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PECULIARITIES OF SPECTRA OF INDUCED EMISSION
OF POLYMETHINE DYE SOLUTION AT LOW TEMPERATURES

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(NASA-TM-76680) PECULIARITIES OF SPECTRA OF
INDUCED EMISSION OF POLYMETHINE DYE
SOLUTIONS AT LOW TEMPERATURES (National
Aeronautics and Space Administration) 12 p
HC A02/BF A01 CSCI 07D G3/25

N82-20261

Unclas
16974

Translation of "Osobennosti spektrov vyzhdennoy izlucheniya
rastvorov polimetinnykh krasiteley pri nizkikh temperaturakh,"
Ukrainskiy fizicheskiy zhurnal, Vol. 20, No. 3, 1975, pp. 360-366.



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 AUGUST 1981

STANDARD TITLE PAGE

1. Report No. NASA TM-76680	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle PECULIARITIES OF SPECTRA OF INDUCED EMISSION OF POLYMETHINE DYE SOLUTIONS AT LOW TEMPERATURES		5. Report Date August 1981	6. Performing Organization Code
7. Author(s) M. V. Melishchuk, Ye. A. Tikhonov, M. T. Shpak		8. Performing Organization Report No.	10. Work Unit No.
9. Performing Organization Name and Address Leo Kanner Associates Redwood City, California 94063		11. Contract or Grant No. NASW-3199	13. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address National Aeronautics and Space Adminis- tration, Washington, D.C. 20546		14. Sponsoring Agency Code	
15. Supplementary Notes Translation of "Osobennosti spektrov vyzhdenno- izlu heniya rastvorov polimetinovykh krasiteley pri nizkikh temperaturakh," <u>Ukrainskiy fizicheskiy zhurnal</u> Vol. 20, No. 3, 1975, pp. 360-366. <i>A 75-31603</i>			
16. Abstract The results are presented of studying the induced emission spectra with monochromatic excitation (superluminescent regime) within a temperature range of 300° - 5.2° K. The significant feature of such operators is the appearance of quasi-lines whose minimum width is realized at 4.2° K. The frequency distribution of the quasi-lines unambiguously characterizes the dye investigated. When interpreting these results, the idea of an inhomogeneous broadening of the polymethine dye spectra in the solution, being studied experimentally by the authors was used for the first time. The quasi-lines observed are interpreted as a manifestation of the electron-vibration structure of singlet states of a complex molecule.			
17. Key Words (Selected by Author(s))		18. Distribution Statement THIS COPYRIGHTED SOVIET WORK IS REPRODUCED AND SOLD BY NTIS UNDER LICENSE FROM VAAP, THE SOVIET COPYRIGHT AGENCY. NO FURTHER COPYING IS PERMITTED WITHOUT PERMISSION FROM VAAP.	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 10	22.

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Introduction

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In previous works [1-3] observations of narrow lines were reported in the induced emission spectra of solutions of polymethine dye with excitation from monochromatic radiation. In reference [2], solutions were studied in which this effect is observed at room temperature. The proposal was put forward and argued as to the affiliation of these lines to the resonance induced combination scattering on molecules of dye. In reference [3], solutions were studied at 4.2°K and it was pointed out that the manifestation of the narrow-line spectrum, along with diffusion, is a typical property of the generation of solutions of dye in these conditions. In the spectra of the system in which the lines were observed at room temperature, at 4.2°K, an additional linear structure was apparent. Similarly to the effect at room temperature, these spectra were also interpreted as spectra of resonance induced combination scattering on molecules of dye; however the possibility of a **fluorescent** origin of the structure is not excluded [2]. The concept existing earlier as to properties of the spectra of absorption and spontaneous **fluorescence** of solutions of dye at low temperatures made it difficult to establish the true origin of the phenomena.

In references [4, 7, 8] also the **property of the narrow-line** part of the spectra for generation of frozen solutions of dye was studied and the affiliation of lines to resonance combination scattering on electron-excited [4-7] and unexcited [8] molecules of dye was indicated.

The study of the nature of expansion of the spectra of solutions

*Numbers in the margin indicate pagination in the foreign text.

of dyes in a broad temperature range¹ made it possible to establish that at low temperatures the spectra of absorption and fluorescence expand unevenly and this causes the dependence of the shape of the curve and the position of maxima of the fluorescent bands on wavelengths and the half-width of the excitation band similar to that observed with combination scattering. In references [9, 10], it was pointed out that with the appropriate selection of the solvent (the Shpol'skiy effect) or the properties of excited light (in particular, the use of a laser source) at low temperatures one can observe an electron-oscillation structure in the spectra of spontaneous fluorescence of such complex molecules as perylene, coronene and phthalocyanine. In ordinary conditions, excitation of the spectrum of solutions of these compounds even at 4.2°K is without a structure.

The presence of a concealed structure in the spectra of dye solutions and the multiple forms of processes of induced emission with resonance excitation of them by a powerful monochromatic radiation creates difficulties for unambiguous interpretation of the phenomena. These difficulties occur during radiation of spectra of spontaneous radiation in resonance conditions where it is possible to have simultaneous observation of the processes of the ordinary and the "hot" fluorescent and spontaneous resonance of combination scattering [11-13]. /361

The purpose of this work was: the study of the spectra of induced radiation of solutions of dye during monochromatic excitation in a broad temperature interval; the study of the principles of manifestation of the fine structure in the spectra with a changing temperature and conditions of generation; the interpretation of the phenomena on the basis of existing data as to nonuniform expansion of transitions in the vitrified matrices.

I. Method of the Experiment

For studying the spectra of induced radiation in a temperature

¹The results of this study will be presented separately.

range from 300 to 4.2°K it is necessary to translate into a vitreous state a comparatively large volume (2-3 m³) of dye solutions. Therefore, alcohol solutions were used: glycerin, diethylene glycol, propyl and ethyl alcohol. The glycerin, diethylene glycol and ethyl alcohol formed transparent matrices with even cooling in the interval from room temperature to the temperature of full hardening T_g. The propyl alcohol with slow cooling transferred to a crystal state at T = 220°K and therefore for obtaining a transparent vitreous matrix it was necessary to have rapid cooling to T ≥ 220°K and then slow cooling at a rate of 0.5°/min to the temperature for hardening of solution T_g. With further cooling of the solution from T_g to 4.2°K, the optical quality of the solution did not depend on the rate of cooling.

For excitation generation, a ruby laser was used with a passive modulation of quality [14]. The impulse of the laser generation had the following parameters: duration at half-height -- 20 ns, peak power -- less than 40 MW. Excitation was accomplished in a longitudinal variation with feedback at the ends of the cuvette which were not strictly parallel. The spectra were recorded on an instrument with inverse dispersion -- Å/mm.

II. The Results of Experiments and Their Discussion

The table presents the wavelengths of the maximum of the absorption bands for solutions of the dyes being studied in glycerin at 300°K and shifts of the fluorescent bands with a transition to T = 77°K.

Number	Dye	λ_{max} , nm	Temperature shift, nm
I	3-3'-diethyl-9, 11, 13-(penta-1", 3", 5"-trityl)-thiathiazolino-tricarbo-cyanine iodide	706	3
II	3-3'-diethyl-9, 11, 13-(penta-1", 3", 5"-trityl)-thiacarbo-cyanine iodide	752	2
III	1-1'-dimethylene dotricarbo-cyanine	750	4
IV	Tricyanine perchlorate	706	2
V	Cryptocyanine	715	5

The temperature change of the spectra of generation can be divided according to characteristics into two temperature intervals 1) from 300°K to T_g , 2) from T_g to 4.2°K.

1. The temperature interval from 300°K to T_g . The basic characteristics of the behavior of the spectra in this interval include a shift in average frequency of generation without a change in the width of the spectrum and in a decreased threshold of generation as the solution cools. These features appear differently in different solutions.

a) Glycerin. With a decrease in temperature from 300 to 190°K, one observes a shift in the average wavelengths of generation toward the shortwave side and here the threshold of generation is almost unchanged. The value of the shift is different for different dyes and hardly depends at all on the optical density of the solution. For example, for dye I (see the table), the shift amounts to 40 Å, for dye III - 90 Å. With further cooling of the solution the spectrum does not shift. In Figure 1, a and b, spectra of generation of dyes I and III are presented at different temperatures greater than T_g .

b) Diethylene glycol. For dye I (Figure 1,c) in the temperature intervals of 300 to 270°K one observes a monotonous shift in average wavelengths of generation toward the long wave side with simultaneous decrease in the threshold (approximately three-fold): in the interval from 270 to 180°K, the spectrum is shifted toward the short wave; the threshold does not change and with further cooling the shift stops.

c) Ethanol. In the entire temperature interval one observes a shift in the spectrum toward the long wave with simultaneous decrease of the threshold of power for excitation in sequence. The shift occurs more rapidly in the high temperature field and reaches saturation close to T_g . In Figure 1,d temperature relationships of the average wavelength of generation of dye I are shown graphically in different solutions. /363

The qualitative explanation of these shifts is the following: a shift in the spectra of generation toward the short wave side correlates

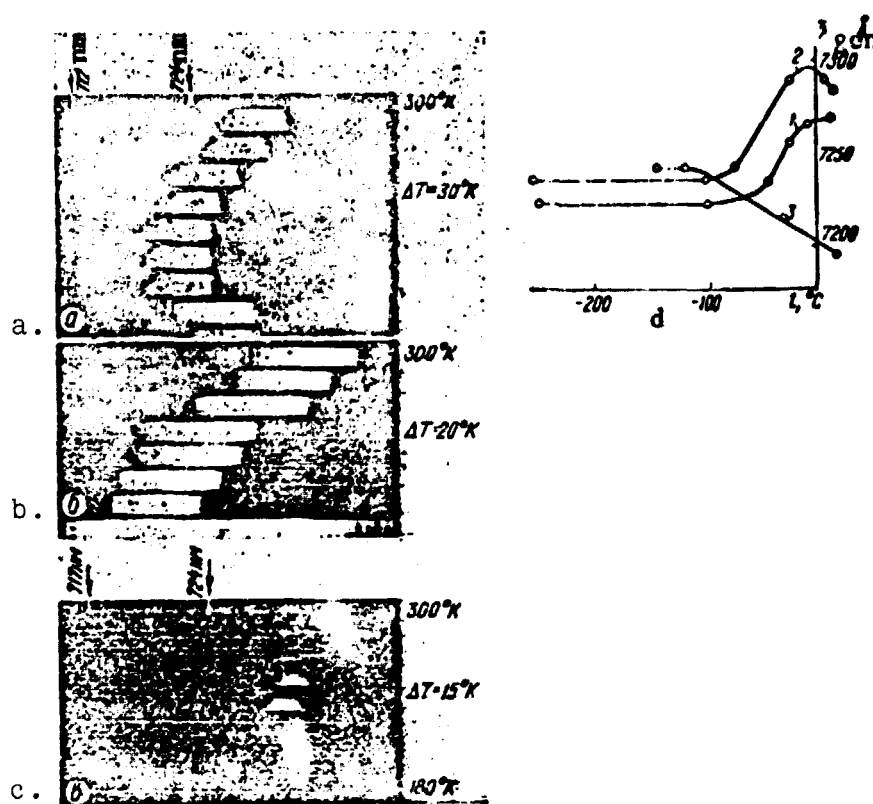


Figure 1. The spectra of generation of solutions of dye at different temperatures: a -- dye I in glycerin, b -- dye III in glycerin, c -- dye I in ethylene glycol; d -- temperature dependences of the average wavelengths of generation of dye I in different solutions: 1 -- glycerin, 2 -- diethylene glycol, 3 -- ethanol ($U_{exc} = \text{const}$). The lower spectra in Figures a and b correspond to T_g .

with a shift in the spectra of fluorescence in this temperature interval (see table). A long wave shift involves an increase in the quantum output of the solution η with decreased temperature: an increase in η results in a decrease in the threshold of generation, and because all spectra were obtained with a uniform value of the excitation power, each spectrum corresponds to a different excess in the excitation power over the threshold power. As was shown in reference [15], the excess of excitation power over the threshold results in a shift in average frequency of generation toward the long wave. This explanation is in agreement with the fact that the curves in Figure 1, d depend on viscosity of the solution at room temperature. In viscous solutions, the change in quantum output with temperature is not great

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and therefore one does not observe a noticeable decrease in the threshold and a long wave shift. In the case of ethanol one observes a stronger change in viscosity and an increase in quantum output, a decrease in the threshold of generation and a shift in the spectrum.

2. The temperature interval from T_g to 4.2°K . When approaching T_g , one observes a significant expansion in the generation band and then the threshold of generation remains as before or increases.

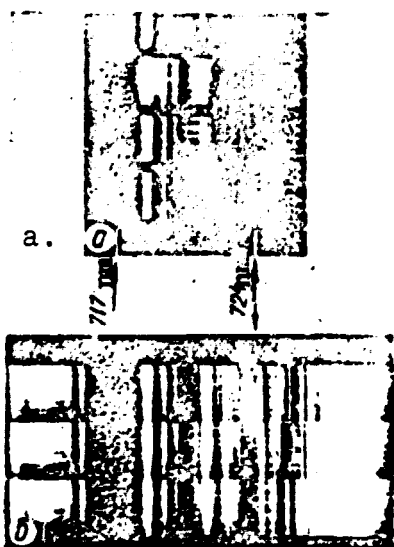


Figure 2. Spectra of generation of dye I in glycerin with different optical densities d of the solutions: $a-d = 2$, $b-d = 5$, $T = 4.2^\circ\text{K}$.

As a rule, the largest increase in the threshold was observed in the more viscous solution. Expansion of the spectrum occurs rapidly in the narrow temperature interval not exceeding $20-30^\circ\text{K}$; the width of the spectrum increases 3-4 times and a larger expansion is observed toward the long wave side (Figure 1, a, b). With a further decrease in temperature, the width of the generation band is almost unchanged but the short wave part of the spectrum spreading close to T_g becomes narrow-line at 4.2°K (Figure 2). The distance of the line from the excitation line remains constant for the

same dye in different solutions and can serve as the characteristic for the dye. At the same time, with the formation of a narrow-line structure, on the background of the diffusion section of the spectrum, narrow absorption bands are apparent. The overall view of the spectrum to a certain degree depends on the optical density of the solution and the power of excitation. With an optical density which is optimum for the threshold of generation ($d(v_H) = 5$) and power of excitation greater than the threshold, in the field of the structural part of the spectrum there is a diffusion background (Figure 2, b). With a density greater than the optimum, the structural part of the spectrum can be absent. With densities smaller than the optimum, one observes only a structural spectrum (Figure 2, a). With an optimum density of the

solution, the number of lines is increased close to the diffusion section of the spectrum and the form of the spectrum in this field is not reproduced (Figure 2, b). The shift in frequency of excitation by 4 cm^{-1} results in a corresponding shift of the lines (Figure 3).

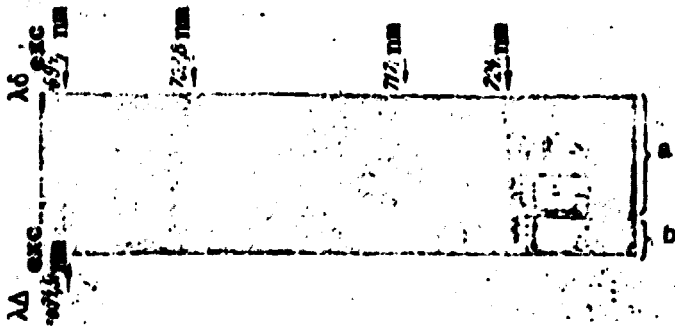


Figure 3. The spectra of generation for dye I in glycerin excited by radiation from a ruby laser with $\lambda = 694.3 \text{ nm}$ (a) and $\lambda = 694.5 \text{ nm}$ (b), when $T = 4.2^\circ\text{K}$.

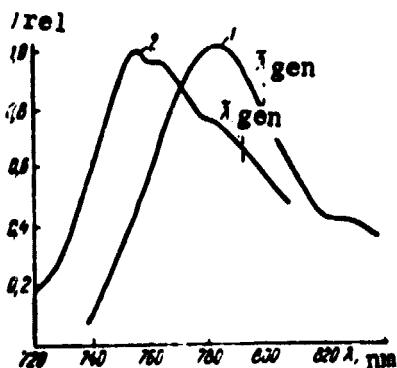


Figure 4. Spectra of fluorescence of dye III in glycerin: 1 -- $T = 300^\circ\text{K}$, 2 -- $T = 130^\circ\text{K}$. $\lambda_{\text{exc}} = 690 \text{ nm}$, $\Delta\lambda = 5.0 \text{ nm}$.

The general principles of change of the spectra of generation with temperatures smaller than T_g can qualitatively be explained, comparing them with the low temperature spectra of fluorescence. As was mentioned above, with T_g and the systems considered, a nonuniform character is apparent for the expansion of spectra and one observes a dependence of the shape of the curve and the position of the maximum on the wavelength of the excited light. Figure 4 shows spectra of fluorescence for dye II in glycerin with excitation by light with a wavelength of $\lambda = 690 \text{ nm}$ and width $\Delta\lambda = 50 \text{ \AA}$ at 300°K (curve 1) and 130°K (curve 2). It is obvious that the low temperature spectrum is shifted toward the short wave, is expanded and the long wave edge of it is gently sloping. Such changes in the spectrum of fluorescence can result in a shift and expansion of the generation band.

A further decrease in temperature results in the formation of a coarse structure in the spectra of fluorescence and a fine structure in the spectra of generation. Figure 5 shows the spectrum of fluorescence for dye IV in glycerin obtained with excitation by light with $\lambda = 694 \text{ nm}$ and width \AA at 4.2°K . Here the spectrum induced radiation

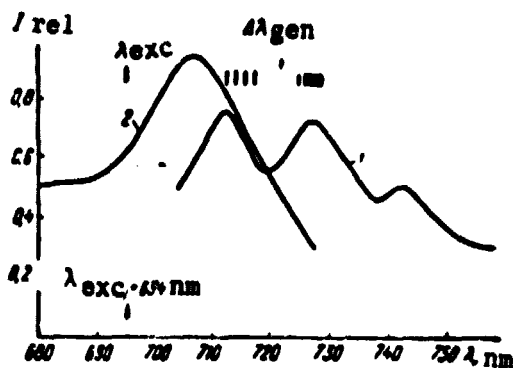


Figure 5. Spectra of fluorescence (curve 1) and absorption (curve 2) of the solution of dye IV in glycerin at $T = 4.2^\circ\text{K}$.

is shown diagrammatically, it was obtained with monochromatic excitation by light with a wavelength of 6.43 nm. It is obvious that the group of narrow bands of the spectrum of generation of the dye are located in the field of maxima of the spectrum of fluorescence.

Starting with the familiar non-uniform expansion of the absorption bands and fluorescence of solutions of polymethene dyes which are manifested in the field of low temperatures with monochromatic excitation, one can propose the following interpretation of narrow-line spectra of induced emission of dyes.

1) During excitation in a short wave field of spectra, groups of centers participate in absorption whose frequency of electron transitions and electron-oscillating transitions are found in resonance with a frequency of the incident light. Therefore, the structure of the spectrum of generation can be a manifestation of separate electron-oscillation transitions in different types of centers. The distances in the scale of frequencies between the lines of excitation and the lines of generation correspond to the oscillating wave number of the basic state (in a case of excitation in the field of a purely electron transition) or their combination with oscillating wave numbers of the excitation electron state (in the case of excitation in the field of an electron-oscillation transition).

2) The shift of lines in the spectrum of generation with a change in wavelength of excitation is the result of the nonuniform expansion of the absorption and fluorescent bands. Because the shift in frequency of excitation even by 4 cm^{-1} results in a shift in the lines of generation, one should assume that in the spectra of fluorescence there is a fine structure involving phonon-less lines. However, this hypothesis

was always confirmed experimentally: for some of the studies of polymethine dyes, the spectra of fluorescence of 4.2°K excited by He-Ne-laser light (6328 Å) do not contain the corresponding narrow lines on the background of a structureless spectrum as is observed in the case of phthalocyanine in reference [9].

3) Irregularity of the appearance of separate lines in the spectra of generation can explain the concurrence of generating modes which exist in lasers with nonuniformly expanded active media.

REFERENCES

1. Melishchuk, M. V., Ye. A. Tikhonov, M. T. Shpak and I. K. Kvitaishvili, Tezisy V Vsesoyuznoy konferentsii po nelineynoy optike [Summaries of the Vth All Union Conference on Non-linear Optics], Kishinev, 1970.
2. Melishchuk, M. V. and Ye. A. Tikhonov, Tezisy mezhdunarodnoy konferentsii po lyuminesstsentii [Summaries of the International Conference on Luminescence], Leningrad, 1972.
3. Melishchuk, M. V., Ye. A. Tikhonov and M. T. Shpak, ZhPS 16, 642 (1972).
4. Bobovich, Ya. S. and A. V. Bortkevich, Opt. i spektr. 26, 1060 (1969).
5. Bobovich, Ya. S. and A. V. Bortkevich, Pis'ma v ZhETF 11/85 (1970).
6. Bobovich, Ya. S. and A. V. Bortkevich, Opt. i spektr. 28, 474 (1970).
7. Bortkevich, A. V., Ya. S. Bobovich and N. M. Belyayevskaya, Opt. i spektr 28, 688 (1970).
8. Pfeifer, M., A. Lau and H. J. Weigmen, Optics Com. 6, 284 (1972).
9. Litvin, F. F. and R. I. Personov, DAN SSSR 136/4 (1961).
10. Personov, R. I. Ye. I. Al'shits and L. A. Bykovskaya, Pis'ma v ZhETF 15, 609 (1972).
11. Hyzhnyakov, V. and I. Tehver, Phys. stat. sol. 39, 67 (1970).
12. Holzer, W., W. F. Morphy and H. J. Bernstein, J. Chem. Phys. 52, 329 (1970).
13. Shorytin, P. P., UFN 109/2 (1973).
14. Smirnova, T. N., et al., inventor's certificate No. 397130, June 4, 1973.
15. Gandel'man, I. L., Ye. A. Tikhonov and A. N. Nikolayenko, Lazery restrai vayemoy chastotoy [Lasers with retuned frequency], Kiev, IF, Academy of Sciences Ukrainian SSR, 1974.