

Anomalous thermal line broadening in the optical spectra of perylene in *n*-octane

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The temperature dependence of the homogeneous width of the nonphonon lines in the vibron spectra of perylene in *n*-octane exhibits a saturation. This saturation cannot be explained on the basis of an interaction with phonons.

There is convincing experimental evidence that the optical dephasing responsible for the thermal broadening of nonphonon lines is caused by a quadratic electron-phonon interaction in the case of impurity crystals.¹⁻⁴ The specific mechanism of this interaction involves a change in the frequencies of crystal vibrations upon an electronic transition in an impurity molecule. We show below that a thermal broadening may occur because an impure crystal contains low-frequency excitations of a nonphonon type, along with phonons. These nonphonon excitations^{5,6} are the so-called two-level systems, which are being discussed widely in connection with optical dephasing in polymers and glasses.²

In this letter we are reporting a study of the thermal broadening of nonphonon spectral lines of the fluorescence excited selectively by monochromatic laser light in impurity perylene crystals in *n*-octane at high pressure. This impurity system has been studied previously at standard pressure.⁷ It exhibits the record high rate of thermal broadening and shift of nonphonon lines. The selective fluorescence which we studied is that of perylene molecules, which are incorporated in the matrix in a manner distinct from that for the molecules which are studied at standard pressure. A discussion of specifically what these differences are goes beyond the scope of the present letter. A selective fluorescence arises as the pressure is raised. It differs from the fluorescence studied in Ref. 7 in terms of both its spectrum and the rate of the thermal broadening of the nonphonon lines.

The experiments were carried out over the temperature interval from 5 K to 30 K at a pressure of about 3 kbar. We used an optical pressure chamber, which compressed the sample in a quasihydrostatic manner. In order to detect effects of the deviation from a perfectly hydrostatic compression on the thermal broadening of the lines, we repeated the experiments several times on the same sample, changing the direction of the temperature variation. We found no hysteresis which would be characteristic of processes associated with a change in the quasihydrostatic compression conditions. The fluorescence was excited with the beam from a single-mode cw He-Cd laser with an output wavelength $\lambda = 441.6$ nm. For study of the fluorescence spectrum we selected the line with the wavelength $\lambda = 448.6$ nm, which corresponds to the most active molecular vibration of perylene, with a frequency of 353 cm^{-1} . After measuring the width of the spectral line, we eliminated the temperature-independent part of this

width, which stems from an inhomogeneous broadening and the finite lifetime of the energy levels. This part of the width was determined by extrapolating an experimental plot of the temperature dependence to 0 K. This component had a value of about 1.15 cm^{-1} .

Figure 1 shows the temperature dependence of the homogeneous width γ of the vibron line at 448.6 nm , after elimination of the temperature-independent component. We see two temperature intervals, differing significantly in the behavior of the thermal broadening of the nonphonon lines. At low temperatures ($5\text{--}10 \text{ K}$), there is a quasilinear broadening ($\gamma \propto T^{1.1}$). In the temperature interval $17\text{--}30 \text{ K}$ we find a characteristic quadratic law ($\gamma \propto T^2$). The most interesting feature of this experimental plot, however, is the fact that there is no broadening in the interval $10\text{--}17 \text{ K}$. This effect—a saturation of the thermal broadening—is impossible in principle to explain theoretically on the basis of an electron-phonon interaction. The reason is that in the low-temperature limit the theory predicts a broadening law $\gamma \propto T^7$ in the case of an interaction with acoustic phonons, while it predicts an activation law in the case of an interaction with local phonons. At high temperatures, both models lead to a $\gamma \propto T^2$ broadening. Obviously, neither of these models is capable of explaining the experimentally observed saturation as the temperature is varied.

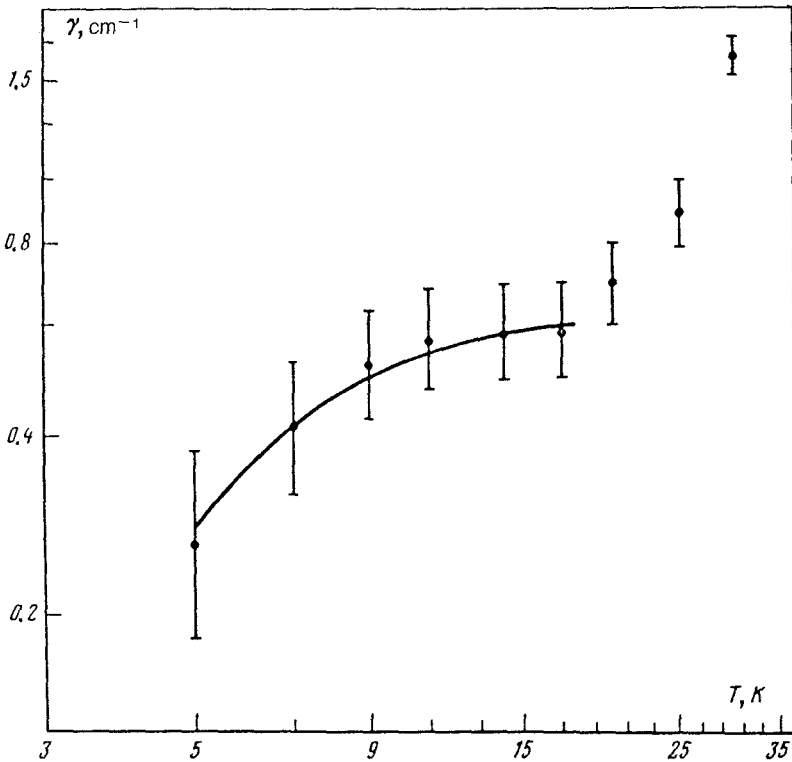


FIG. 1.

Our interpretation of these results runs as follows. The thermal broadening in this case is determined by two distinct mechanisms, operating simultaneously. At $T > 17$ K, the broadening is caused primarily by an interaction with local phonons. To explain the anomalous broadening at low temperatures, we need a fundamentally new broadening mechanism for impure crystals. We believe that a suitable mechanism is the tunnelon mechanism which was originally proposed by Osad'ko⁸ to explain the thermal broadening of impurity spectra in polymers and glasses.^{9,10} According to that mechanism,⁸ the thermal broadening results from the creation and annihilation of tunnelons, which are the quanta of excitation in two-level systems. These two-tunnelon processes are analogous to the two-phonon processes which are believed to be (exclusively) responsible for the thermal broadening in crystals. In contrast with phonons, however, tunnelons are Fermi excitations, so their laws governing broadening are quite different. In particular, both the quasilinear behavior of the thermal broadening and the saturation can be explained in a completely natural way on the basis of a two-tunnelon theory.

Under the assumption that only one tunnelon senses the electronic excitation at the impurity center, the homogeneous half-width of the spectral line, γ , is given as a function of the temperature by²

$$\gamma(T) = \gamma_g \cos h^{-2}(\epsilon/kT), \quad (1)$$

where ϵ and γ_g are the energy and the reciprocal lifetime of the tunnelon. A calculation carried out on the basis of (1) with the values $\epsilon = 6.9 \text{ cm}^{-1}$ and $\gamma_g = 0.7 \text{ cm}^{-1}$ leads to a good agreement with experiment in the temperature interval 5–17 K (Fig. 1). This agreement lends support to the suggestion that a tunnelon mechanism is operating to cause a broadening in this impure crystal. Note the unusually high energy of the tunnelon (which is one or two orders of magnitude greater than in amorphous media). Because of this high energy, this mechanism continues to operate up to 17 K. In amorphous media, saturation is reached at 0.05–0.5 K, and the broadening at higher temperatures is caused by a phonon mechanism. We should also point out that for crystals, in particular, *n*-octane, we know of no data demonstrating the existence of two-level systems, in contrast with the case of glasses, in which the presence of two-level systems is confirmed by independent data on thermodynamic, acoustic, and certain other properties.

We note in conclusion that the two-tunnelon theory is at present the only theory capable of explaining our experimental results. Nevertheless, a final resolution of the question of whether a tunnelon mechanism is responsible for the thermal broadening in impure crystals will require further research.

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