

# Fine structure of luminescence spectra of laser-excited organic molecules and the nature of the broad spectral bands of solid solutions<sup>1)</sup>

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Experiments in which fluorescence was excited with monochromatic laser emission were performed in order to identify the causes of the large width ( $\sim 200 \text{ cm}^{-1}$ ) of the spectral bands in the luminescence and absorption spectra of organic molecules and solid solutions at 4.2°K. It was observed that if the laser excitation is produced in an appropriate region of the absorption spectrum, then the fluorescence spectrum contains a large number of narrow lines instead of the smeared-out bands. The widths of a number of lines are much less than  $1 \text{ cm}^{-1}$ , and some of them have an internal structure. This effect takes place both in crystalline and in vitreous solvents, and was observed in the present study in five different organic substances. The fluorescence excitation spectra were investigated. It was shown experimentally that when the emission is registered in a sufficiently narrow spectral interval of the excitation spectrum, it is possible to reveal a fine structure in the smeared absorption spectra. The scheme whereby the broad spectral bands are produced is discussed. Certain new possibilities of spectroscopic investigations of complex organic molecules in solid solutions, which are made possible by the discovered regularities, are discussed.

## INTRODUCTION

1. The present paper is devoted to experimental investigations of the nature of the smeared-out absorption and luminescence spectra of polyatomic organic molecules in solid solutions at low temperatures. The first results of this study were recently published in the brief communications<sup>[1,2]</sup>. By now these investigations have been substantially expanded and detailed. Corresponding new results will be considered below. However, to make clear both the formulation of the problem and the interpretation of the results, we shall recall to begin with some of the known premises of the theory.

2. From the point of view of present-day concepts<sup>[3,4]</sup>, each electron-vibrational transition can correspond to a spectral band in the spectrum of the impurity center of the crystal in the general case; this band consists of a narrow phononless line (PLL), which is the optical analog of the resonant Mossbauer  $\gamma$  line, and of a broad phonon wing (PW), corresponding to transitions with creation and annihilation of the matrix phonons. The ratio of the integrated intensity of the PLL to the summary intensity of the entire band (PLL + PW) is determined by the Debye-Waller factor:

$$\frac{I_{\text{PLL}}}{I_{\text{PLL}} + I_{\text{PW}}} = \exp \left\{ - \int_0^{\infty} f(\omega) \left[ 1 + \frac{2}{e^{\hbar\omega/kT} - 1} \right] d\omega \right\}, \quad (1)$$

where  $f(\omega) = \xi^2(\omega)\rho(\omega)$  is the weighted density of the phonon states of the impurity crystal;  $\rho(\omega)$  is the density of states in the phonon band, and  $\xi^2(\omega)$  is a function of the electron-phonon coupling (the square of the displacement of the equilibrium position of a crystal oscillator with frequency  $\omega$  following an impurity phototransition).

It is seen from (1) that the smaller the electron-phonon coupling the more intense the PLL. At a fixed coupling force, a temperature rise leads to a weakening of the PLL and to "pumping over" of its intensity into the PW.

Optical bands consisting of narrow PLL and their accompanying broad PW were observed in the spectra of many impurity-containing inorganic and organic crystals, and in particular in the quasi-line spectra of organic molecules in Shpol'skiĭ n-paraffin matrices<sup>[5]</sup>.

The structure of the optical bands in the quasi-line impurity spectra in n-paraffins, the shapes of the PLL and the PW in these spectra, and their temperature dependence have been discussed in a large number of papers (see, e.g.,<sup>[6-9]</sup>) and will not be considered here. The main problem considered in the present paper is connected with the nature of the smeared-out electron vibrational spectra of complex organic molecules in solid solutions in the absence of the Shpol'skiĭ effect.

3. It is well known that in most solvents (particularly in vitreous media), the luminescence and absorption spectra of organic molecules remain smeared out down to helium temperatures. The fundamental question arises: what causes the large width of the bands in these cases?

From the point of view of the concepts considered above regarding the spectra of the impurity centers, the broad bands in the electronic spectra of solid solutions at low temperatures can appear in two extreme cases:

1) The electron-phonon interaction is weak and the individual impurity molecules have spectra consisting of narrow PLL. However, individual impurity molecules are under somewhat differing local conditions, and there is a statistical scatter in the positions of the corresponding PLL. In this case each broad band observed in the spectrum represents the envelope of a family of PLL, and the band broadening is inhomogeneous.

2) A strong electron-phonon interaction occurs, and therefore the intensity of the PLL is negligibly small. The observed broad bands represent in this case PW, and the broadening is in this case mainly homogeneous.

To determine which of these cases is actually realized, we performed experiments on a number of objects with laser excitation of fluorescence by a narrow line of a gas laser. One should expect in the case of inhomogeneous broadening that going to monochromatic excitation of the luminescence in the 0-0 transition region would excite only those centers for which the wavelength of the PLL coincides with the wavelength of the exciting light. Then narrow lines belonging only to these centers would appear in the emission spectrum. On the other

hand, if the band broadening is homogeneous, then a transition from ordinary excitation to laser excitation should not lead to a significant change in the character of the luminescence spectrum.

Our experiments on a number of objects have shown that under definite excitation conditions, a spectrum with a fine structure can be obtained in practically any solvent (both crystalline and vitreous).

## CONCERNING THE EXPERIMENTAL PROCEDURE

To obtain the spectra at 4.2° K and to investigate the temperature changes of the spectrum, the cell with the solution was placed in a metallic optical helium cryostat fitted with a system for automatically controlling and stabilizing the temperature<sup>[6,7]</sup>.

To excite the luminescence, we used, along with the customarily employed mercury-quartz superhigh pressure lamps (DRSh-1000 and DRSh-250) the following gas lasers: a) a cadmium laser with  $\lambda = 4415.6 \text{ \AA}$ , line width  $\Delta\nu \approx 0.05 \text{ cm}^{-1}$ , and power  $\approx 30 \text{ mW}$ ; b) a helium-neon laser with  $\lambda = 6328 \text{ \AA}$ ,  $\Delta\nu \approx 0.03 \text{ cm}^{-1}$ , and approximate power 30 mW; c) a nitrogen laser with  $\lambda = 3371 \text{ \AA}$ , pulse repetition frequency 100 Hz, and average power 2 mW.

The luminescence spectra were registered in the region 4000–6000 Å with a DFS-12 spectrometer (inverse dispersion 5 Å/mm) and in the regions 3000–5000 and 6000–8000 Å with an SDL-1 spectrometer (inverse dispersions 8 and 16 Å/mm, respectively, at a relative aperture 1:3).

The widths of the narrow lines (at  $\Delta\nu < 1 \text{ cm}^{-1}$ ) were measured photographically with the aid of a Fabry-Perot interferometer crossed with an ISP-67 spectrograph (with a camera having  $F = 1500 \text{ mm}$ ).

To obtain the excitation spectra, we assembled an installation containing two monochromators. The excitation source was in this case a DKSSH-1000 xenon lamp with a VMS-1 diffraction monochromator (dispersion 13 Å/mm at a relative aperture 1:5). The spectral width of the scanned exciting beam was 0.8 Å in all the experiments. The required section of the fluorescence spectrum was separated with a DFS-12 spectrometer. To obtain the excitation spectra of narrow fluorescence-spectrum sections it was necessary to measure weak light fluxes. The standard recording part in the DFS-12 spectrometer was therefore replaced by a photon counter system with a specially selected FEU-79 photomultiplier.

## PRINCIPAL RESULTS AND THEIR DISCUSSION

1. Fluorescence spectra with laser excitation. For convenience in the exposition that follows, all the basic results will be demonstrated with one compound as an example, the pentacyclic aromatic hydrocarbon perylene, and only in two solvents. We shall then present the results obtained with a number of other objects.

Figure 1 shows the fluorescence spectra of perylene in two solvents that are essentially different in their properties: in a neutral crystalline solvent (n-undecane) and in a polar vitreous solvent (absolute ethanol) under ordinary excitation (DRSh-1000 mercury-quartz lamp,  $\lambda = 365 \text{ nm}$ ) at 4.2° K. The two spectra are very similar and consist of relatively broad bands ( $\Delta\nu \sim 200 \text{ cm}^{-1}$ ). The absorption spectra of these solutions are similar. The long-wave maxima of the absorption bands are shown dotted in Fig. 1.

Figure 2 shows the fluorescence spectra of the same samples but under monochromatic excitation in the 0–0 transition region by light from the cadmium laser with  $\lambda = 4415.6 \text{ \AA}$ . It is easily seen that the transition to monochromatic excitation leads to a radical transformation of the fluorescence spectra, namely, the spectra now contain surprisingly narrow lines accompanied by PW on the long-wave side.

As a result of a vibrational analysis of these fine-structure spectra, we determined the fundamental frequencies, with the aid of which all the spectral lines can be determined (see the table). All the obtained frequencies are frequencies of the perylene molecule's vibrations in the electronic ground state<sup>[10]</sup>. This proves that the narrow PLL observed under laser excitation are undoubtedly due to the perylene impurity molecules<sup>2)</sup>.

2. Line width. It was of undisputed interest to estimate the line width in the fluorescence spectra under laser excitation. It turned out that some of the lines were so narrow that their widths could not be measured with the DFS-12 spectrometer at a resolution

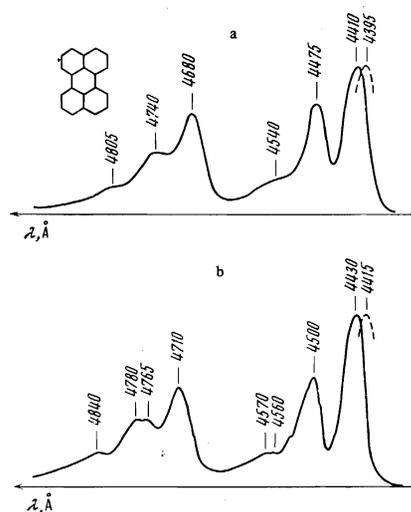
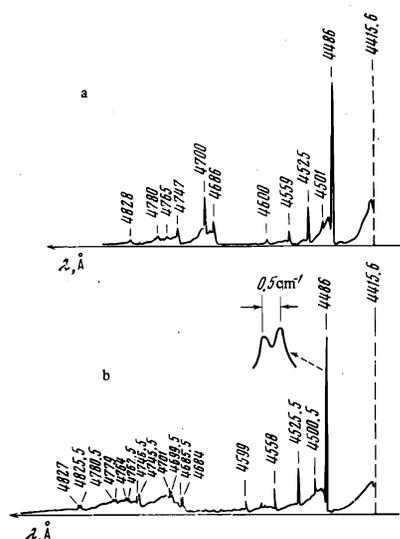


FIG. 1. Fluorescence spectra of perylene at 4.2° K: a—in ethanol; b—in n-undecane. Excitation with  $\lambda_{Hg} = 365 \text{ nm}$ . Solution concentration  $2 \times 10^{-5} \text{ mole/liter}$ .



Impurity-molecule normal-vibration frequencies obtained from an analysis of the fluorescence spectra under laser excitation (in  $\text{cm}^{-1}$ )

Perylene			Phenanthrene in ethanol	3,4,8,9-dibenzopyrene in ethanol
In n-undecane	In ethanol	In ethanol*		
354 in	355 in	350 in	252 w	265 in
427 w	430 w	425 w	409 in	650 w
550 med	550 med	545 med	547 w	1170 w
1298 med	1305 med	1295 med	619 w	1245 in
1368 med	1370 med	1390 med	714 med	1380 med
1375 med	1580 med	1590 med	833 med	1470 w
1577 med			877 med	1580 med
1582 med			1043 med	
			1205 w	
			1354 in	
			1448 in	
			1605 in	

\*The third column lists the vibration frequencies obtained from the excitation spectrum for perylene in the excited electronic state.

Notation: in—intense, med—medium intensity, w—weak.

$0.7\text{--}0.9\text{ cm}^{-1}$ , and it was necessary to use for this purpose a Fabry-Perot interferometer. The interferometric measurements have shown that many of the lines have widths less than  $1\text{ cm}^{-1}$ . In addition, some of them reveal a complicated structure, the origin of which still remains unclear and calls for a further investigation. Thus, for example, the  $4525.5\text{ \AA}$  line in the perylene spectrum in n-undecane has a width  $0.4\text{ cm}^{-1}$ , and the  $4486\text{ \AA}$  line is a doublet with a distance  $0.5\text{ cm}^{-1}$  between the components (Fig. 2b). The same line in ethanol are somewhat broader ( $2$  and  $3\text{ cm}^{-1}$ , respectively).

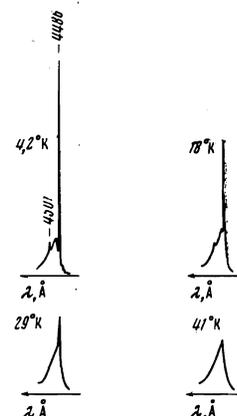
All the narrow PLL lines observed in the spectrum correspond to vibronic transitions in the impurity molecule. Their width in our case can already be determined to a considerable degree by the relaxation times of the vibrational excitations of the impurity molecules. The corresponding times, estimated from the widths of these vibronic lines, turn out to be of the order of  $10^{-11}$  sec, which agrees with the results of [13, 14]. The width of the 0-0 transition line, which coincides in wavelength with the exciting laser line, has not yet been measured. One can assume that the 0-0 line is much narrower than the electron-vibrational lines.

**3. Temperature dependence of the spectra.** As already noted at the start of the article, a characteristic attribute of the PLL is the decrease of its intensity with increasing temperature. It was therefore of interest to investigate the temperature dependence of the fluorescence spectra under laser excitation. Figure 3 shows a section of the spectrum of perylene in ethanol at different temperatures. It is easily seen that a rise in temperature leads to a very strong attenuation of the PLL. At a temperature near  $40^\circ\text{K}$ , the PLL practically vanish and only the relatively broad PW remain in the spectrum. The PLL behaves similarly in the spectra of perylene in other solvents.

**4. Nature of the broad bands.** We turn now to an interpretation of the results. They show, in particular, that neither of the two extreme causes of the spectral lines that were considered in the introduction is realized in pure form. The inhomogeneous broadening does, however, play the decisive role. In this case it seems to us that the scheme for the formation of the broad bands is the following:

In the region of the 0-0 transition (and also in the region of any vibronic transition), each impurity mole-

FIG. 3. Part of the fluorescence spectrum of perylene in ethanol following excitation with a cadmium laser at four different temperatures.



cule has both a narrow intense PLL and an accompanying relatively broad PW (on the long-wave side of the PLL in the case of emission, and on the short-wave side in absorption). The differences between the local conditions for the different impurity molecules lead to a scatter in the positions of the corresponding PLL and PW. The width of the PLL is then small, and the width of the PW is comparable with the maximum value of the indicated scatter. As a result, the PLL belonging to different centers overlap to a lesser degree than the PW. Therefore when the optical bands of many centers are added up, the summary peak intensity of the PLL increases much more slowly than the summary peak intensity of the strongly overlapping PW. Although the PLL intensity at the maximum for each individual impurity center can greatly exceed the intensity of the PW, a broad structureless band is produced when many optical bands of this type are added together.

Fluorescence excitation by a laser line affects principally those centers for which the PLL wavelength coincides with the laser emission wavelength. As a result, it is precisely these impurity centers that fluoresce most intensely, and the corresponding PLL are clearly observed in the spectrum<sup>3)</sup>.

We emphasize finally that the "phonon wings" observed in the fine-structure fluorescence spectra have a complicated nature. They include first of all the PW connected with the PLL of the resonantly excited centers. In addition, they receive a contribution from the relatively weak emission of centers of other types, which are excited by the laser in the region of the corresponding PW in absorption.

**5. Excitation spectra.** The monochromatic-excitation method considered above enables us to obtain emission line spectra. Of no lesser interest, however, is the detection of an analogous fine structure in absorption spectra, which carry information on the vibronic levels of excited electronic states. Our investigation has demonstrated experimentally the feasibility of revealing a fine structure in smeared-out absorption spectra by means of the fluorescence excitation spectra.

It is known that to obtain an excitation spectrum, one scans the wavelength of the exciting light, and the ensuing variation of the fluorescence intensity is measured in a fixed, usually broad, spectral interval. In the case of sufficiently dilute solutions and in the absence of a dependence of the fluorescence quantum yield on the exciting-light wavelength, the excitation spectrum duplicates the absorption spectrum exactly<sup>[15]</sup>. Assuming that the

scheme considered above for the formation of broad electron-vibrational absorption and emission bands is correct, it is to be expected that if a sufficiently narrow spectral interval is separated in the fluorescence spectrum, then the radiation registered in this interval is connected predominantly with centers of one type<sup>4</sup>. Then the corresponding excitation spectrum duplicates the absorption spectrum of only these centers, and a fine structure should appear in it. This is indeed the case.

Curve a of Fig. 4 shows the fluorescence excitation spectrum of perylene in ethanol, with the fluorescence registered in a broad spectral interval. This spectrum consists of several broad bands and duplicates the absorption spectrum of the investigated solution. An entirely different picture is obtained if the excitation spectrum is recorded with the fluorescence registered in a narrow spectral interval. Curve b of Fig. 4 is the excitation spectrum for a fluorescence spectral interval  $0.8 \text{ \AA}$  ( $\approx 4 \text{ cm}^{-1}$ ) in the region of the first vibronic fluorescence band  $0-355 \text{ cm}^{-1}$ . (The spectral width of the exciting beam was the same in both cases and also amounted to  $0.8 \text{ \AA}$ .) Now, as was assumed, the excitation spectrum has an entirely different character: instead of the broad bands it contains narrow PLL accompanied on the short-wave side by PW. This excitation spectrum is practically a mirror reflection of the fine-structure fluorescence spectrum obtained by laser excitation. The frequencies obtained on vibrational analysis of the excitation spectrum (see the table) coincide with the frequencies of the normal vibrations of the perylene molecule in the first excited electronic state<sup>[10]</sup>. Temperature investigations show that the intensity of the PLL in the excitation spectrum decreases with increasing temperature in perfect analogy with the situation in the fluorescence spectrum.

It should be noted that the ratio of the intensity maxima of the PLL and PW is smaller and the PLL themselves much broader in the excitation spectrum than in the fluorescence spectrum. This is a reflection of the fact that when the excitation spectra were recorded the width of the exciting beam was much larger than the width of the laser line. The inhomogeneous broadening is therefore not lifted to the same full degree in the case of the excitation spectrum. One can hope that the use of a laser with continuously tunable frequency and a suffi-

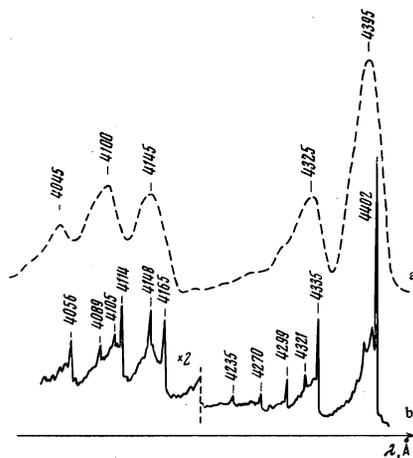


FIG. 4. Fluorescence excitation spectra of perylene in ethanol at  $4.2^\circ\text{K}$ : a—fluorescence registered in a broad spectral interval ( $\Delta\lambda > 20 \text{ \AA}$ ); b—fluorescence registered in a narrow spectral interval ( $\Delta\lambda = 0.8 \text{ \AA}$ ,  $\lambda = 4472 \text{ \AA}$ ).

ciently narrow line for investigation of the spectra will reveal new and finer details in the spectra.

6. Other molecules. All the spectra presented above belong to a single compound, perylene. This raises the question: are the regularities considered above also observed in other molecules?

The following question is also natural: As noted above, the fluorescence of the perylene solution was laser-excited in the region of a pure electronic  $0-0$  transition. What will be the character of the fluorescence spectrum when laser-excited to higher vibronic levels? In this case the effect of the narrowing of the spectral bands should also be observed, but it may be less strongly pronounced. Indeed, the vibronic levels

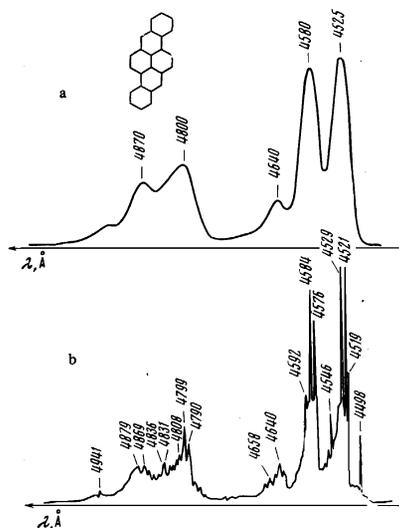


FIG. 5. Fluorescence spectra of 3,4,8,9-dibenzpyrene in ethanol at  $4.2^\circ\text{K}$ : a—usual excitation ( $\lambda_{\text{Hg}} = 365 \text{ nm}$ ); b—excitation with a cadmium laser ( $\lambda = 4415.6 \text{ \AA}$ ). Concentration  $10^{-5}$  mole/liter.

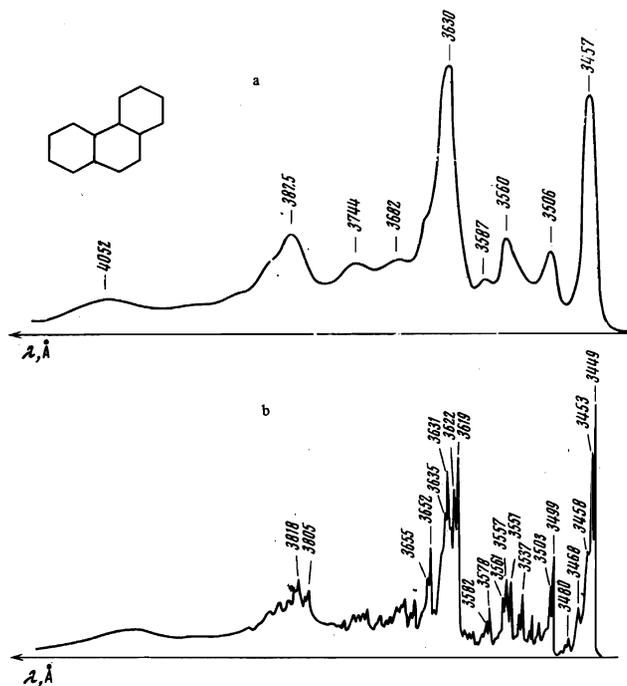


FIG. 6. Fluorescence spectra of phenanthrene in ethanol at  $4.2^\circ\text{K}$ : a—usual excitation (DKSSh-1000,  $\lambda = 220 \text{ nm}$ ); b—excitation with nitrogen laser ( $\lambda = 3371 \text{ \AA}$ ). Concentration  $5 \times 10^{-5}$  mole/liter.

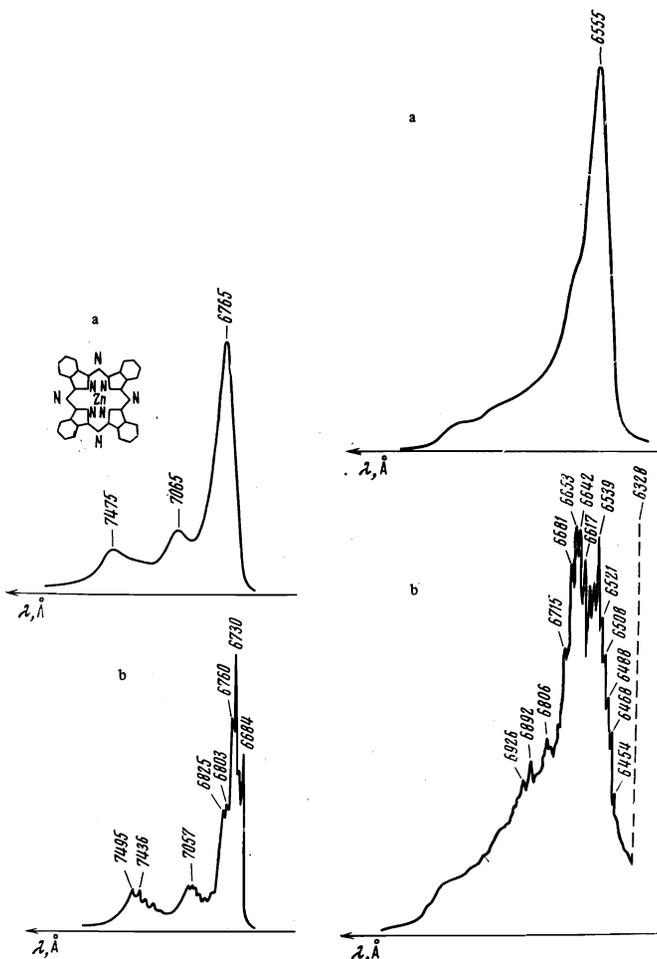


FIG. 7

FIG. 8

FIG. 7. Fluorescence spectra of Zn-phthalocyanine in paraffin oil at 4.2°K: a—usual excitation ( $\lambda_{Hg} = 405$  and 435 nm); b—excitation with helium-neon laser ( $\lambda = 6328$  Å). Concentration  $5 \times 10^{-6}$  mole/liter.

FIG. 8. Fluorescence spectra of chlorophyll "b" in n-undecane at 4.2°K: a—ordinary excitation ( $\lambda_{Hg} = 436$  nm); b—excitation with helium-neon laser ( $\lambda = 6328$  Å). Concentration  $5 \times 10^{-6}$  mole/liter.

and the corresponding PLL are broader than the pure electronic levels, and the overlap of the PLL of different centers in the region of the vibronic transitions is larger. Therefore laser excitation will affect the PLL of a larger number of centers than following excitation in the region of the 0-0 transition, and the inhomogeneous broadening will be eliminated to a lesser degree.

Figures 5 and 6 show the fluorescence spectra of two aromatic hydrocarbons, namely, 3,4,8,9-dibenzpyrene a and phenanthrene, in ethanol under ordinary and laser excitation (in the region of one of the first vibrational levels of the excited electronic state). It is easily seen that in this case, too, laser excitation produces a fine structure (although measurements show that the lines are somewhat broader here than in the case of perylene).

Line groups—"multiplets"—are observed in the region of the 0-0 transition in both fine-structure spectra. The most intense lines in the 0-0 region are those of the 4521-4529 Å doublet in the spectrum of dibenzpyrene and those of the 3449-3453 Å doublet in the spectrum of phenanthrene. Similar doublets can be traced through the entire fluorescence spectrum<sup>5)</sup>. The results of vibrational analysis of these spectra are listed in the

table. The frequencies obtained by us for the normal vibrations of these molecules agree well with the results of [18, 19].

Figures 7 and 8 show the spectra of two compounds of the porphyrin class, namely Zn-phthalocyanine and the important photosynthetic pigment chlorophyll "b", under two methods of excitation. The effect here is likewise distinctly observed<sup>6)</sup>.

## CONCLUSION

Summarizing all the foregoing, we can conclude that the appearance of a fine structure in luminescence spectra following monochromatic excitation can be observed in various compounds and in most diverse solvents. The question of the general validity of the considered mechanism whereby the broad spectral bands are formed calls for further study. It can already be stated, however, that it holds for molecules of different classes.

The established regularities uncover new possibilities for spectroscopic investigations of complex molecules in both crystalline and vitreous media. These include, in particular: 1) the study of the subtle effects of external actions on the optical spectrum of impurities (for example, the influence of the surroundings of the impurity; the influence of external electric and magnetic fields, etc.); 2) investigation of vibrational relaxation in impurity centers by determining the widths of the vibronic lines, since it appears that when suitable laser excitation is used this relaxation is indeed determined by these processes; 3) study of the phonon-spectrum characteristics of different matrices by determining the PW in the fine-structure spectra of the impurity: one impurity adequately excited by a laser can be used to investigate a large number of matrices. This brief list is, of course, far from complete.

<sup>1)</sup>This article reflects the content of a paper delivered at the 11th European Congress on Molecular Spectroscopy (Tallin, 28 May-1 June 1973).

<sup>2)</sup>We note that when a solution of perylene in ethanol is exposed at 4.2°K to light from a 30-mW cadmium laser, a decrease of the fluorescence line intensity with time is observed [1]. This process may be due to two-photon ionization of the perylene molecule via the triplet state [11, 12]. To exclude this process when working with perylene solutions in ethanol, we decreased the laser radiation intensity by a factor of 100 with the aid of filters.

<sup>3)</sup>From the point of view of the scheme considered above, in the case of the quasi-line Shpol'skiĭ spectrum a situation is realized in which the inhomogeneous broadening is small if the electron-phonon interaction is weak enough.

<sup>4)</sup>We note that excitation spectra were successfully used to prove the existence of several types of spatially-separated radiating centers in the case of quasi-line spectra [16, 17].

<sup>5)</sup>It is known that "multiplets" are frequently observed in spectra of different impurity crystals. It appears that this is the first time they have been observed in a vitreous medium. The interesting question of their origin will be considered in a separate paper.

<sup>6)</sup>The chlorophyll "b" compounds were isolated and purified in the laboratory of G. P. Gurinovich of the Physics Institute of the Belorussian Academy of Sciences and also in the laboratory of F. F. Litvin in the Soil-Biology Department of the Moscow State University. We are sincerely grateful for the supply of these compounds. It should be noted that the intensity distributions in the fine-structure spectra of different samples of chlorophyll "b" varied noticeably. In addition, changes took place in the fluorescence spectra during the course of laser irradiation. It was not our task to investigate these chemical transformations of chlorophyll. The laser-excitation method can be presumed to be useful in their study.

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