**, 113, (1990).
328. U. Asaf, K. Rupnik, W. S. Felps and S. P. McGlynn, "Scattering of Electrons of High-Molecular Rydbergs in Dense Atomic and Molecular Gases," in "Nonequilibrium Effects in Ion and Electron Transport," J. W. Gallagher et al., Eds., Plenum, New York, 1990.
329. Lj. Pasa-Tolic, B. Kovac, L. Klasinc, S. M. Shevchenko, and S. P. McGlynn, "Photoelectron Spectroscopy of Biologically active Molecules. 20. para-Quinones, Semiquinones, and Aromatic Ketones," *Int. J. Quant. Chem.: Quant. Chem. Symp.* **24**, 799 (1990).
330. L. Klasinc and S. P. McGlynn, "Photoelectron Spectroscopy of Biologically Active Molecules. 21. Thiooxamides," *Int. J. Quant. Chem: Quant. Chem. Symp.* **24**, 813 (1990).
331. Lj. Pasa-Tolic, B. Kovac, L. Klasinc, and S. M. Shevchenko, "Photoelectron Spectra of Lignin Model Compounds," *Croat. Chem. Acta* **63**, 37 (1990).
332. D. Kumar and S. P. McGlynn, "Ionization and Photoacoustically Mediated Optogalvanic Signals," *Chem. Phys. Lett.* **176**, 536 (1991).
333. S. P. McGlynn, V. Asaf, D. Kumar, S. Felps, K. Rupnik, and L. Klasinc, "Solvent Effects in Dense Gases," *Int. J. Quant. Chem.* **39**, 399 (1991).
334. K. Rupnik, V. Asaf, and S. P. McGlynn, "Reply to the Comment on : Electron Scattering in Dense Atomic and Molecular Gases," *J. Chem. Phys.* **94**, 3285 (1991).
335. L. Nyulaszi, T. Vezpremi, J. Reffy, G. Zsombok, T. Cvitas, B. Kovac, L. Klasinc and S. P. McGlynn, "Photoelectron Spectra of Halogenofurans," *Int. J. Quant. Chem: Quant. Chem. Symp.* **25**, 479 (1991).
336. L. Klasinc, Lj. Pasa-Tolic, H. Spiegl, J. V. Knop, and S. P. McGlynn, "Positional and Conformational Dependence of Long-Range Interaction in 3,16 - and 3,17 - Androstanediones," *J. Math. Chem.* **8**, 179 (1991).
337. Lj. Pasa-Tolic, L. Klasinc, H. Spiegl, J.V. Knop, and S. P. McGlynn,

- "Ab-initio Calculations on 5 α - Androstanes," Int. J. Quant. Chem.: Quant. Biol. Symp. 41, 815 (1992)
338. D. Kumar and S. P. McGlynn, "Analysis of Radiofrequency Discharges in Plasma," Patent Application; Accepted 1992; Patent Number to be issued.
339. Annual Report for 1990-1991. A Bibliography of Titles, Report of Work in Progress and Work Completed (items 326-339) for the period 1990-1991 of Research Grant Number DE-FG05-87ER60503.
340. S. P. McGlynn and M. N. Varma, "Radiation Signatures", Proceedings of the Council of the European Community Workshop on Biophysical Modelling of Radiation Effects, Padova, Italy, September 1991, Adam Hilger (IOP), Bristol, England (in press).
341. S. P. McGlynn, K. Rupnik, M. N. Varma and L. Klasinc, "Radiation Signatures for Biology," Int. J. Quant. Chem., Quant. Biol. Symp. 1992 in preparation for submission.
342. M. Eckert-Maksic, Z. B. Maksic, M. Hodoscek, and K. Rupnik, "Intra- and Extramolecular Electrostatic Potentials in Vitamin C" J. Mol. Struct. THEOCHEM, (in press).
343. S. P. McGlynn and D. Kumar, "The Laser Optogalvanic Effect in Radiofrequency Discharges," Proceedings of the International Society for Optical Engineering Meeting on *Lasers, Sensors and Spectroscopy*, Los Angeles, California, January 1992 (in press).
344. A. Alebic-Juretic, T. Cvitas and L. Klasinc, "Ozone Destruction on Powders," Ber. Bunsenges. Phys. Chem. 1992 (in press).
345. T. Pasinszki, T. Veszpremi, M. Feher, B. Kovac, L. Klasinc and S. P. McGlynn, "The Photoelectron Spectra of Methyl Pseudohalides," Int. J. Quant. Chem., Quant. Chem. Symp. 1992 (in press).
346. K. Rupnik, and S. P. McGlynn, "Molecular Lesion Spectra as Radiation Signatures", Radiation Research 1991 (submitted).
347. U. Asaf, R. Reininger, K. Rupnik and S. P. McGlynn, "Pressure Shift and Electron Scattering Length in Atomic and Molecular Gases," J. Phys. Chem. (prepared for submission).
348. U. Asaf, S. Felps, K. Rupnik, and S. P. McGlynn, "Electron Scattering in Dense Hydrogen-Argon Gas Mixtures: A Pressure Shift Study," Phys. Rev. A. (submitted).

349. M. Surgi, D. Giamalva and L. Klasinc, "Correlation Between Ozonolysis Rate and π -Ionization Potential of 10,10'-Dimethyl,-9,9'-Biacridylidene." Bull. Slov. Chem. Soc. (submitted).
350. S. P. McGlynn, K. Rupnik and M. N. Varma, "Molecular Lesion Spectra are Radiation Signatures," Patent Application 1991; Patent pending.
351. R. Armstrong, "A Study of the Optogalvanic Effect in Water and Argon," a report presented to LaSER (Louisiana Stimulus for Excellence in Research), January 1992.
352. Annual Report for 1991-1992. A Bibliography of Titles, Report of Work in Progress and Work Completed (Items 340-353) for the period of 1991-1992 of Research Grant Number DF-FG05-87ER 60503.
353. Comprehensive 3-Year Report 1989-1992. A Bibliography of Titles Submitted in 1989-1992. A Brief Resume of Research Activities and Principal Results Obtained During 1989-1992, with Comments on the Research Performed under Contract No. DE-FG05-87ER 60503.

COMMENTS

The bibliography of titles consists of 39 titles. These may be divided as follows:

Articles:

Published	22
Accepted for publication or in press	06
Submitted for publication	<u>04</u>
SUB-TOTAL	32

Reports and Patents:

Reports to the Department of Energy	04
Report to LaSER (Louisiana Stimulus for Excellence in Research)	01
Patents Granted	01
Patents Submitted	<u>01</u>
TOTAL	39

Disregarding Dissertations and Reports, the average cost per publication was ~ \$11,000. This number takes no account of the extent to which grant expenditures contributed to the training and education of the persons employed on DOE monies.

The above numbers do not take into account the extent to which grant expenditures contributed to the caliber of the Undergraduate Programs in this Department. This contribution was so pervasive, yet so ill-defined, that it cannot be categorized. However, such effects did occur and they were important.

No graduate students are listed for the 1989-1992 period. One of the Principal Investigators (S. P. McGlynn) was Vice-Chancellor of the University during that period and a conscious decision was made not to accept graduate students. Now that S. P. McGlynn has returned to full-time faculty status, that decision has been reversed: one graduate student is contracted to enter the program in August, 1992; one other during Fall, 1992; and a full complement of 5 to 6 graduate students should be on board by December of 1993.

B. SYMPOSIA ATTENDED

1989-1992

1. I. Novak, B. Kovac and S. P. McGlynn, "Photoelectron Spectra and Long-Range Interactions in Dihaloalkanes," 11th Meeting of Chemists of Croatia, Zagreb, Yugoslavia, February 16-17, 1989.
- - -submitted, poster
2. Lj. Pasa-Tolic and L. Klasinc, "The He(1) Spectrum and Electronic Structure of Nitroethene," 11th Meeting of Chemists of Croatia, Zagreb, Yugoslavia, February 16-17, 1989.
- - -submitted, poster
3. L. Klasinc, "Electronic Structures and Long-Range Interaction in Androstanes," Math. Chem. Comp., Dubrovnik, Yugoslavia, June 26-30, 1989.
- - -Invited lecture
4. K. Rupnik, "Scattering of Electrons of High-Molecular Rydbergs in Dense Atomic and Molecular Gases," Sixth International Swarm Seminar, New York, NY, August 2-5, 1989.
- - -submitted, poster
5. K. Rupnik, "Phase-space approach to the calculation of Rydberg constant," OSA Annual Meeting, Orlando, FL, October 15-20, 1989.
- - -Invited, seminar
6. S. P. McGlynn, "Spin-Uncoupling and Scattering of a Rydberg Electrons," Chemistry Department, University of British Columbia, Vancouver, B. C., Canada, September 14, 1989.
- - -Invited Seminar
7. K. Rupnik, "VUV and Laser Raman Study of the Correlation Between Atomic Molecular Polarizabilities and Number Density Shifts", Lasers '89 Conference, New Orleans, LA December 3-8, 1989.
- - -submitted, oral
8. S. P. McGlynn, "Laser Optogalvanic (LOG) Spectroscopy", Lasers '89 Conference, New Orleans, LA, December 3-8, 1989.
- - -Invited, lecture
9. D. Kumar, "Role of Photoacoustics in Optogalvanics," Lasers '89 Conference, New Orleans, LA, December 3-8, 1989.
- - -submitted, oral
10. L. Klasinc, "Photoelectron Spectra and Electron Transfer in Steroids," The 1989 International Chemical Congress of Pacific Basin Societies, December 17-22, 1989.
- - -submitted, oral

11. K. Rupnik, "Lasers Without Inversion in Molecular Systems-First Thoughts," 20th Winter Colloquium on Physics of Quantum Electronics, Snowbird, UT, January 2-5, 1990.
- - -submitted, poster & oral
12. K. Rupnik, "Neural Network Models and Their Application to the VUV and Optical Spectroscopy of Molecular Systems," International Joint Conference on Neural Networks, Washington, DC, January 15-19, 1990.
- - -submitted, poster
13. L. Klasinc, "Photoelectron Spectra and Electronic Structure of Thiooxamides" 30th Sanibel Symposia, St. Augustine, FL, March 17-24, 1990.
- - -submitted, poster
14. S. P. McGlynn, "Scattering of Rydberg Electrons," Chemistry Department, Texas A&M University, College Station, Tex, May 22, 1990.
- - -Invited Seminar
15. D. Kumar, "Optogalvanics and Photoacoustics," Radiological and Chemical Physics Contractors' Meeting, Department of Energy, Berkeley, CA, June 26-28, 1990.
- - -Invited Lecture
16. S. P. McGlynn, "Scattering of Rydberg Electrons," Radiological and Chemical Physics Contractors' Meeting, Department of Energy, Berkeley, CA, June 26-28, 1990.
- - -Invited Lecture
17. S. P. McGlynn and G. L. Findley, "Geometry of Genetic Code," 2nd World Congress of Theoretical Organic Chemists (WATOC), University of Toronto, Toronto, Canada, July 8-14, 1990.
- - -Invited Lecture
18. S. P. McGlynn, "Geometry of Genetic Code," Symposium on Recent Developments in Mathematical Chemistry, WATOC Congress, Toronto, Canada, July 8-14, 1990.
- - - Invited Lecture
19. S. P. McGlynn, "Scattering of Rydberg Electrons," III. Brioni International Conference on Interdisciplinarity in Chemistry and Physics, Brioni, Croatia, Yugoslavia, September 10-14, 1990.
- - - Invited Lecture
20. L. Klasinc, Lj. Pasa-Tolic, H. Spiegl, J. V. Knop and S. P. McGlynn, "Electronic Structure and Long-Range Interactions in Steroids," III. Brioni International Conference on Interdisciplinarity in Chemistry and Physics, Brioni, Croatia, Yugoslavia, September 10-14, 1990.
- - - Invited Lecture

21. D. Kumar and S. P. McGlynn, "Laser Intensity Dependence of Optogalvanic Signals in a Neon rf Discharge," Sixth Interdisciplinary Laser Science Conference, Minneapolis, Minnesota, September 16-19, 1990.
- - -submitted, poster
22. K. Rupnik, W. S. Felps, and S. P. McGlynn, "VUV Electronic Absorption and Magnetic Circular Dichroism Study of HI Molecules," Annual Meeting of the Optical Society of America, Boston, Massachusetts, November 4-9, 1990.
- - -submitted, poster
23. Lj.Pasa-Tolic, D. Srzic, and L. Klasinc, "FTMS Fragmentation Study of 5α - Androstane - 3,16 - Dione and 5α - Androstane - 3,17 - Dione," 12th. Meeting of Chemists of Croatia, Zagreb, Croatia, February 11-13, 1991.
- - -submitted, poster
24. Lj.Senkovic, D. Srzic, and L. Klasinc, "Laser Desorption FTMS of Humic Acid," 12th. Meeting of Chemists of , Zagreb, Croatia, February 11-13, 1991.
- - -submitted, poster
24. D. Srzic, A. Vrancic, and L. Klasinc, "FTMS of Deuterated Stilbenes," 12th. Meeting of Chemists of Croatia, Zabreb, Croatia, February 11-13, 1991.
- - -submitted, poster
25. L. Nyulaszi, T. Veszpremi, J. Reffy, G. Zsombok, B. Kovac, L. Klasinc, S. P. McGlynn and T. Cvitas, "Photoelectron Spectra of Halogen Substituted Furans," 12th. Meeting of Chemists of Croatia, Zagreb, Croatia, February 11-13, 1991.
- - -submitted, poster
26. Lj. Pasa-Tolic, L. Klasinc, and D. Vikić-Topic, "Long-Range Interactions in Androstanes," 12th. Meeting of Chemists of Croatia, Zagreb, Croatia, February 11-13, 1991.
- - -submitted, poster
27. S. P. McGlynn, "Scattering of Rydberg Electrons," Department of Physics and the Institute for Non-Linear Optics and Non-Linear Materials, Alabama A & M University, Huntsville, Alabama, February 26-27, 1991.
- - - Invited Seminar
28. Lj. Pasa-Tolic, L. Klasinc, H. Spiegl, J. V. Knop, and S. P. McGlynn, "Ab initio Calculations on 5α - Androstane," Sanibel Symposia, St. Augustine, Florida, March 9-16, 1991.
- - -submitted, poster

29. L. Nyulaszi, T. Veszpremi, J. Reffy, G. Zsombok, T. Cvitas, B. Kovac, L. Klasinc and S. P. McGlynn, "Photoelectron Spectra of Halogenofurans," Sanibel Symposia, St. Augustine, Florida, March 9-16, 1991.
- - -submitted, poster
30. S. P. McGlynn, V. Asaf, W. S. Felps, L. Klasinc, and K. Rupnik, "Scattering of Rydberg Electrons," Sanibel Symposia, St. Augustine, Florida, March 9-16, 1991.
- - -submitted, poster
31. D. Kumar, "The Optogalvanic Effect," Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana, April 2, 1991.
- - - Invited Seminar
32. S. P. McGlynn, "How to Model Molecular Lesions?" Radiological and Chemical Physics Contractors' Meeting on "Radiation Signatures: Facts or Fancy," Department of Energy, Columbia University, New York, April 15-17, 1991.
- - - Invited Lecture
33. K. Rupnik, "Adaptive Lesion Models," Radiological and Chemical Physics Contractors' Meeting on "Radiation Signatures: Facts or Fancy," Department of Energy, Columbia University, New York, April 15-17, 1991.
- - - Invited Lecture
34. L. Klasinc, Lj. Pasa-Tolic, S. P. McGlynn and T. P. Zivkovic, "Low-Rank Perturbation Approach Applied to Steroids," IV. International Conference on Mathematical and Computational Chemistry, in Bled, Slovenia, June 4th, 1991.
- - -Invited Lecture
35. S. P. McGlynn, "Spin Uncoupling In Rydberg States," IV. International Conference on Mathematical and Computational Chemistry, Bled, Slovenia, June 5th, 1991.
- - -Plenary Lecture
36. S. P. McGlynn, G. Findley and A. Findley, "The Geometry of Genetics", IV. International Conference on Mathematical and Computational Chemistry, Bled, Slovenia, June 6th, 1991.
- - -Plenary Lecture
37. S. P. McGlynn, G. Findley and A. Findley, "The Geometry of Genetics", to the faculties of Biochemistry and Biophysics, The University of Split, Split, Croatia, June 11th, 1991.
- - -Invited Lecture

38. S. P. McGlynn, "Scattering of Rydberg Electrons", given to the faculty of Arts & Sciences at The University of Split, Split, Croatia, June 13th, 1991.
- - -Invited Lecture
39. S. P. McGlynn, "Technology Transfer: University to Industry," given at the University of Ljubljana, Ljubljana, Slovenia and the Ministry of Science, Research and Technology of the Republic of Slovenia on June, 14th, 1991.
- - -Invited Lecture
40. L. Klasinc, "Quantum Chemical Calculations on Steroids," given at the International Conference on Mathematics, Chemistry and Computers, Dubrovnik, Croatia, June 24-29, 1991.
- - -Invited Lecture
41. S. P. McGlynn, "Molecular Lesion Spectra: Radiation Signature and Biological Gateway" Workshop on Biophysical Modelling and Radiation Effects. Organized by the U. S. Department of Energy and The Radiation Protection Research Program of the Commission of European Communities, Padova, Italy, September 1-5, 1991.
- - -Invited Lecture
42. S. P. McGlynn visited the new synchrotron research center in Trieste, Italy on September 6th and 7th, 1991. This center, funded by the U. N. and Italy, hosted a discussion concerned with a joint U. S. /Eastern European/Italian research program on radiation signatures. Professor McGlynn was one of the discussants.
- - -Discussion Leader
43. S. P. McGlynn reviewed the research program of the Radiation and Solid State Laboratory of New York University, October 17th, 18th and 19th, 1991; on behalf of the U. S. Department of Energy. His co-reviewers were Harel Weinstein (Mt. Sinai Medical Center) and A. W. Castleman (Penn State).
- - -Reviewer
44. D. Kumar and S. P. McGlynn, "Dependence of Optogalvanic Signal on Laser Excitation Region in a Low Power Neon RF Discharge," 44th Annual Gaseous Electronic Conference, Albuquerque, New Mexico, October 22-25, 1991.
- - -submitted, poster
45. S. P. McGlynn, "Radiation Signatures," Fourth Winter Conference of the Inter-American Photochemical Society at Clearwater Beach, Florida on January 1-5, 1992.
- - -Session Chairman
46. S. P. McGlynn and D. Kumar, "The Laser Optogalvanic Effect in Radiofrequency Discharges," International Society for Optical Engineering Meeting on *Lasers, Sensors and Spectroscopy*, Los Angeles, California, January, 1992.
- - -Invited Lecture

47. S. P. McGlynn, K. Rupnik, M. N. Varma and L. Klasinc, "Radiation Signatures for Biology," Sanibel Symposia, on Atomic, Molecular and Condensed Matter Theory, St. Augustine, Florida; March 14-21, 1992.
- - -submitted, poster
48. T. Pasinszki, T. Veszpremi, M. Feher, B. Kovac, L. Klasinc and S. P. McGlynn, "The Photoelectron Spectra of Methyl Pseudohalides," Sanibel Symposia on Atomic, Molecular and Condensed Matter Theory, St. Augustine, Florida; March 14-21, 1992.
- - -submitted, poster

D. PERSONNEL
(1989-1992)

1. PERSONNEL DEPARTING

1. Uri Asaf Post Doctorate Fellow Now a Research
Scientist at
The Racah Institute of
Physics in Jerusalem,
Israel.

2. PRESENT SCIENTIFIC PERSONNEL

Tanya Ducre	Student Worker
T. Eaton	Visiting Assistant Professor from McNeese State University Lake Charles, Louisiana
Margaret Edwards	Secretary
W. S. Felps	Senior Research Associate
L. Klasinc	Visiting Professor from Ruder Boskovic Institute, University of Zagreb, Zagreb, Croatia
D. Kumar	Associate Professor-Research
S. P. McGlynn	Boyd Professor of Chemistry
R. C. Mohanty	Visiting Professor from Southern University Baton Rouge, Louisiana
K. Rupnik	Research Associate
J. D. Scott	Senior Staff Scientist from Center for Advanced Microstructures and Devices, Louisiana State University

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A. RADIATION SIGNATURES

A major goal of biophysical modelling is to relate physical events such as ionization, excitation, etc. to the production of radiation carcinogenesis. All types of radiations are of concern since each one is potentially carcinogenic. A description of the physical events is provided by track or ion distribution structures. The track structure is determined by radiation quality, and it can be considered to be the "physical signature" of the radiation. Unfortunately, the uniqueness characteristics of these signature are dissipated in biological systems in $\sim 10^{-9}$ s. Nonetheless, it is our contention that this physical disturbance of the biological system eventuates later, at 10^0 - 10^2 s or greater, in molecular lesion spectra, which we dub the "lesion signature" or "radiation signature" and which also characterize the causal radiation.

The best way to understand the radiation signature paradigm is by a representation of a spatio-temporal path from a normal, just insulted cell to a fully transformed carcinogenic cell. Much radiation physics work has been concentrated on the track structures at the $\leq 10^{-11}$ s level and ion distribution at the 10^{-7} s level. Unfortunately, the observed tracks are too far removed, in a spatio-temporal sense, from clinical manifestations of cancer. Clinical manifestations of cancer may take more than 20 years to develop, which places any possible radiation signature based on malignancy or mutation type at 10^8 to 10^9 s. Thus it becomes necessary to follow the radiation track through a whole host of chemical, biochemical, biological repair and emergent cellular happenings before its manifestation as cancer. The radiation signature paradigm is aimed at finding an intermediate point on the spatio-temporal path. We suggest that the most appropriate place to seek such a "signature" is at the junction of the chemical and biological regimes. If such a signature exists at a point which provides identification capability for the causal radiation, it should also serve as a gateway point for the bioprocessing which ultimately ends in malignancy. The correlation of the two ends of the spatio-temporal path might then be significantly facilitated by relating both ends to the midway point.

It is our contention that such a signature is provided by the spectrum (or histogram) of DNA molecular lesions. These signatures have the advantages of (1) high fidelity, (2) persistence times some ten orders of magnitude greater than track structures, and (3) a space-time cellular position which is approximately half way between initial insult and ultimate biological dysfunction.

Molecular lesion spectra contain information about the mechanism of radiation damage at the molecular level. That is, the types of lesions produced

by a given radiation surely reflect the variety of different physico-chemical-biological processes that take place after radiation insult. In fact, some lesions may be a result of some particular radiation: for example, double strand breaks and multiply locally damaged sites that are mainly (but not solely) associated with high density radiations.

In this work, in order to clarify terminology in radiation signature research we introduce certain definitions:

(i) Molecular Lesion: A molecular lesion in DNA is defined differently in different fields. For example, definitions at the organismal, cellular and sub-cellular levels vary widely. We shall adopt an operational definition, and take a molecular lesion in DNA to be any damage, whether constitutional or conformational, that can be measured reproducibly by different investigators. It is implied, then, that a good assay method exists for the lesion. It is also implied, for now anyway, that irradiations and measurements be done in the vicinity of 0°C since, otherwise, differential repair rates might vitiate reproducibility.

(ii) Sub-lesion: We suppose sub-lesions to be post-radiative damage usually consisting of loci at which energy has been deposited or ionizations have occurred. We suppose them to lie in the time domain in which physics has terminated and chemistry (but not biology) has initiated. The important point is that they are unstable and that processing of them may produce more than one type of molecular lesion. That is, branching may take place.

(iii) Molecular Lesion Spectra: We define a molecular lesion spectrum (MLS) as a plot of lesion frequency (or probability), usually in bar graph form, versus lesion type (categorized, for example, by indices 1,2,3,...). The sum of bars is normalized to 100. The set of lesions should be complete; that is, every lesion, regardless of how low its frequency, should be represented. Reality, however, intrudes: we have neither detected all possible lesions produced by a particular radiation nor learned to perform reliable assay for the limited set that has been detected. Thus, we must make do with a constrained definition which replaces "complete set" with "maximal detected set that can be reliably assayed".

(iv) Radiation Signature: The term radiation signature implies the existence of a set of post-irradiation properties of DNA that can be used to identify the radiation which caused them. The search for such a property set is an urgent desideratum of the radiation safety, insurance and environmental fields. It is our contention that molecular lesion spectra provide such a signature. Any individual possesses a variety of signatures: the "name" signature is used to validate a contract; the bank card microchip to obtain money from an automatic teller; the metallized parking card to gain entry to an automobile lot; or a voice

recognition system to open a pension door. In any event, signature and purpose must be related. The purpose of this work is to define a radiation signature in DNA which not only serves as an identifier of the radiation which produced the signature but also functions as an appropriate gateway to the cellular processings which ultimately result in cell carcinogenesis. We contend that molecular lesion spectra serve as such a nexus.

(v) The Spatio-Temporal Pathway: There is a path (perhaps many paths) from normal to carcinogenic cell. The point of reference for a signature based on track structure is $\leq 10^{-10}$ s, at the lower left of the curve. The point of reference for a signature based on carcinogenesis (i. e., on medicine) is years. These two points are too far removed in both organismal (or cellular) space and in time to permit other than an allusive correlation of one with the other. It our contention that an intermediate point provides signature for one end (i. e., radiation) and gateway to the other (i. e., cancer), and permits a real two-fold correlation which, in a single end-to-end correlation, might forever remain suppositional. We contend that molecular lesion spectra fit those requirements.

In this work , which is part of a long-term radiation signature study, the focus is on molecular lesion spectra as radiation identifiers. The objects of the research are: (1) to demonstrate that MLS can serve as radiation signatures for various radiations and to study the "sensitivity" and precision of these signatures; (2) to expand the data bases for such research; and (3) to develop tools for feature recognition and extraction. We have shown that these goals are realistic and we have made much progress with respect to items 1 & 3. However, those goals that involve any relationship between signatures and carcinogenesis, if any, are still in process of formulation. Indeed, we intend, at least for now, to keep the accent solely on molecular lesion spectra as signatures of a causative radiation.

The experimental data bases for the great majority of radiations (i. e., item 2) are very fragmented, so much so that a systematic study of radiation signatures is largely inhibited. The situation would improve enormously if more and better data were available. However, the advent of new experimental techniques, such as the polymerase chain reaction or laser technology promise much in unraveling the difference between high and low intensity radiation effects, in generating new data on the intensity-dependent photochemistry of DNA, in elucidating the effects of biphotonic processes, etc. In sum, the systematic elucidation of lesion types and frequencies, with proper regard paid to dosimetry (e.g., energy absorbed, cell concentration of insult, etc.) and biology (e.g., *in vitro*, *in vivo*, cell cycle stage, etc.), is a massive task that must be engaged in order to put the concept of spectrum as signature on a firm footing.

The concept of a signature (i.e., feature recognition) implies the existence of a set of object characteristics that can discriminate between different objects and /or classes of objects. A signature should possess such characteristics as repeatability (i.e., confidence) and ease of recognition (i.e., ease of discrimination from threshold "noise"). However, since the characteristics of a signature need not always be explicitly circumscribed by rules, some element of adaptability in the models used for feature extraction, particularly when the experimental data are collected under conditions that are exceedingly difficult to standardize, appears to be mandatory. For that reason, we have also introduced methods for the extraction of radiation signatures from diverse data sets: that is, an adaptive lesion model, which originates in parallel distributed processing (PDP) methods and which is related to adaptive nonlinear (neural) networks (ANN) and/or genetic algorithms (GA). It might be argued that that the use of feature (or pattern) recognition techniques in the present instance is redundant in the cases where the MLS are visually different. One answer is that visual differentiation is a qualitative sorting, and that one should make the sorting quantitative. To that end, each of the MLS is viewed as a "vector" in a space spanned by the MLS (or patterns), and the distinctiveness of patterns is quantified as the degree of orthogonality of the representative vectors. A second, and more relevant answer is that feature recognition techniques become necessary when one deals with data bases that are less than optimal, when one queries the minimum number of lesions adequate for a signature, or when one pursues any presumptive connection of a causal radiation and clinical outcome.

There are a variety of network architectures available. The counter-propagating network used here happens to be particularly advantageous for handling data sets that are either restricted in the number of lesions for which frequency data are available or of mixed quality because of lesion assay methods. Other network architectures, such as the backpropagating network, are also under study. The results of this study, indicate that the radiation signature approach can indeed identify the causative radiation and also provide valuable information on the role that specific lesion types play in the radiation signature. As a result, we expect to be able to limit molecular lesion spectra to a "minimum set" of lesions and to define those lesions which are the crucial identifiers for a given radiation.

THE SPECTRUM OF MOLECULAR LESIONS: AN EXAMPLE

Somewhat complete assays exist for only three different electromagnetic radiations, namely

Radiation	Energy	Source of data
VIS (limit of UV-A)	405 nm	Peak and Peak, (1987)
UV-C	254 nm	Setlow and Setlow, (1972)
γ -RAY	^{137}Cs (~0.6 MeV) ^{60}Co (~1.1 MeV)	Ward, (1988)

The molecular lesion spectra (or histograms) for these three radiations have been constructed as bar graphs of lesion frequency versus lesion type. The bar sum in any one graph is arbitrarily normalized to 100 .

The molecular lesions assayed in the three data sets are

Index	Name	Abbreviation
1	cytidine hydrate	ch
2	thymine dimer	d
3	pyrimidine adduct	pa
4	DNA-protein cross-link	dpc
5	DNA-DNA cross-link	ddc
6	single strand break	ssb
7	double strand break	dsb
8	locally multiply damaged sites	lmbs

Indeed, these eight lesions are those for which assay data are most generally available.

The three data sets refer to the DNA of various cells and of different biological entities. All data refer to the number of lesions produced by an F37 (D37) radiation fluence. Intercomparison of the three data sets must be accompanied with certain reservations:

-- Peak and Peak studied DNA lesions in mammalian cells at 405 nm. The F37 fluence was equivalent to $\sim 4\text{MJ}/\text{m}^2$. The cell line was a cultured P3 teratocarcinoma strain.

-- The Setlow and Setlow data for 254nm refer to vegetative mammalian cells at room temperature, again at an F37 fluence which, in this case, corresponded to $10\text{J}/\text{m}^2$.

-- The Ward data also refer to mammalian cells at an F37 dose. However, in this instance of ionizing radiation, the kill efficiency was much higher than for either 405 or 254nm. That is, in a relative sense, the γ -rays produced low levels of DNA damage. The high mortality level is apparently attributable to the ability of γ -rays to produce damage in which more than one moiety in a localized region of the DNA suffers damage, the so-called "locally multiply-damaged sites" (LMDS). It is important to point out that the LMDS category, index 8, encompasses a large variety of lesions, many of them categorizable under indices 1 through 7.

The defects then, are: (i), the supposition that F37 is an appropriate standard for radiation dosage; (ii), the use of different cell lines under different experimental conditions, both physical and biological; (iii), the lack of fluence considerations, and a disregard for the manner in which lesion interactions relate to fluence and fluence rate on the one hand and mortality and lesion production on the other.

The 405nm distribution is quite similar to the γ -ray distributions if the lmds lesion category, category 8, of the latter is disregarded; and both the 405nm and γ -ray distributions are markedly different from the 254nm spectrum.

According to radiation quality considerations, on the other hand, it is the 405 and 254nm distributions which should exhibit similarity, and both should be quite different from the γ -ray distribution. It is clear, then, that radiation quality does not provide an apt classification of DNA damage at the molecular level, and that the nature and loci of the energy deposition events is the significant descriptor. In specific, the 254nm distribution reflects direct absorption by, and deposition in the DNA bases, events which are totally impossible at 405nm and statistically improbable at $\sim 1\text{MeV}$; the similarity of the 405nm and γ -ray spectra, the lmds category of the latter excepted, is probably a consequence of energy deposition in the aqueous environment, directly for γ -rays and through the intermediacy of some third-party-chromophore for 405nm.

The construction of a portfolio of trustworthy radiation signatures is inseparable from the existence of reliable, quantitative data sets of molecular lesions. The imposition of the reliability consideration probably implies that repair processes be inoperable. That is, irradiation must be made at temperature

near 0°C in order to inhibit repair. Enzymatic repair rates are functions of lesion type and, hence, the relative concentrations of lesions types may change with post-irradiation time. Should that be the case, the fidelity of radiation signatures would be diminished.

Apart from a subcategorization of existing lesion sets (e.g., the dimer set), the signature fidelity would also be enhanced by the discovery and assay of new lesion sets. In view of the importance of the OH· radical and other oxygen-hydrogen entities, it is surprising, for example, that nitrogenous species are not implicated in the indirect production of molecular lesions. It is known that irradiation of protein produces generous amounts of NH₂·, a radical isoelectronic with and no less reactive than OH·, yet lesions produced by NH₂· seem not to occur or, at least, not to have been detected.

At this time, there is no unique, generally acceptable standard for biological dose. The data used in this work are based on a biological normalization related to the "efficiency of killing", namely the dose (D37) or fluence (F37) which permits a survivor fraction of 37%. This type of normalization presents at least two difficulties. Firstly, it appears that the ratio of lesion production to cell mortality may be a function of the radiation. For example, if 405nm is, as it appears to be, inefficient in killing, a D37 dose at 405nm implies measurement of the lesion production at very high fluence. That is (D37/F37) for the γ-ray region may well be more than 10⁶ times larger than (D37/F37) for the 405nm region. This question, in turn, generates the second difficulty: if the quadratic component in the linear-quadratic dependence of effect on dose is dominant, or merely important, the distribution of lesion intensity in the lesion spectra will vary with dose (and fluence), and the concept of a signature will run into difficulty. Thus, it is imperative that the effects of fluence on lesion distribution be investigated in detail. If it is found that lesion distributions are dose dependent, this will require an extension of the concept of a signature promulgated here to one which acquires multidimensionality in the sense that, for electromagnetic radiation of wavelength λ, the signature S = S(F) will have to be replaced by S = S(λ, F). In terms of the adaptive PDP approach advocated here, such a change poses no problem. In fact, it should produce better signature discrimination characteristics. However, it surely would increase the experimental workload, and reasons of economy alone could cause the signature concept, even if fully validated in a multidimensional sense, to lose utility.

COMPUTATIONAL SPACE

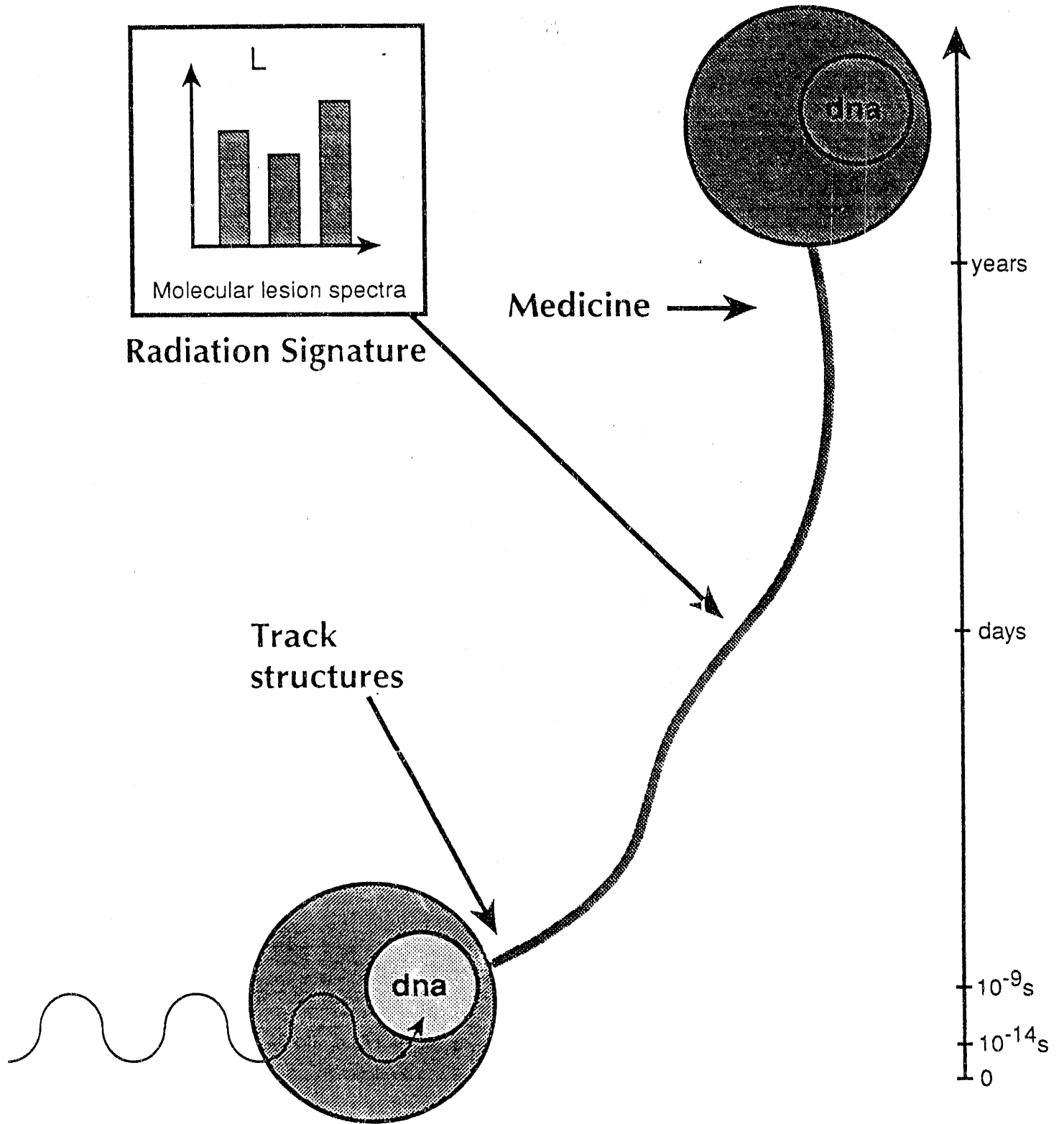


FIGURE 1

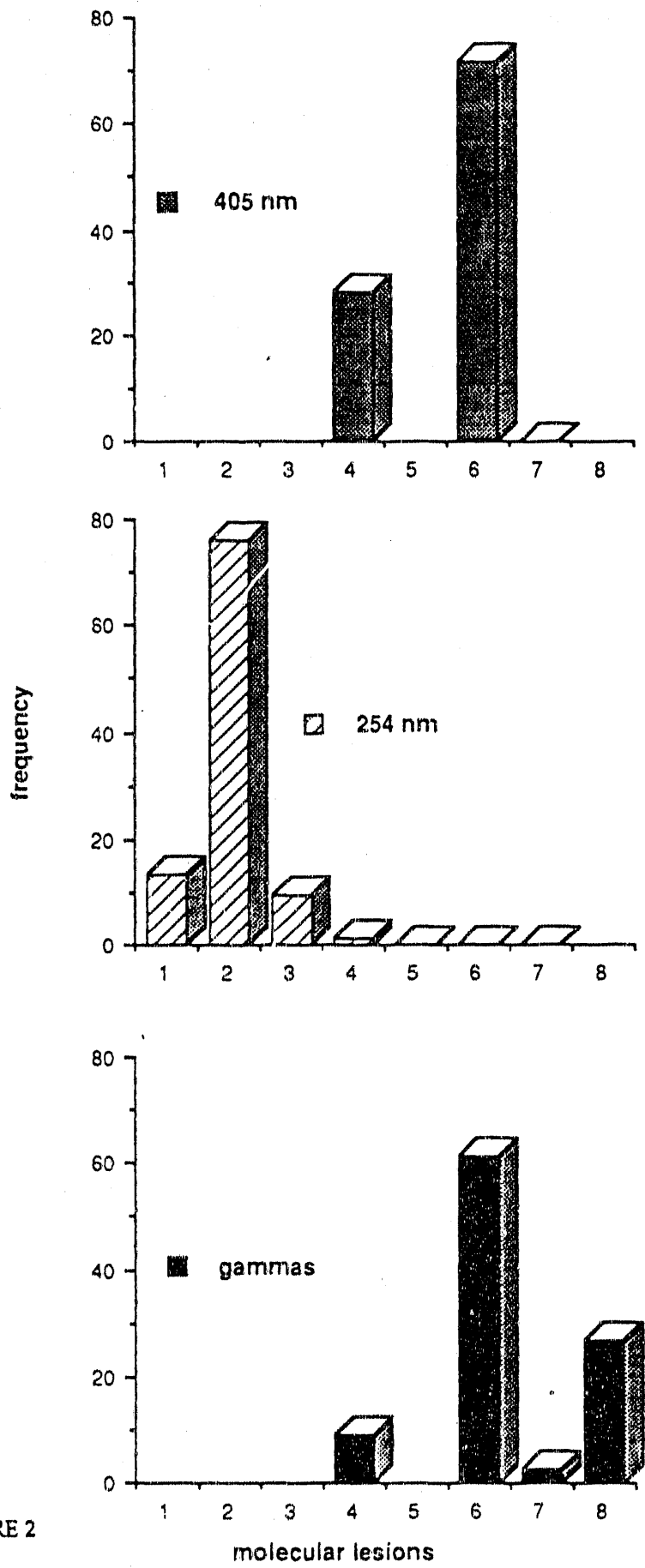


FIGURE 2

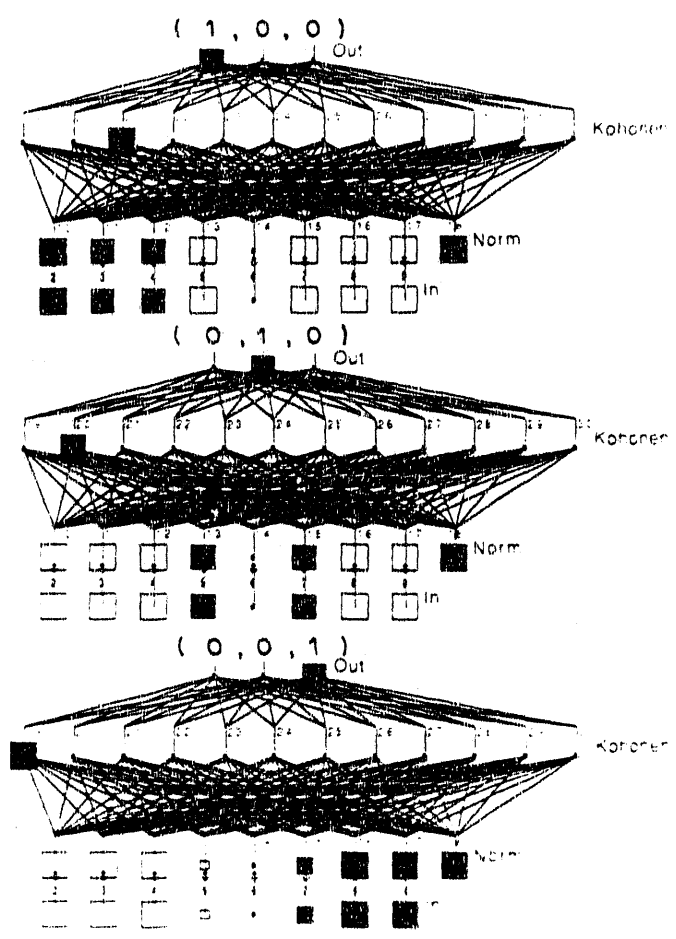
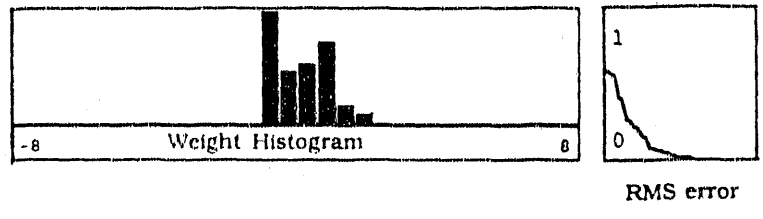


FIGURE 3

FIGURE CAPTIONS

FIGURE 1

The post-radiative spatio-temporal development of a cell from "normal" to "abnormal". The radiative insult occurs at the lower left. Clinical effects occur at the extreme upper right. The molecular lesion spectra introduced in this work are located about midway along the curve. In the same way as MLS are mapped onto the radiations, there exists the possibility that clinical effects might be mapped onto MLS.

FIGURE 2

Examples of molecular lesion spectra (lesion type versus lesion frequency) for 405nm, 254nm and γ -ray radiations. The numbers on the abscissae correspond to the lesion indices in the text.

FIGURE 3

Test of the trained counterpropagating network for 254nm, 405nm, and γ -ray radiations. This network is discussed in the text. Input occurs in the bottom layer (8 elements or lesions), normative and selection (competition) processes occur in the middle layers, and output occurs in the top layer. A normalized histogram of all variable weights in the network and the RMS error of the output layer during the process are shown at the top.

Abstracts

340. S. P. McGlynn and M. N. Varma, "Radiation Signatures", Proceedings of the Council of the European Community Workshop on Biophysical Modelling of Radiation Effects, Padova, Italy, September, 1991, Adam Hilger (IOP), Bristol, England (in press).

ABSTRACT: A new concept for modelling radiation risk is proposed. This concept is based on the proposal that the spectrum of molecular lesions, which we dub "the radiation signature", can be used to identify the quality of the causal radiation. If the proposal concerning radiation signatures can be established then, in principle, both prospective and retrospective risk determination can be assessed on an individual basis.

346. K. Rupnik, and S. P. McGlynn, "Molecular Lesion Spectra as Radiation Signatures", Radiation Research, (submitted).

It is proposed that the distribution of DNA molecular lesions (i.e., molecular lesion spectra, MLS) produced by a particular electromagnetic radiation characterizes that radiation, and that these distributions serve as radiation signatures. These signatures have the advantages of (1) high fidelity, (2) persistence times at least ten orders of magnitude greater than track structures, and (3) a space-time cellular position which is approximately half way between initial insult and ultimate biological dysfunction. Examples of such spectra are presented for 405nm, 254nm and γ -ray radiations, and are visually distinctive. Unfortunately, the data bases for other radiations, particulate and electromagnetic, are incomplete. We propose the application of adaptive feature recognition and classification techniques to the extraction of radiation signatures for such incomplete data sets. We illustrate the use of an unbiased adaptive network, one trained on the experimental lesion data, using the three data sets discussed in this work. The nature and quality of data bases required to validate and extend the signature concept are discussed.

350. S. P. McGlynn, K. Rupnik and M. N. Varma, "Molecular Lesion Spectra are Radiation Signatures," Patent Application (pending).

Patent Disclosure Forms have been filed at this time. Confidentiality requirements prevent us from giving details of this application at this time.

341. S. P. McGlynn, K. Rupnik, M. N. Varma and L. Klasinc,
"Radiation Signatures for Biology," Int. J. Quant. Chem.,
Quant. Biol. Symp. in preparation for submission.

The distribution of DNA molecular lesions produced by a particular electromagnetic radiation is shown to be a characteristic of that radiation. Such molecular lesion spectra (MLS) can serve as radiation signatures. Based on experimental results for 405nm, 254nm, and γ -ray radiation, the minimum number of lesions adequate for a signature (minimal experimental set) is investigated encompassing two different network architectures and different lesion sets consisting of 8, 5, 4, 3 and 2 lesions. It appears that a two lesion set will suffice for the three radiations of interest, but the quality of the signature suggests that a specific three lesion set is the best.

B. ELECTRONIC STRUCTURE

1. Steroids

Investigations of the electronic structure of steroids were continued experimentally (PES, NMR, FTMS, Synthesis of model compounds) and theoretically (SCF, MNDO, MM2, *ab initio* STO-3G and 3-21G calculations), the emphasis being the determination of the electronic distributions within the frontier ("ribbon-like") orbitals of the steroid hydrocarbon androstane and, the role of these orbitals in coupling substituents, particularly those in the 3-and/or 11- and/or 16- and/or 17- positions. The 3-, 11- and 17- positions are those which are usually found to be substituted in biologically-active steroids. The theoretical and experimental evidences suggest that the coupling between substituents in steroidal systems is provided by interactions with the frontier orbitals of the intervening molecular fragments. Efficient intramolecular electron transfer has been found for 3,16-disubstituted androstanes. It follows that the "ribbon-like" orbitals of saturated polycyclic hydrocarbons can "conduct" electrons over ten or even more single CC bonds.

According to its photoelectron (PE) spectrum 5α -androstane has two characteristic low energy ionizations of 9.21 eV and 9.49 eV which, assuming Koopmans' theorem, correspond to the release of electrons from the two highest occupied MO's of the molecule. These energies, both absolutely and relatively, are in excellent accord with the STO-3G results.

The 3-21G calculations are still underway because of the extensive optimization procedures that are required. Qualitative arguments indicate that these two topmost orbitals contain C2p AO's aligned somewhat in the molecular plane. Indeed, MNDO calculation yields a HOMO with constituent C2p AO's aligned along the short molecular axis (T-type MO) and a SHOMO in which the C2p AO's are aligned along the long molecular axis (L-type MO). It is believed that such MO's, best described as a mixture of σ_{CC} and π_{CH_2} orbitals and colloquially termed "ribbon orbitals," are essential for the transmission of electronic effects in large saturated polycyclic hydrocarbon molecules.

According to MNDO calculations for the androstanones, the T-type MO interacts with 3-substituents, while the L-type MO interacts with 17-substituents, the same exclusivity being retained for 3,17-disubstitution. The 16-substituent, however, interacts with both types of MO and, as a consequence, so also do dual substituents, one each in the 3 and 16 positions. This behavior leads one to

assume that, in 3,16- disubstitution, long range electronic interaction should be heavily promoted. In the STO-3G calculation the order of the two orbitals is reversed relative to the MNDO situation: that is, the HOMO is now L-type and the SHOMO is T-type. The electron distribution of these L-and T-type MO's is somewhat lumped on the inner B and C ring carbons according to MNDO results, but is more evenly distributed over all four rings in the STO-3G calculation. In particular, the electron density at C3 of the L-type HOMO and C16 of the T-type SHOMO is considerably higher in STO-3G than in MNDO. Thus, the STO-3G calculations suggest ribbon-like MO's that are better suited for the transmission of electronic effects. They also suggest that such transmissions will be particularly effective in the case of 3,16-disubstitution. The energy inversion of L-and T-type MO's that occurs in the two computations is not really discriminatory because of the near accidental degeneracy of these ribbon-like MO's ($\Delta_{\text{MNDO}} = 0.117\text{eV}$ and $\Delta_{\text{STO-3G}} = -0.154\text{eV}$). The salient point is that the STO-3G computation both validates and enhances the concept of ribbon-like MO's for both the SHOMO and HOMO of 5 α -androstane and, by extension, for steroids generally.

Abstracts

317. Lj. Pasa-Tolic, B. Kovac, L. Klasinc, J. V. Knop, C. Kubli-Garfias and S. P. McGlynn, "Photoelectron Spectra, MNDO Calculations and Electronic Structure of Some Saturated Steroids," *Croat. Chem. Acta* **62**, (4) 813 (1989).

Photoelectron (PE) spectra in connection with semiempirical MNDO SCF MO calculations (assuming validity of Koopmans' theorem) and empirical arguments (i.e. composite molecule method) are used to derive (valence) electron structure of 5 α -androstane (1), 5 α -androstan-3-one (2), 5 α -androstan-11-one (3), 5 α -androstan-17-one (4), 5 α -androstane-3,17-dione (5) and 5 α -androstane-3,11,17-trione (6).

324. L. Klasinc, Lj. Pasa-Tolic, H. Spiegl, J. V. Knop and S. P. McGlynn, "Electronic Structures and Long-Range Interaction in Androstanes," *Computers Chem.*, **14**, 287 (1990).

Abstract—The results of semiempirical MNDO calculations with full geometry optimization are reported for 5 α -androstane, 5 α -androstan-3-one, 5 α -androstan-11-one, 5 α -androstan-16-one, 5 α -androstan-17-one, 5 α -androstane-3,16-dione, 5 α -androstane-3,17-dione, 5 α -androstane-3,11,17-trione, and five of its unsaturated keto derivatives: androst-5-en-17-one, androst-4-ene-3,16-dione, androst-4-ene-3,17-dione, androst-5-ene-3,17-dione and androsta-1,4-diene-3,17-dione. Emphasis is placed on the long-range effects of carbonyl group(s) located at the biologically important 3-, 11- and/or 17-positions, and on the dependence of these effects on the presence of interpolated localized double bonds. The effects of placing the carbonyl group in the 16- rather than the 17-position were studied and it was found that the former location produced a more efficient mixing of longitudinal and transversal ribbon-like σ -orbitals of the steroidal skeleton and, hence, enhanced the long-range coupling with substituents in the 3-position. Such long-range effects seem to exert considerable influence on conformation and activity, and, particularly, on the fast intramolecular electron transfer that has been observed recently in steroid solutions.

336. L. Klasinc, Lj. Pasa-Tolic, H. Spiegl, J. V. Knop, and S. P. McGlynn, "Positional and Conformational Dependence of Long-Range Interaction in 3,16 - and 3,17 - Androstanediones," J. Math. Chem. 8, 179 (1991).

The 5α - and 5β -conformations of androstane, androstan-3-one, androstan-16-one, androstan-17-one, androstane-3,16-dione and androstane-3,17-dione have been calculated by the SCF MNDO method, using full geometry optimization, in order to assess the dependence of long-range electronic interactions of the carbonyl groups on their location and on the conformation of the steroid ring system.

337. Lj. Pasa-Tolic, L. Klasinc, H. Spiegl, J.V. Knop, and S. P. McGlynn, "Ab-initio Calculations on 5α - Androstanes," Int. J. Quant. Chem.: Quant. Biol. Symp. 41, 815 (1992)

The electronic structure of 5α -androstande, the parent hydrocarbon of the hormonal steroids, has been computed by ab initio scf methods in an STO-3G basis. The results are compared with existing MNDO computations and are used to discuss long-range electronic interactions between distant substituents that might be appended to rings A and D of 5α -androstande. It is thought that these interactions are mediated by the ribbonlike π system of the parent molecule.

2. Vitamins

This work continues the study of solid-state binding energy shifts of inner-shell levels in biologically-important molecules. In these processes, energy is deposited in volumes of the order of nanometers³, and the specific atomic characteristics, which are dependent on the atomic environment, may be elucidated. Indeed, these processes serve as very precise probes of energy transfer and deposition. As a result, we are able to probe the positions of potentially sensitive sites in biomolecular structures exposed to radiation insult. In this work, the inner shell levels of ascorbic acid (AA) and some related model compounds were examined. The intramolecular and extramolecular electronic structures and electronic redistributions occurring during the process of radiation insult were investigated. *Ab initio* and semiempirical (SCC-MO) models were used to interpret the observed phenomena.

We plan to continue the present study of binding energy shifts in the X-ray energy region. However, we will now focus on radiation-induced damage in DNA, which fits well with our concerns in the radiation signature field and in the valence photoelectron spectroscopy of the DNA bases.

The major goal is the development of biophysical/biochemical models of radiation damage in DNA. The photoelectron spectroscopic data will be used to test the assumptions of current models of biophysical/biochemical mechanisms of radiation damage. For example, we believe that theoretical research in this area can model or distinguish between models of the mechanisms of sub-lesion to lesion branching and lesion-lesion interactions.

Following Siegbahn's development of ESCA, we were among the first to develop and apply an effective computational technique to the study of X-ray induced electronic processes (ionization, excitation, Auger, etc.,) in biologically-important molecules. However, the whole area needs reinvestigation. It is expected that the use of synchrotron radiation and VUV lasers the last of which are still being developed, could add much to this area.

In sum, the present theoretical work and the potential for more precise experimental data suggest that we have opened up a very fertile, very important area.

Abstract

342. M. Eckert-Maksic, Z. B. Maksic, M. Hodoscek, and K. Rupnik, "Intra- and Extramolecular Electrostatic Potentials in Vitamin C" J. Mol. Struct. THEOCHEM, (in press).

Solid state binding energy shifts of inner-shell levels in ascorbic acid (AA) and in some related model compounds are examined by the SCC AMEP model. The relaxation effects are approximately but explicitly taken into account by employing transition potential (TP) and equivalent core (EC) concepts. It is shown that that final state polarization (relaxation) effect is decisive in determining the most favourable site of protonation. The calculated *ab initio* extramolecular electrostatic potential (MEP) contours proved useful in this respect. Results discussed in the present paper are in accordance with chemical intuition and available experimental findings. They provide a rather nice illustration of the importance of the electrostatic potential in rationalizing chemical phenomena.

3. General

Much of the attraction of photoelectron spectroscopy (PES), in its early years at least, was vested in the belief that one of the most basic concepts of modern chemistry, namely the orbital concept, would be interpretively sufficient and, further, that this belief was experimentally vindicated by the existing PES data. Now, after a quarter of a century, it is clear that PES has outgrown this convenient, but naive expectation, that the whole area has become much less transparent and quite multilayered, and that a particular interpretive mode will often be determined by the viewpoint, intention and purpose of the modern investigator. None the less, while the "now" investigator tends to move away centrifugally from the familiar picture of photoejection of electrons from orbitals and photo-creation of holes in these orbital levels, and while he may, for example, present his story as time-dependent scattering process, he and/or the users of his results will invariably refer the conclusion back to the orbital concept because of the simplicity and utility which this referral confers. Indeed, if the orbital concept were to lose such utility vis-a-vis PES data, it is quite sure that the PES technique would lose its somewhat special status and become no more than another physical method for the investigation of matter.

In the work performed during this 3-year period we have used the orbital interpretive model to combine PES experimental results with quantum chemical calculations. We have elucidated the electronic structure of numerous biologically active or otherwise important molecules: nitroethene, p-quinones, semiquinones, aromatic ketones, thiooxamides, numerous lignin model compounds, halogenofurans and methyl pseudohalides. We have been particularly interested in the assignment of lone-pair ionizations, which, because of a lack of HeII/HeI intensity ratios and sufficient spectral resolution have been often incorrectly assigned in previous works. The lone pair electrons play a crucial role in determining the properties of biologically active molecules.

A continuation of work along these lines on biologically active molecules is important for a number of reasons:

- (i) It provides chemists and biologists an interpretive mode that is a part of their existing theoretical armamentarium.
- (ii) Increased computer power brings high quality *ab initio* methods more and more into the range of big biomolecules. In addition many of the existing semiempirical many- and one-electron-methods have been specifically

parametrized for PES, and they provide a convenient, first-run interpretive approach that can be refined using various correlative techniques.

(iii) It is a technique which, when wedded to experience, is usually pretty much on target relative to ion-state assignments.

Abstracts

323. S. P. McGlynn, K. Wittel and L. Klasinc, "The Orbital Concept as a Foundation for Photoelectron Spectroscopy," of Theoretical Models of Chemical Bonding, Part 3 of Molecular Spectroscopy, Electronic Structure and Intramolecular Interactions, ed. Z. B. Maksic, Springer Verlag, Berlin, 1991, p. 63

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327. Lj. Pasa-Tolic, L. Klasinc and S. P. McGlynn, "The He I PE Spectrum and Electronic Structure of Nitroethene," *Chem. Phys. Lett.* **170**, 113, (1990).

The HeI photoelectron (PE) spectrum of nitroethene is presented. Four groups of bands are observed, the group ranges being 11–12.5, 14–15.5, 16–17 and 17–18 eV. Fine structure analysis of the first group (assigned empirically as π_{O}^* , π_{CC} , n_{O}^* and n_{C}^* , with the specific order of the last two being uncertain) indicates that the electrons of the NO_2 group are distributed much the same in both nitromethane and nitroethene. A comparison with quantum chemical results is given.

329. Lj. Pasa-Tolic, B. Kovac, L. Klasinc, S. M. Shevchenko, and S. P. McGlynn, "Photoelectron Spectroscopy of Biologically active Molecules. 20. para-Quinones, Semiquinones, and Aromatic Ketones," *Int. J. Quant. Chem.: Quant. Chem. Symp.* **24**, 799 (1990).

We have recorded and analyzed the HeI PE spectra of the following molecules: 9,10-dihydroanthracene (1); 9,10(H)-anthracenone (2); 9,10-anthracenedione (3); 1,2,3,4-tetrahydro-9,10-anthracenedione (4); 1,4,1a,4a-tetrahydro-9,10-anthracenedione (5); 10-methylene-9,10(H)-anthracenone (6); and 10-(phenylmethylene)-9,10(H)-anthracenone (7). The PE spectra are assigned by comparison with those of the composite parts (i.e., by employing an orbital interaction model such as the composite molecule method). This approach, which works surprisingly well in the present instance, indicates that the carbonyl lone pair and the carbonyl π electrons interact negligibly with the outer π electrons of the aromatic unit(s). If no change in conformation of the component aromatic parts occurs, the spectrum of the composite molecule exhibits the additivity property. This result agrees with previous studies of benzophenones [3]. However, it is argued that the ordering of the strongly overlapped, low energy ionization bands of benzaldehyde and acetophenone should be changed to $I_1(\pi)$, $I_2(\pi) \approx I_3(n_{\text{O}})$ and $I_1(\pi)$, $I_2(n_{\text{O}})$, $I_3(\pi)$, respectively.

330. L. Klasinc and S. P. McGlynn, "Photoelectron Spectroscopy of Biologically Active Molecules. 21. Thiooxamides," *Int. J. Quant. Chem: Quant. Chem. Symp.* 24, 813 (1990).

The He I photoelectron (PE) spectra of N^O, N^O -dimethyl-monothiooxamide (1), its analogue N^S, N^S -dimethylmonothiooxamide (2), dithiooxamide (3), N, N' -dimethyldithiooxamide (4), and N, N', N', N' -tetramethyldithiooxamide (5) are presented. The results of CNDO/2 calculations, the PE spectra of the related compounds acetamide, thioacetamide, thiourea, and their methyl derivatives, and He I/He II intensity considerations are used to assign the spectra.

331. Lj. Pasa-Tolic, B. Kovac, L. Klasinc, and S. M. Shevchenko, "Photoelectron Spectra of Lignin Model Compounds," *Croat. Chem. Acta* 63, 37 (1990).

The He I photoelectron (PE) spectra of the 77 lignin subunits were measured and arranged in classes of compounds according to the following functional groups: aldehydes, ketones, alcohols, carboxylic acids, functionalized polymethyl benzenes and miscellaneous lignin subunits. In all spectra the highest occupied molecular orbital (HOMO) was assigned to a π -orbital.

335. L. Nyulaszi, T. Vezpremi, J. Reffy, G. Zsombok, T. Cvitas, B. Kovac, L. Klasinc and S. P. McGlynn, "Photoelectron Spectra of Halogenofurans," *Int. J. Quant. Chem: Quant. Chem. Symp.* 25, 479 (1991).

The UV photoelectron spectra of 2-halogenofurans, together with 3-iodo and 2,5-diiodofurans, have been studied. The assignment of the lower energy region of the spectra was based on correlation of the ring π - and halogen levels in the related compounds, resolved vibrational structure, and in case of 2- and 2,5-diiodofurans by considering the relative intensities of their He I/He II spectra.

345. T. Pasinszki, T. Veszpremi, M. Feher, B. Kovac, L. Klasinc and S. P. McGlynn, "The Photoelectron Spectra of Methyl Pseudohalides," *Int. J. Quantum Chem. Quantum Chem. Symp.* (in press).

The He I and He II photoelectron (PE) spectra of methyl pseudohalides (MeNCO, MeNCS, MeNCSe, MeSCN and MeSeCN) have been recorded. Assignments are based on 3-21G *ab initio* quantum-chemical calculations, and their comparison with high-resolution He I spectra and He I/ He II band intensity ratios. Contradictions found in previous works are largely resolved. The strikingly different spectra of the isomeric forms are interpreted using a consistent model for a methyl-distorted $^{\#}\text{NCX}$ substructure. The effects of the heavy atoms are also discussed.

C. LASER OPTOGALVANIC EFFECT

The laser optogalvanic (LOG) technique is an extremely versatile and sensitive detection/spectroscopic tool. It has found important applications in such diverse areas as combustion diagnostics, plasma studies, atomic and molecular spectroscopy, gas laser stabilization, environmental monitoring, etc. Despite these applications, the exact mechanism(s) for the generation of LOG signals were not clearly understood. Obviously, full exploitation of this technique requires a better understanding of these mechanisms.

The LOG effect is the change of electrical impedance of a plasma produced by resonant absorption of laser radiation by a plasma moiety. This effect was discovered by Penning in 1928. However, the technique remained dormant until after the development of tunable dye-lasers and gained prominence in early eighties.

Our initial objective in the LOG area was to understand the mechanisms involved in the generation of LOG signals, to find the optimum experimental configuration for a particular application, and to develop it as a sensitive analytic and spectroscopic tool. We discovered rather rapidly that the optogalvanic effect was not properly understood, and that the comprehension of the basic physics underlying the phenomenon was in part wrong and/or incomplete. Thus, we had to devote ourselves to extensive investigations into the characteristics and mechanisms of production of LOG signals. These attempts have been largely successful and, as a result, we have shown that:

- (i) The temporal profile of a LOG signal contains two physically distinct components: one attributable to ionization rate changes, the other to an optoacoustic effect.
- (ii) Under suitable conditions, these two components are uniquely separable, even when they exhibit extensive temporal overlap, by an experimental method which treats the plasma as an integral of circuit component.
- (iii) The physical origins of these two components may be understood using simple term diagrams for the laser excited species. In this regard, we have emphasized some halogens and rare gases (I₂, Br₂, Ne, Ar).
- (iv) The plasma, as sensed by the LOG effect, is a very sensitive optoacoustic detector.
- (v) The physical processes, underlying the LOG effect, whether produced by radiative or collisional ionization, or by the movement of bulk positive ions, can be disentangled.
- (vi) Capacitively (or inductively) coupled rf discharge (with no internal electrodes) in conjunction with transverse laser (pulsed) excitation provides an excellent experimental configuration.

These are significant findings. Plasma is a complex mixture of different species (neutrals, ions, etc.) in various states of excitation. In addition, lack of knowledge about various rates/cross-sections prohibits accurate quantitative modeling. The separation and identification of the IRC and OA components in the temporal profile of a LOG signal can provide important information about various excited states and plasma processes. Our patent application regarding these findings has recently been approved by the U. S. Patent Office.

Our interpretation of the various components in the temporal profile of a LOG signal provides a simple and accurate procedure for investigation of radiation trapping of strongly self-absorbed atomic emission lines. Our initial attempts to investigate OH⁻ generated in an rf discharge in water were not successful, primarily because of the lack of a tunable IR laser. This experimental apparatus we hope, will be acquired in the near future.

Since the LOG signal is generated either by one or both of ionization rate changes and optoacoustic effects, both of which are inherently sensitive processes, the detectivity limits for plasma species can be extremely low. For example, detectivity limits for Xenon can readily approach the fmole range. This suggests an important application for low-level monitoring of environmental Radon. This will, of course, involve some developmental work involving two and multi-component mixtures. This specific application will form the basis of a separate research proposal which will be submitted to the Department of Energy in the near future.

Our ability to disentangle and identify the individual IRC and OA components in the temporal profiles of pulsed LOG signals will permit us to discriminate between two interfering species. This is a serious problem which besets some prominent detection/analysis technologies (e.g., Inductively-coupled Plasma (ICP)). Thus, the LOG technique can evolve as a sensitive environmental monitoring tool, either as a complementary adjunct to ICP fluorescence or as a real time monitor for simultaneous maximizing burn energy production and minimizing burn pollutant generation. It will also evolve into a superb probe of plasma characteristics, particularly as these relate to etching/deposition applications in microelectronics.

The full impact of our contribution to this area of research can only be assessed in the future. We believe it will be large.

Abstracts

321. D. Kumar and S. P. McGlynn, "Nature of Laser Optogalvanic Signals," Proceedings of International Conference on LASERS '89, D. B. Harris and T. M. Shay, Eds. STS Press, 1990, p. 757.

Laser optogalvanic (LOG) signals are believed to be generated primarily by laser-induced changes in the equilibrium ionization rate of a discharge. Recent work has shown that photoacoustic (PA) effects can also play an important role in the generation of LOG signals [Kumar et al., J. Chem. Phys. 90, 4008 (1989)] and that no thermal effects or ionization rate changes are involved in the final step of such signal production. The PA mediated components may be superimposed on the other components and a complex temporal profile of the LOG signal may result.

We report a technique by which the two types of components may be distinguished even when they overlap temporally. This technique is applicable to rf discharges, and concerns marked changes induced in the temporal profiles of LOG signals as the rf frequency is altered about the resonance frequency. Results from time-resolved studies in a ~30 MHz rf discharge in ~5-torr neon are presented.

322. D. Kumar and S. P. McGlynn, "Laser Optogalvanic Spectroscopy," Proceedings of International Conference on LASERS '89, D. B. Harris and T. M. Shay, Eds. STS Press, 1990, p. 753.

Various configurations for laser optogalvanic (LOG) studies are discussed. Emphasis is placed on pulsed laser optogalvanic spectroscopy of atoms and molecules (Xe, Cs, Ne, I₂) in a radiofrequency discharge. The photoacoustic effect is found to be a major contributor to the LOG signal. The nature and magnitude of this contribution is assessed.

326. D. Kumar and S. P. McGlynn, "Role of Photoacoustics in Optogalvanics," J. Chem. Phys. 93, 3899 (1990).

Time-resolved laser optogalvanic (LOG) signals have been induced by pulsed laser excitation ($1s_1 - 2p_k$, Paschen notation) of a ~30 MHz radio-frequency (rf) discharge in neon at ~5 torr. Dramatic changes of the shape/polarity of certain parts of the LOG signals occur when the rf excitation frequency is scanned over the electrical resonance peak of the plasma and the associated driving/detecting circuits. These effects are attributed to ionization rate changes (i.e., laser-induced alterations of the plasma conductivity), with concomitant variations in the plasma resonance characteristics. In addition to ionization rate changes, it is shown that photoacoustic (PA) effects also play a significant role in the generation of the LOG signal. Those parts of the LOG signal that are invariant with respect to the rf frequency are attributed to a PA effect. The similarity of LOG signal shapes from both rf and dc discharges suggests that photoacoustics play a similar role in the LOG effect in dc discharges. Contrary to common belief, most reported LOG signal profiles, ones produced by excitation to levels that do not lie close to the ionization threshold, appear to be totally mediated by the PA effect.

332. D. Kumar and S. P. McGlynn, "Ionization and Photoacoustically Mediated Optogalvanic Signals," Chem. Phys. Lett. 176, 536 (1991).

We report a technique which permits distinction between conventional optogalvanic signals, ones produced by ionization rate changes, and photoacoustically mediated optogalvanic signals, ones which do not involve ionization rate changes. The effects of rf frequency changes near resonance on the temporal profiles of the optogalvanic signals produced by pulsed laser excitation of an rf neon discharge permit this distinction. The results show that many temporal profiles reported in the literature (even for laser excitation into the discharge) are dominated by the photoacoustic effect.

338. D. Kumar and S. P. McGlynn, "Analysis of Radiofrequency Discharges in Plasma," Patent Application (Patent Granted) 1992.

Separation of laser optogalvanic signals in plasma into two components: (1) an ionization rate change component, and (2) a photoacoustic mediated component. This separation of components may be performed even when the two components overlap in time, by measuring time-resolved laser optogalvanic signals in an rf discharge plasma as the rf frequency is varied near the electrical resonance peak of the plasma and associated driving/detecting circuits. A novel spectrometer may be constructed to make these measurements. Such a spectrometer would be useful in better understanding and controlling such processes as plasma etching and plasma deposition.

343. S. P. McGlynn and D. Kumar, "The Laser Optogalvanic (LOG) Effect in Radiofrequency Discharges," Proceedings of the International Society for Optical Engineering Meeting on *Lasers, Sensors and Spectroscopy*, Los Angeles, Calif., January, 1992 (in press).

The laser optogalvanic (LOG) technique is an extremely versatile and sensitive detection/spectroscopic tool. Full exploitation of this technique requires a better understanding of the mechanisms involved in the generation of LOG signals. The temporal profile of a LOG signal consists, in general of two overlapping but distinctly generated components, one mediated by ionization rate changes and the other by acoustic effects. These components, when resolved, can provide considerable information about various excited states and plasma processes. Some sample results are presented for neon and iodine, and the use of energy level diagrams for the isolation of various physical processes is demonstrated.

351. R. Armstrong, "A Study of the Optogalvanic Effect in Water and Argon," a report presented to LaSER (Louisiana Stimulus for Excellence in Research), January, 1992.

The behavior of the laser optogalvanic (LOG) effect in ~30MHz radiofrequency discharge in Argon, and water vapor was studied with a pulsed, tunable dye laser. The Argon pressure was unknown, whereas the pressure of water vapor corresponded to vapor pressures at temperatures ranging from ~ -40°C to ~20°C. In Argon, a LOG signal was observed at ~452nm for the transition $1s_3 \rightarrow 3p_{10}$ (Paschen notation). In water vapor a strong, wavelength independent, LOG signal was determined to be due to excitation into the ionization continuum. A weak LOG signal observed at ~656nm was assigned to the $2s \rightarrow 3p$ transition in atomic hydrogen, which is produced by dissociation of water molecules.

D. VACUUM ULTRAVIOLET SPECTROSCOPY

1. Electron Scattering

Most of our spectroscopic work has been confined to the measurement of electron scattering cross sections for a number of reasons, all of them derivative of our own work. These are:

- - -The spectroscopic method is much quicker than either time-of-flight (TOF) or swarm measurements (days as opposed to weeks or months).

- - -The spectroscopic method appears to yield zero-energy cross-sections, whereas a MERT extrapolation must be used to remove residual energy effects in both TOF and swarm experiments before zero-energy cross-sections become available. MERT extrapolations are neither easy nor accurate, and sometimes they can be wrong.

- - -We have performed spectroscopic density effect measurements at 70atm and see no reason why we cannot go to even higher pressures. Thus, the ability to cross the gas/liquid boundary is at hand. Consequently, we are in a position to study band development, scattering changes, etc. as we cross the pressure boundary between gas and liquid. This capability is not inherent in either the TOF or swarm methods.

- - -Since data can be generated quickly, we are in a position to investigate many scatterer entities and, hence, to delineate empirically the dependence of scattering length on scatterer polarizability. Indeed, we have already generated some very salient insights on this dependency.

- - -The spectroscopic method provides a direct measure of scattering length. The other methods do not. The scattering length can be either negative or positive, and provides some direct insights into the scattering potential. Indeed, one could say that our work has directed attention to the lengths, and away from the cross-sections where, unfortunately, it should not have focussed.

- - -The plus/minus nature of lengths provides a very simple means of devising mixtures with tailored scattering lengths and, hence, cross-sections.

- - -The demonstration that autoionization effects may be used in the same way as found Rydberg absorptivities opens up the ability to study opaque perturbers, and hence to greatly expand the data base.

In view of the above, it is clear that this is an important research venture. Hence, we now provide a more rambling and, therefore, more informative discussion.

We have shown that spectroscopic studies of perturber number density effects for both atomic and molecular perturbers is the most efficient approach to a study of the mechanisms of momentum and energy transfer and energy deposition in density dependent, highly-energetic electronic processes. Indeed, our recent VUV study of CH_3I and C_6H_6 and H_2 was the first measurement of the effects of a molecular perturber on the high- n Rydberg transitions of molecular absorbers.

The measured spectral shifts may be used to generate scattering cross-sections and electronic scattering lengths for perturbers. The shifts of molecular absorbers, even in the large number density range (~ 70 atm), have been found to vary linearly with densities for both atomic (Ar) and molecular (H_2) perturbers. The results indicate that this sort of experiment can approach perturber densities comparable to those of liquids. In view of these results, well-known criteria, which suppose that Rydberg series should be broadened or disappear in highly dense and liquid media whereas valence transitions should not, demand further examination.

A new experimental method, using autoionization spectra for the determination of pressure shifts, was also developed. All in all, photoabsorption and autoionization spectra of CH_3I have generated pressure shift data for 11 perturber gases. The perturbers include molecules such as CO_2 , CH_4 , C_2H_6 and C_3H_8 . As a result, electron scattering lengths have been obtained for these perturber gases, some for the first time.

Recent experiments on the CH_3I /nitrogen systems have addressed the role of polarizability in electronic scattering processes and, in particular, have used the Alekseev-Sobel'mann polarizability dependence.

We have compared three sets of scattering length data: one from density effects on high- n Rydberg states of CH_3I , a second from TOF data, and a third from the drift of electron swarms. The latter two data sets yield a scattering length A only after a MERT extrapolation to zero energy.

The primary adjustable parameter in the MERT expression is the electron scattering length. A comparison of scattering lengths from pressure shift data for the Rydberg states $n=10-16$ (0.13-0.05eV) with those from MERT expansions yields generally good agreement.

We have investigated mixtures of rare gases of different signs in order to make mixtures with an effective, net scattering length of zero. Perturber gases of positive scattering length (He, Ne, H_2) exhibit a blue spectral shift, while those of negative scattering length (Ar, Kr, Xe, CH_4 , CO_2 , C_2H_6 , etc.) produce a red shift.

The observed "additivity" in mixtures of gases provides the ability to tailor any value, including zero, for an effective cross-section.

We have investigated the role of atomic and molecular polarizabilities in scattering. For example, following atomic effective-range theory, which applies to neutral electron scatterers, we find that a simple linear correlation brings the rare gases into a common frame: that is, a linear correlation exists between the electron scattering length, A , of the atomic perturbers and the polarizability of the rare gases. This correlation, evades any MERT extrapolation, in the sense that the direct results of measurement provide scattering lengths at the low-energy limit. Finally, it also illumines the nature of the scattering potential, whether repulsive or attractive, since the correlative behavior predicts both the size and sign of the electron scattering length.

Our recent work has begun to focus in on the polarizability. We find two separate correlations: one for the rare gases and CH_4 which uses α , the other for H_2 , N_2 , C_2H_6 and C_3H_8 which uses $\bar{\alpha}$, the average polarizability. The two lines have essentially the same intercept of ~ 1.23 but quite different slopes. The results indicate that the more anisotropic molecular systems "see" electrons in a different way than do isotropic systems. This behavior is the subject of much of our present work.

These correlations between electron scattering lengths and polarizabilities indicates that Rydberg electron scattering by atomic and molecular perturbers should be described in terms of spatio-temporal response functions for the perturbers.

Abstracts

315. U. Asaf, W. S. Felps, K. Rupnik, G. Ascarelli and S. P. McGlynn, "Density Effects on High- n Molecular Rydberg States: CH_3I and C_6H_6 in H_2 and Ar". J. Chem. Phys. 91, 5170 (1989).

The absorption spectra of high- n Rydberg states of methyl iodide and benzene perturbed by varying number densities of hydrogen or argon, range 0.9×10^{20} – $10.5 \times 10^{20} \text{ cm}^{-3}$ for H_2 and 0.6×10^{20} – $7.5 \times 10^{20} \text{ cm}^{-3}$ for Ar, have been investigated. The high- n molecular states of both absorbers were found to shift linearly with the number density of atomic Ar and molecular H_2 scatterers. The Fermi formula modified by the Alekseev–Sobel'man polarization term provides an excellent fit of the shift data. The electron scattering lengths obtained are: $0.93 a_0$ for H_2 and $-1.63 a_0$ for Ar using the CH_3I absorber; and $0.99 a_0$ for H_2 and $-1.57 a_0$ for Ar using the C_6H_6 absorber. The electron scattering lengths for H_2 and Ar agree with the results of an empirical model that correlates scattering lengths and the polarizabilities α (spherical) for inert atoms and α_2 (nonspherical) for H_2 molecule.

316. U. Asaf, W. S. Felps and S. P. McGlynn, "Electron Scattering in Dense He-Ar Gas Mixtures: A Pressure Shift Study". Phys. Rev. A, 40, 5458 (1989).

The dependence of the energies of high- n Rydberg states of CH_3I on the molar composition of helium-argon mixtures (in the number density range 1.3×10^{20} – $5.6 \times 10^{20} \text{ cm}^{-3}$) is reported. The energy shifts, when normalized to a given density value, are found to vary linearly with the mole fraction of either component of the binary, rare-gas mixture. The observed change in sign of the energy shift is attributable to the different signs of the electron scattering lengths for the two rare-gas components. As a result, there exists a mixture composition, at a mole ratio $[\text{He}]/[\text{Ar}] = 2.0$, at which the shift is null. The experimental results for the gas mixture agree with the Fermi formula, as modified to include the Alekseev–Sobel'man polarization term. Effective electron scattering lengths and cross sections, polarizabilities, and thermal velocities are used to characterize the effects of the binary gas perturber system.

318. K. Rupnik, U. Asaf and S. P. McGlynn, "Electron Scattering in Dense Atomic and Molecular Gases: An Empirical Correlation of Polarizability and Electron Scattering Length," J. Chem. Phys., 92, 2303 (1990).

A linear correlation exists between the electron scattering length, as measured by a pressure shift method, and the polarizabilities for He, Ne, Ar, Kr, and Xe gases. The correlative algorithm has excellent predictive capability for the electron scattering lengths of mixtures of rare gases, simple molecular gases such as H₂ and N₂ and even complex molecular entities such as methane, CH₄.

320. K. Rupnik, "VUV and Laser Raman Studies in the Correlation Between Atomic and Molecular Polarizabilities and the Number Density Shifts," Proceedings of Laser's '89 International Conference on LASERS '89, "D. B. Harris and T. M. Shay, Eds. STS Press, 1990, p. p. 757.

This work is the first attempt to investigate the possible mechanisms of the radiative (VUV field induced) momentum transfer or coupling between the molecular perturbers and high-*n* Rydberg absorbers. A phase space approach using correlation functions is proposed for the interpretation of these processes in the gases. It is found from the density shift study, that the atomic and the anisotropic molecular polarizabilities are related to a single "active" correlation function component which is coupled to the correlation function describing high-*n* Rydberg transitions. We propose VUV and Raman study of the number density effects for some of the following systems (HF, NH₃, C₂H₄, H₂CO, CO₂, HCN, C₂H₂, and CH₃CN). In order to give a proper description of the total response function of the medium (the polarizabilities and their correlation functions) we are also interested in the investigation of their Raman and Rayleigh spectra (from ~ 0 to 5000cm⁻¹). The Raman spectra of some substituted iodomethanes (CH₃I, CHD₂I and CD₃I) are presented. The results of the study indicate that the role of electrons in the observed VUV transitions should be questioned and investigated in terms of their correlation functions. While it is commonly believed that the electron excitation mechanism is a requirement for all Rydberg transitions and the appearance of progressions, this may not be so. Indeed, these high-*n* transitions may be too "slow"- "dephasing" in absorption is too fast- to reach the electron excitation processes, so that they have no real physical significance.

328. U. Asaf, K. Rupnik, W. S. Felps and S. P. McGlynn, "Scattering of Electrons of High-Molecular Rydbergs in Dense Atomic and Molecular Gases," in "Nonequilibrium Effects in Ion and Electron Transport," J. W. Gallagher et al., Eds., Plenum, New York, 1990.

The effect of rare gases, rare gas mixtures and hydrogen on the high- n Rydberg states of methyl iodide and benzene has been discussed recently (Köhler et al., 1987; Asaf et al., 1989a; Asaf et al., 1989b; Reininger et al.,). According to the experimental evidence, the pressure induced energy shift of these molecular Rydbergs varied linearly with density up to relatively high perturber densities ($\sim 1 \times 10^{21} \text{cm}^{-3}$). These linearities can be reproduced accurately by the Fermi model modified by the Alekseev-Sobel'man polarization term (Alekseev and Sobel'man, 1966).

Electron scattering cross sections of rare gases obtained from these experimental results (Table 1) agree well with existing data for "classical" pressure shift studies using atomic Rydbergs. Electron scattering cross sections of rare gases as measured by pressure shift agree with cross sections near or at zero electron energies obtained from swarm data (Gilardini, 1972); however, large differences exist relative to H_2 swarm (Gilardini, 1972) and TOF (Ferch et al., 1980) data which are higher by 50 - 100%.

A recent empirical model (Rupnik et al.) provides a linear correlation of the electron scattering lengths of H_2 , Ne, Ar, Kr and Xe gases and atomic polarizabilities. This model suggests the use of the non-spherical polarizability for hydrogen and predicts a scattering length $a = 0.83a_0$ ($\sigma = 2.43 \times 10^{-16} \text{cm}^2$) in agreement with the result of the pressure shift study.

333. S. P. McGlynn, V. Asaf, D. Kumar, S. Felps, K. Rupnik, and L. Klasinc, "Solvent Effects in Dense Gases," *Int. J. Quant. Chem.* **39**, 399 (1991).

The effects of perturber gases, partial pressures in the range 0-50 atm, on the absorption spectra of high- n Rydbergs, $n \geq 10$, in methyl iodide and benzene have been investigated. The perturbers were rare gases and H_2 . It has been shown that the spectroscopic energy shift $\Delta = \Delta(\rho, n)$ is given by $\Delta = \Delta^0 \rho$, where ρ is the number density of the perturber, for $n \geq 10$. The shift data can be interpreted using a Fermi model, and values of scattering lengths for perturbers can be extracted. These scattering lengths are internally consistent, independent of the absorber, and in excellent agreement with electron-swarm results. Given that the Fermi model is nonspecific and microscopic, scattering shifts and lengths for mixtures of perturber gases can be predicted. These predictions, having been verified by experiment for He/Ar mixtures, provide a means of "tailoring" any required scattering length. Finally, it is shown empirically that the determinative scattering parameter is the polarizability of the perturber, and a universal relationship $a = -0.26\alpha + 1.18$ between scattering length a , in Bohr radii, and polarizability α is found to exist.

334. K. Rupnik, V. Asaf, and S. P. McGlynn, "Reply to the Comment on : Electron Scattering in Dense Atomic and Molecular Gases," J. Chem. Phys. 94, 3285 (1991).

The Freeman Comment¹ raises two issues. The first of these relates to the values of polarizability used by us.² The second relates to the need to develop new theoretical approaches to the scattering of very low-energy electrons. We shall treat each separately.

(1) We agree with Freeman that the empirical relationship between polarizability and scattering length for the rare gases is linear. Freeman also agrees with our *empirical* observation that the use of the nonspherical static polarizability, α_2 , for the diatomics H_2 and N_2 permits an excellent inclusion of their molecular scattering lengths into the linear rare gas correlation. However, for *theoretical* reasons, he would have preferred to use the mean polarizability, α_0 ; unfortunately, the use of α_0 for H_2 and N_2 does not yield correlation. The single disagreement of an *experimental* nature between Freeman and us concerns the value of the polarizability of methane, CH_4 . By analogy to H_2 and N_2 , we used $\alpha = 2/3 \alpha_0$ for CH_4 , whereas Freeman

prefers α_0 . Unfortunately neither value provides a fit to the rare gas correlation line.

(2) We agree with Freeman that new approaches to the theory of scattering for low-energy electrons are needed. In this regard, we believe that the nature of our experimental measurement of scattering shifts, namely, the energy perturbation of high- n Rydberg states of probe molecules by otherwise inert scatterer gases, is itself suggestive. In specific, this experiment suggests that radiative coupling of the absorber probe and perturber scatterer, as described by spatiotemporal correlation functions related (among other things) to scatterer polarizabilities, should provide an apt framework. Consequently, we are developing such a description.³

¹G. R. Freeman, J. Chem. Phys. 94, xxx (1991), previous comment.

²K. Rupnik, U. Asaf, and S. P. McGlynn, J. Chem. Phys. 92, 2303 (1990).

³K. Rupnik, *Proceedings of the International Conference LASERS '90* (STS Press, McLean, VA, 1990), p. 774.

347. U. Asaf, R. Reininger, K. Rupnik and S. P. McGlynn, "Pressure Shift and Electron Scattering Length in Atomic and Molecular Gases," J. Phys. Chem. (submitted).

Recent photoabsorption and autoionization spectra of CH_3I have generated pressure shift Rydberg data for 11 perturber gases. The asymptotic energy shift of these high- n Rydberg states have yielded "near zero energy" electron scattering lengths for the perturber gases. A compilation of these electron scattering lengths, as well as those obtained from swarm and time of flight electron scattering data, is presented and comparisons are made. The "zero energy" electron scattering length or cross section correlates with the polarizability of the non-polar perturber gas atoms and molecules. This correlation is discussed.

348. U. Asaf, S. Felps, K. Rupnik, and S. P. McGlynn, "Electron Scattering in Dense Hydrogen-Argon Gas Mixtures: A pressure Shift Study," Phys. Rev. A. (submitted).

Absorption spectra of high- n Rydbergs of CH_3I perturbed by varying molar compositions of hydrogen-argon mixtures in a density range $2.16\text{-}3.14 \times 10^{20} \text{ cm}^{-3}$ are reported. The energy shifts when normalized to a fixed density value, are found to vary linearly with mole fraction composition of the binary mixture. The observed change of sign in the pressure-induced energy shift is attributable to the different signs of the electron scattering length of the two components. At a mole ratio $[\text{H}_2]/[\text{Ar}] = 3$, the shift is null. The experimental pressure shift results can be reproduced by substituting effective scattering lengths, thermal velocities and polarizabilities into the Fermi equation as modified by the Alekseev-Sobel'man polarization term.

2. Photochemistry

We have analyzed the electronic absorption spectra of the cyanogen halides in a way that accounts for their electronic molecular spectroscopy and photochemistry. We have shown that intravalence excitations may not be ignored in the analysis of the electronic spectra of those polyatomic molecules in the VUV. We have discussed the relevance of our analysis to the photochemistry of the cyanogen halides. Specific predictions are presented for the production, as primaries, of various states of the CN radical and halogen atoms fragments. These predictions, in most instances, are verifiable by further photochemical investigations.

Abstract

242. W. S. Felps, K. Rupnik and S. P. McGlynn, "Intravalence Transitions of the Cyanogen Halides," This manuscript has been published with revised title, "Electronic Spectroscopy of the Cyanogen Halides," J. Phys. Chem. 95, 639 (1991).

The electronic absorption spectra of the cyanogen halides, XCN where X = Cl, Br, and I, have been investigated in the range 3100–1050 Å. The spectra are analyzed in terms of vibronic structure, oscillator strengths, and effective quantum numbers. The spectra of the cyanogen halides exhibit no regular Rydberg structure. The absence of regularity is shown to be a direct consequence of the presence of intravalence excitations and Rydberg/valence interactions. In confirmation of the above, the intravalence transitions arising from the $2\pi \rightarrow (5\sigma, 3\pi, \text{ and } 6\sigma)$ configurational excitations are observed and assigned. In addition, we presume to extract "term values" for the antibonding $5\sigma, 3\pi, \text{ and } 6\sigma$ MOs and then use these to predict the energies of the remaining nine low-energy intravalence excitations of the cyanogen halides, $\{4\sigma; 1\pi; 3\sigma\} \rightarrow \{5\sigma; 3\pi; 6\sigma\}$. There is a danger in this, in that we seem, too blithely perhaps, to make use of a simple one-electron MO model in situations where it is known that many-electron effects may dominate. We believe that the use of one-electron considerations is moderated by the extensive use of a vast amount of empirical, correlative experimental data. Finally, all excited states that arise from the 12 low-energy intravalence excitations are correlated with the states of the separated halogen atom and CN radical such that photoprocesses in the cyanogen halides may be rationalized. The A-band and α -band continua are assigned as $2\pi \rightarrow 5\sigma, {}^1,3\Pi$ and $2\pi \rightarrow 3\pi, {}^1,3\Delta, {}^1,3\Sigma^+, {}^1,3\Sigma^-$ configurational excitations, respectively. The $4\sigma \rightarrow 5\sigma, {}^1\Sigma^+$ transition is associated with the discrete structure atop the α continuum; the intense, discrete band systems that lie to the blue of the B and C Rydberg band systems are associated with the $2\pi \rightarrow 6\sigma, {}^1,3\Pi$ intravalence transitions. The states that arise from the remaining eight configurational excitations are shown to be mostly dissociative in nature. The correlation scheme predicts (i) CN ($X^2\Sigma^+$) to be the primary product of photolysis within the A continua; (ii) CN ($A^2\Pi_1$) to be the primary product of photolysis from the onset of the α continua up to photon energies of 80 000 cm^{-1} for each of the cyanogen halides, and (iii) CN ($B^2\Sigma^+$) to be a primary product for photon energies greater than $\sim 105\,000, 94\,000, \text{ and } 80\,000 \text{ cm}^{-1}$ in ClCN, BrCN, and ICN, respectively.

3. Magnetic Circular Dichroism

In this work, the emphasis is on the VUV MCD of HI. Experimental MCD work in this Laboratory has always focussed on the VUV region and on particular groups of molecules and atoms: simple gaseous molecular systems such as CH_3I which exhibit both Rydberg and valence electronic spectral structures. Our aim has been to develop an MCD VUV technique which is both easy to use and for which the results are easy to interpret.

MCD is a spectroscopic method that probes the earliest, electronic events in photophysics/photochemistry. In MCD spectroscopy, which measures the difference of absorptivity of right and left circularly polarized light, one applies a static magnetic field parallel to the incidence direction of a polarized light beam. In Circular Dichroism (CD) spectroscopy, on the other hand, one measures the difference of absorption of left and right circularly polarized light caused by the torques exerted on the molecular constituents by the electromagnetic field. Consequently, CD measurements are dependent on the molecular structure as well as on the changes that occur during interactions with the field and/or with the molecular environment. In MCD measurement the two forces, circularly polarized light and (static) magnetic field, are coupled.

Circular dichroism spectroscopy has been applied to a great variety of structures ranging from small chiral molecules to larger structures such as eukaryotic cells in solutions. MCD spectra are not so readily available. Indeed, MCD spectra are very scarce even for small molecules and are virtually non-existent in the VUV. . .this, despite the fact that all molecular systems must exhibit electronic MCD spectra whereas chirality is a prerequisite for CD spectra. Because of its general presence, MCD could

become the spectroscopy of choice for the study of molecular DNA damage, in particular local DNA molecular lesions.

The VUV absorption and MCD spectra of the first Rydberg transitions of gaseous HI have been studied at $\lambda > 140\text{nm}$, at various pressures below 1 Torr. This molecule is a simple diatomic with resolved rotational and vibrational electronic structures above the CaF_2 cutoff at 140nm. Progress in MCD measurements beyond the 140nm limit requires optics that are not presently available. An expansion of MCD spectroscopy below this limit was one of the subjects discussed at a recent Synchrotron Workshop on MCD. Analysis of the MCD spectra provides quantitative information concerning the large spin-orbit parameters ($>5000\text{ cm}^{-1}$) of the HI molecule. Indeed, the observed MCD spectra encompass the two most intense absorption bands which are the result of a spin-orbit splitting. A small shift of $\sim 20\text{ cm}^{-1}$ is observed at the center of the 62320 cm^{-1} line. The interpretation of this shift demands a quantitative interpretation of high resolution rotational and vibrational electronic spectra. Secondly, unexpectedly strong MCD signals are observed in the region of all absorption bands, some of which appear to be in complete discord with some existing state assignments, *s*, *d* or *p*. Thirdly, many of the observed (low resolution) MCD spectral structures do not meet either of the two specifications for A (derivative) or B (absorption) signal types, a simple typing which frequently is used for the analysis of low-resolution MCD spectra. Thus, the need for a model, which incorporates explicit rotational and vibrational structures is established.

Magnetic field strength effects are observed in the MCD spectrum: the intensity of the MCD lines is linear, as expected, with field, and no peak to peak shifts are observed in the A signatures. An analysis of the observed spectra as a combination of A structures, an approach similar to that used in earlier studies of opto-magnetic activity, indicates that a field induced

"mixing" of electronic states may be taking place. The observed MCD spectra may be fitted extremely well with two derivative functions, extracted from the MCD spectra in the energy region around 56740 cm^{-1} , the separation (or splitting) between the pairs of "doublets" for the first four MCD bands being in the range 20 to 90 cm^{-1} . We do not yet know the nature of the "states" implied by this analysis.

The magnetic momentum ratio obtained from the MCD spectra for the first (around 55830 cm^{-1}) and second (around 56790 cm^{-1}) bands is: $m_1/m_2 \sim 2.25$, and the ratio between the first and fourth (around 67330 cm^{-1}) bands is $m_1/m_4 \sim 2$. The magnetic moment of from the MCD spectrum in the region of the third band (around 60840 cm^{-1}) is difficult to estimate.

The MCD results call attention to the coupling mechanisms of electronic and nuclear motions in the rovibronic levels of Rydberg states. Thus we have begun an analysis based on a previously - developed spin-uncoupling model. This model was recently applied to a study of the VUV spectra of CH_3I . It was shown that uncoupling of the spin angular momentum of the optical electron from the molecular axis was essentially complete in some s- Rydberg states. We believe that this same model can account for the main MCD characteristics found in the HI spectra.

We have also initiated a computational analysis of the observed spectra, using Fourier convolution and deconvolution procedures. The results of the analysis indicate that the observed roelectronic envelope of the first electronic transition can be correlated directly to the observed MCD spectra. If successful, this study will provide direct and very specific information about low-n Rydberg electrons in magnetic fields.

Abstract

K. Rupnik, W. S. Felps, and S. P. McGlynn, "VUV Electronic Absorption and Magnetic Circular Dichroism Study of HI Molecules," in OSA Annual Meeting Technical Digest 1990, Vol. 15 of the OSA Technical Digest Series (Optical Society of America, Washington, D. C., 1990), p. 144.

We present the results of the first VUV (250–146 nm) magnetic circular dichroism (MCD) study of HI molecule in the gaseous state at various pressures below 1 Torr. MCD spectroscopy¹ measures the difference in the absorption of right and left circularly polarized light, and refers to the situation in which a static magnetic field is applied parallel to the direction of the polarized beam. This molecule is of particular interest since it is a simple diatomic that exhibits resolved rotational, vibrational and electronic structure below the CaF₂ cutoff of 140 nm. Progress in MCD measurements beyond this limit requires optics not presently available. We are investigating pressure effects and the dependence of spectra on magnetic field strength (1–5 T). The analysis of the absorption spectrum of HI molecule is also important to the proposed models of electron-nuclear momentum coupling. We are also investigating the possible role of spin-orbit mechanisms in the VUV electronic absorption and MCD of HI molecules.

Reference

1. J. D. Scott, W. S. Felps, and S. P. McGlynn, *Nuc. Instrum. and Meth.* 152, 231 (1978).

E. OZONE

Ozone is one of the most important microconstituents of Earth's atmosphere. In the stratosphere it acts as a shield against harmful UV radiation; however, in the troposphere it enters numerous reactions some of which are harmful and of considerable environmental importance. Within the report period we here investigated the rate of destruction of ozone on various powder materials and the heterogeneous reaction of ozone with polycyclic aromatic hydrocarbons (PAH's) adsorbed on the surface of a (silica-gel) carrier.

As adjunct to an earlier work on the correlation of ozone reaction rates with the ionization potentials of conjugated molecules (e.g., L. Klasinc, H. Güsten, S. P. McGlynn, Title 272 in Comprehensive Report 1983-86) we have extended the correlation almost to the diffusion controlled limit by including new results for 10,10-dimethyl-9,9' biacridylidene.

Abstracts

347. A. Alebic-Juretic, T. Cvitas and L. Klasinc, "Ozone Destruction on Powders," *Ber. Bunsenges. Phys. Chem.*, (in press).

The destruction of ozone on silica-gel, alumina, sodium chloride, calcite, Saharan sand and wood ash as model powders was studied in a fluidized bed reactor. An elevated ambient concentration of ozone (100 ppb) in the filtered air stream was applied during the experiments. The relative effectiveness of ozone destruction was in the order alumina > wood ash > silica-gel, followed by Saharan sand > calcite > sodium chloride. The implication of this result on ozone measurements in particle-rich atmospheres is discussed.

319. A. Alebic-Juretic, J. Cvitas and L. Klasinc, "Heterogeneous Polycyclic Aromatic Hydrocarbon Degradation with Ozone in Silica Gel Carrier," *Environ. Sci. Technol.* 24, 62 (1990).

■ Heterogeneous degradation of five polycyclic aromatic hydrocarbons (PAHs), perylene (Pe), pyrene (Py), benzo[a]pyrene (BaP), benz[a]anthracene (BaA), and fluoranthene (Flo), adsorbed on nonactivated (moisture-containing) silica gel with ozone in a fluidized-bed reactor has been studied. The concentrations of ozone employed varied from 0.050 to 0.400 ppm. The results obtained show that, concerning their kinetics, there is a clear difference between reactions with less than and more than monolayer coverage of the particle surface with PAHs, those carrying a submonomolecular layer being faster and indicating the effect of the particle surface. In more highly covered samples, the observed degradation obeys two distinct first-order laws, the slow one changing into the faster at monomolecular coverage; the relative reactivities are as follows: Pe > BaP > BaA > Py \gg Flo, and BaP > Pe > BaA > Py \gg Flo, respectively. According to the present results, heterogeneous degradation of PAHs by ozone on particle surfaces is one of important pathways for their removal from the atmosphere.

349. M. Surgi, D. Giamalva and L. Klasinc, "Correlation Between Ozonolysis Rate and π -Ionization Potential of 10,10'-Dimethyl,-9,9'-Biacridylidene." Bull. Slov. Chem. Soc. (submitted)

The bimolecular rate constant of ozonolysis of 10,10'-dimethyl--9,9'-biacridylidene can be correlated with its vertical ionization potential (IP). This behaviour continues a trend begun by other π -electron systems and this behaviour can be described by the equation:

$$\log (k/M^{-1}s^{-1}) = - (4.13 \pm 0.35) (IP/eV) + (35.3 \pm 8.1); r = -0.97$$

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