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APPEARANCE OF FINE STRUCTURE IN FLUORESCENCE SPECTRA OF LASER-EXCITED COMPLEX MOLECULES

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1. It is well known that the absorption and luminescence spectra of polyatomic organic molecules in solutions usually consist of one or several broad bands. In a large number of cases, at low temperatures, it is possible to obtain spectra with a fine structure by introducing the investigated molecules into a suitably chosen crystal n-paraffin matrix (the Shpol'skii effect [1]). Narrow phononless lines in these spectra are accompanied by phonon wings occurring in transitions with creation or annihilation of the matrix phonons [2, 3].

In most solvents, however, particularly in a vitreous medium, the spectra remain smeared down to helium temperatures.

In the present communication we present the first results of our investigations of the nature of broad bands in spectra of organic molecules in solid solutions, using laser excitation of the fluorescence in the region of a purely electronic 0-0 transition. During the course of these investigations we have observed that in a number of compounds, under definite excitation conditions, a spectrum with a fine structure can be obtained practically in any solvent.

2. Figures 1a and 2a show the fluorescence spectra of an aromatic hydrocarbon (perylene) at 4.2°K in two solvents having essentially different

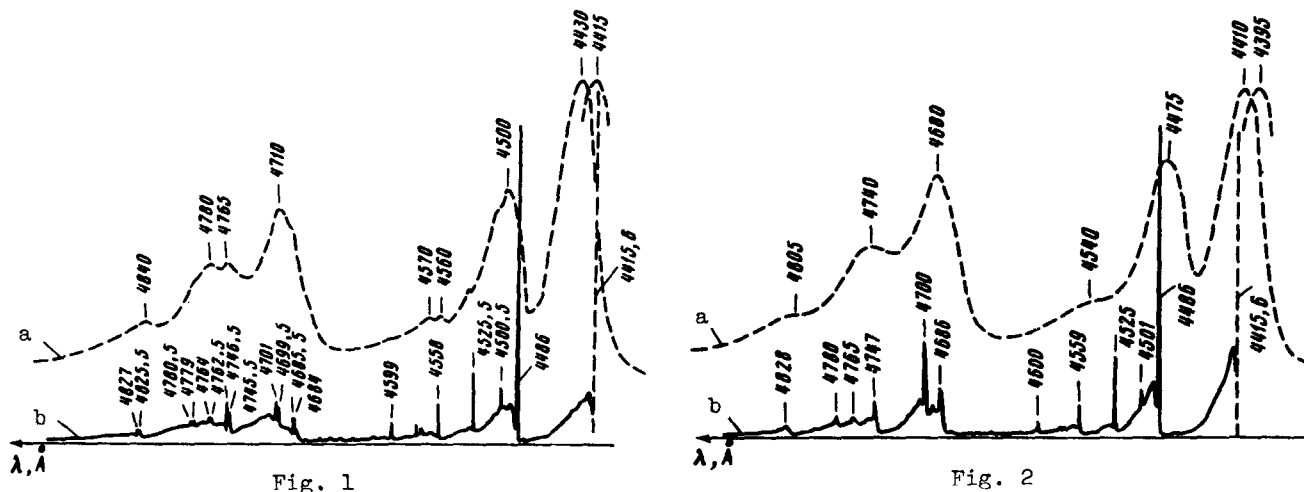


Fig. 1. Fluorescence spectra of perylene in n-undecane at 4.2°K: a - ordinary excitation ($\lambda = 365$ nm, DRSh-1000 lamp); b - laser excitation at $\lambda = 4415.6$ Å. The 4415 Å maximum belongs to the longest-wavelength absorption band. Concentration $\sim 2 \times 10^{-5}$ mole/liter. DFS-12 spectrometer.

Fig. 2. Fluorescence spectra of perylene in ethanol at 4.2°K: a - ordinary excitation, b - laser excitation.

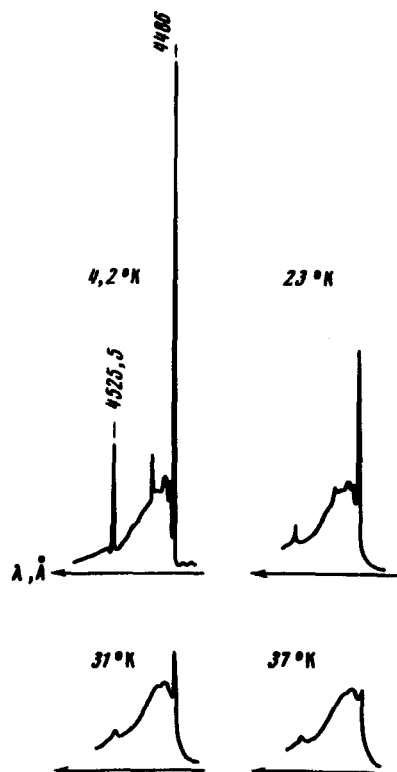


Fig. 3. Section of fluorescence spectrum of perylene in n-undecane when excited with a cadmium laser ($\lambda = 4415.6 \text{ \AA}$) at four different temperatures.

frequencies: 355, 430, 550, 1300, 1370, and 1580 cm^{-1} (the last three are split into doublets in undecane). All these frequencies are the vibrational frequencies of the perylene molecule in the electronic ground state [4]. This proves that the narrow lines observed in our case are due to the perylene impurity molecules.

We estimated the widths of the 4486 and 4525 Å lines. In undecane, the width of the first line turned out to be $\sim 1 \text{ cm}^{-1}$, while the second line was much narrower. In ethanol the widths of these lines were approximately 3 and 2 cm^{-1} , respectively.

As is well known, a characteristic attribute of phononless lines is the decrease of their intensity with increasing temperature. Figure 3 shows the dependence of a section of the fluorescence spectra of perylene in undecane at four different temperatures. We see that when the temperature is increased the intensity of the narrow lines decreases sharply and they practically vanish near 40°K . The lines of the spectrum of the perylene solution in ethanol behave in exactly the same manner.

3. We now turn to an interpretation of the results. In this case we consider the following scheme of formation of the broad spectral bands as possible. In the region of the 0-0 transition each impurity molecule has both a narrow intense phononless line and an accompanying phonon wing (on the short-wave side of the phononless line in absorption, and on the long-wave side in emission).

properties: in a neutral crystalline solvent (n-undecane) and in a polar vitreous solvent (absolute ethanol). The fluorescence was excited in these cases by the usual method (DRSh-1000 lamp, $\lambda = 365 \text{ nm}$). In both cases the spectra are very similar and consist of relatively broad ($\sim 200 \text{ cm}^{-1}$) bands. The absorption spectra of these solutions are similar in character.

In principle, there are two limiting causes of such broad bands: (i) The individual impurity molecules have spectra made up of narrow phononless lines, but these molecules are under slightly differing local conditions, and this causes inhomogeneous broadening. (ii) Owing to the strong interaction of the impurity electrons with the matrix vibrations, the intensity of the phononless lines is low and only the broad phonon wings appear in the spectra. In this case the broadening is mainly homogeneous. To ascertain which of the two cases is realized in fact, we have excited perylene fluorescence with a cadmium laser ($\lambda = 4415.6 \text{ \AA}$, line width 0.05 cm^{-1}).

Figures 1b and 2b show the fluorescence spectra of perylene in undecane and in ethanol when excited with a laser in the region of the 0-0 transitions. We see that these spectra contain surprisingly narrow lines accompanied by phononless wings on the long-wave side. As the result of a vibrational analysis of these spectra (assuming that the 0-0 line coincides in frequency with the laser line), we found the following fundamental

The differences in the local conditions for the different impurity molecules lead to a scatter in the positions of the corresponding phononless line and phonon wing. The width of the phononless line is small in this case, and the width of the phonon wing sufficiently large in comparison with the magnitude of this scatter. Therefore, when several narrow phononless lines add up, a broader line is produced without a significant increase of the intensity at the maximum and when phonon wings overlap strongly, a broad band with a large intensity at the maximum is produced. Although for each individual impurity center the intensity of the phononless line at the maximum can greatly exceed the intensity of the phonon wing, when many optical bands of this type add up, an intense broad band is produced, formed mainly as a result of the superposition of many phonon wings. When the fluorescence is excited by a laser line, we affect principally only those centers in which the phononless-line wavelength is close to the laser emission wavelength. Consequently it is only these impurity centers that fluoresce most intensely, and their corresponding phononless lines appear clearly in the spectrum. The indicated scheme, however, calls also for additional experimental verification.

4. We note one more circumstance. When an alcohol solution of perylene is irradiated at 4.2°K by light from a 30-mW laser, a decrease of the phononless-line fluorescence with time is observed in the fluorescence spectrum. When the solution is heated to 20°K and then cooled again to 4.2°K, the initial spectrum is completely restored. When the laser radiation is attenuated by a factor of 100, there is practically no decrease of the line intensity. In the case of intense excitation this decrease can be connected with two-photon ionization of the perylene molecule via the triplet state [5]. To exclude this process, the measurements with alcohol solutions were performed at 0.3 mW excitation power.

5. In conclusion we note that the appearance of a fine structure in the fluorescence spectra following monochromatic excitation in the region of the 0-0 transition uncovers a new possibility of subtle spectroscopic investigations of complex molecules in both crystalline and vitreous media. We have observed this effect also in a few other molecules besides perylene.

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OBSERVATION OF SUPERHEAT INSTABILITY IN A FULLY IONIZED CURRENT-CARRYING PLASMA

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An investigation of plane gas discharges, in which the magnetic pressure is insignificant, is of interest for the study of force-free superheat-ionization instabilities that develop in a current-carrying plasma. Thus, in [1 - 3] the instability that develops when current flows in a weakly ionized plasma and is due to superheating of the ionizing gas was investigated. This instability, naturally, should not develop in an isothermal fully ionized plasma, but a superheat instability connected with the emission of radiation can develop in such a plasma. A manifestation of the latter instability may be, for example,