

Transformation of the vibron spectra of perylene in *n*-octane induced by external pressure

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A transformation of the quasiline spectra of perylene in *n*-octane has been observed upon a change in pressure. The effect is attributed to a complex shape of the adiabatic potential, which must have at least two minima in both the ground state and the excited state.

A study has been made of how the quasiline spectra of perylene in *n*-octane vary with the external pressure over the range from standard pressure to 2 kbar at a temperature of 4.2 K. It has been observed that these spectra exhibit an unusual behavior at liquid-helium temperatures. Specifically, as the pressure is raised to 1–2 kbar, the fluorescence spectrum of perylene is quenched, and a new spectrum appears. This new spectrum is identical to the old one, but shifted 13 cm^{-1} away from it in the long-wave direction. The first results of a study of this effect are reported below.

The experiments were carried out with the help of a special high-pressure optical chamber in a cryostat. The test sample was subjected to quasihydrostatic compression in this chamber. The pressure in the chamber was measured with a precision dynamometer or by measuring the shift of *R* lines of Rb; in the latter case a microscopic crystal of this element was frozen in the solution under study. The fluorescence was excited by the beam from a cw helium–cadmium laser with a wavelength of 441.6 nm. The excitation was carried out over the broad phonon wing of the purely electronic 0–0 line with a wavelength of 444.7 nm. Since this phonon wing was broad, the excitation was nonselective. Consequently, the lines in the fluorescence spectrum of perylene were broadened nonuniformly; they had a width of $3\text{--}5\text{ cm}^{-1}$. The spectra were recorded with a DFS-12 spectrometer with a linear inverse dispersion of 5 \AA/mm .

The spectrum of perylene at standard pressure, shown in Fig. 1, contains the 0–0 line along with a large number of vibron repetitions. Among the latter we focus on the line at 451.8 nm, which corresponds to the most active molecular vibration of perylene, with a frequency of 353 cm^{-1} . The effect of pressure on the spectra of impure crystals usually takes the form of a broadening and a long-wave shift of the spectral lines.^{1,2} In the case at hand, the lines did broaden slightly as the pressure was raised from standard pressure to 2 kbar at 4.2 K, but there was no noticeable shift.

The most interesting and unexpected result is that the intensity of the spectrum begins to fall off rapidly with increasing pressure starting at 0.6 kbar. This effect is demonstrated in Fig. 2 for the particular case of the vibron line at 451.8 nm. We see from this figure that the decrease in the intensity of this line is accompanied by the appearance and progressive intensification of a new line on the long-wave side of the

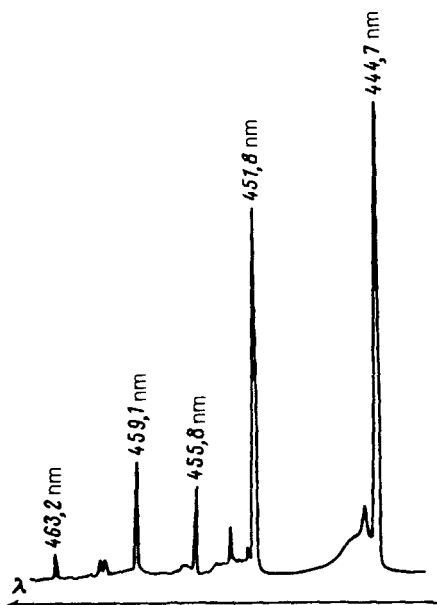


FIG. 1. Fluorescence spectrum of perylene in *n*-octane at $T=4.2$ K.

former line, at a separation of about 13 cm^{-1} . The same picture was observed near the 0-0 transition and for all significant vibrational repetitions. The original fluorescence spectrum thus disappears, and it is replaced by a new spectrum which is identical to the original spectrum but shifted 13 cm^{-1} away from it in the long-wave direction. No substantial changes occur in the absorption spectrum under these conditions. When the pressure is withdrawn, the original fluorescence spectrum is restored. This original

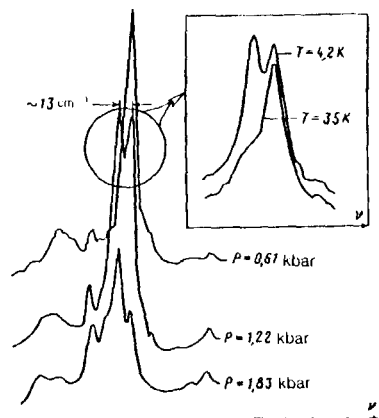


FIG. 2. Redistribution of intensity among the components of the multiplet (451.8 nm) in the fluorescence spectrum of perylene in *n*-octane upon changes in the pressure (at $T=4.2$ K) and the temperature.

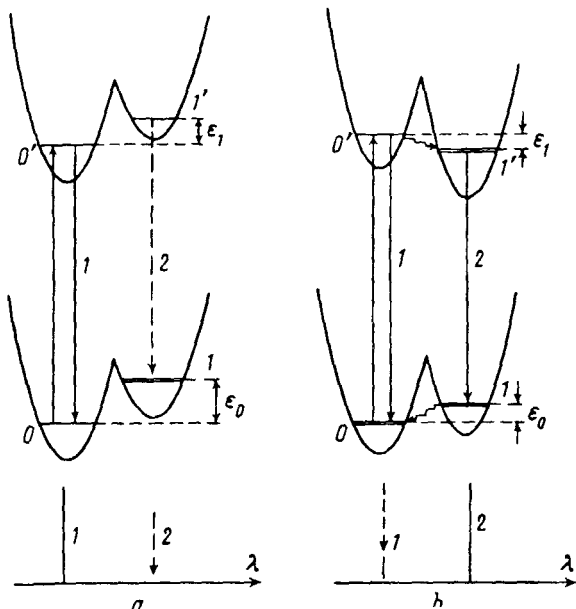


FIG. 3. Model of a two-well adiabatic potential which explains the redistribution of intensity in the fluorescence spectrum of perylene upon a change in pressure.

spectrum can also be partially restored without withdrawing the pressure—by raising the temperature 20–30 °C. We see in Fig. 2 that the intensity of the original line is partially restored as the temperature is raised.

How do we interpret this effect? It might be due to an inversion of two closely spaced excited electronic levels as the pressure in the sample is raised. However, there are no experimental or theoretical data on the existence of such levels near the 0–0 transition of perylene. In addition, in a three-level system of that sort (a ground level and two excited levels), a spectral shift of the lines should have been observed if there were a change in the relative positions of the upper levels. As we mentioned above, however, the spectral lines did not shift; they simply changed in intensity.

A noncontradictory explanation of these experimental results can be found on the basis of a four-level scheme (Fig. 3). In this case the system has two levels in both its ground state and its excited state. The reason for this situation is that the adiabatic potential has two minima. Such two-level systems have been invoked previously (see, for example, Refs. 3 and 4) to explain numerous anomalous properties of polymers and glasses. Our experimental data can be explained on the basis of this scheme as follows: We assume that at standard pressure the arrangement of levels corresponds to Fig. 3a. The purely electronic line 1 in the absorption and fluorescence spectra is then due to a transition between levels 0 and 0'. A rise in pressure distorts the adiabatic potential. As a result, level system 1–1' shifts in an identical way with respect to levels 0 and 0', as shown in Fig. 3b. The wavelengths of lines 1 and 2 therefore do not change. In this case the excited impurity centers undergo a transition from the 0' level to the 1' level as a result of relaxation. The transition erases line 1 and generates line 2, corresponding to the 1' ← 1 transition, on the long-wave side of former line 1. As

the temperature is raised, the population of level $0'$ increases as a result of thermal scattering, and line 1 is partially restored.

In a previous study⁵ on the same impurity system, we observed an anomalous optical dephasing, which we were able to explain only by assuming that the crystal contains two-level systems. In the present study, the same conclusion—that there are two-level systems in the crystal—follows from an analysis of a completely different phenomenon. The fact that two different effects can be explained in a common theoretical model gives us confidence in the conclusion that these crystals contain two-level systems.

Further research will be necessary in order to determine which specific coordinate—intramolecular or crystalline—is associated with the presence of several minima of the adiabatic potential. Further research is also required in order to find a joint quantitative description of the anomalous optical dephasing and the pressure-induced transformation of the spectra of perylene. We plan to carry out such studies in the near future.

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