

FLUORESCENCE OF ANTHRACENE CRYSTALS AT HIGH EXCITON CONCENTRATIONS

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A parallel study was made of the decrease of the quantum yield of the integral emission and of the increase of the relative intensity of one of the vibronic bands in the fluorescence spectrum of an anthracene crystal excited by a nitrogen laser. Control methods that permit the investigation of each of these phenomena separately are obtained.

Two phenomena were observed in the fluorescence spectrum an anthracene that is intensively pumped, namely a decrease in the quantum yield of the integral emission (nonlinear quenching) [1, 2] and an increase in the relative intensity of one of the vibronic bands [3, 4]. Since these two processes were observed in the same samples in one temperature interval and at comparable pump levels, it was deemed to be of interest to investigate the relation between the two. We shall show in this paper that the gain of the vibronic band with participation of the 1400 cm^{-1} oscillation (band I) is due to the onset of light generation in the crystal. Methods for controlling the quenching and the generation are found and make it possible to investigate the two phenomena separately.

We investigated the fluorescence of sublimated anthracene flakes $0.5 - 3\ \mu$ thick, excited by nitrogen-laser pulses of 12 nsec duration and 1.5 kW power at a focusing-spot diameter 1.2 mm. The crystals were freely secured in paper envelopes on the post of a helium thermostat with adjustable bath temperature. The fluorescence from the rear face of the sample was fed through a DFS monochromator to an FEU-36 photomultiplier, the signal from which was fed to a stroboscopic oscilloscope triggered by a reference pulse with adjustable delay. The output voltage, which was proportional to the pulse on the photomultiplier at a specified instant of time, was registered with an automatic recorder, so that the luminescence spectra at this instant could be registered. All the data reported below pertain to the instant of time of maximum luminescence. The measurements of the integral quenching were performed in the same manner as in [2].

Owing to various possible nonradiative transitions, intense pumping causes the temperature of the illuminated region of the crystal to rise. The total heating was determined from the half-width of the vibronic band with participation of the 395 cm^{-1} oscillation (band II), the temperature dependence of which was measured independently and coincided with the data of [5]. At a pump intensity $4 \times 10^{22}\text{ cm}^{-2}\text{sec}^{-1}$ and at a bath temperature 4.2°K , the half-width of band II in different samples corresponded to temperatures $10 - 21^\circ\text{K}$. To eliminate this temperature variation, the bath temperature in the measurements of the intensities of individual bands and of the integral quenching was varied in such a way that the half-width of band II remained constant.

The following can be concluded from an analysis of the experimental data obtained under these conditions concerning the intensity gain of band I:

1. It occurs in the presence of nonlinear quenching of the integral intensity of the entire spectrum, and the quenching takes place at all temperatures and for all sample thicknesses, whereas the gain was observed only when the temperature of the illuminated region was lower than 27°K , and was not observed in crystals thicker than $2\ \mu$.

2. It consists of a faster-than-linear growth of both the peak and integrated intensity of the band and a sharp narrowing of the remaining bands of the spectrum.

3. It increases with decreasing crystal thickness, and for the thinnest crystal the relative peak intensity at maximum pump ($10^{23} \text{ cm}^{-2}\text{sec}^{-1}$) increases by a factor 1000.

4. It is also observed when fluorescence from the side face of the crystal is measured, accurate to within a factor of 2 - 3 in terms of the pumping.

Figure 1 shows typical characteristics of the emission from the crystal. At maximum pumping, band II is much more attenuated than the integral fluorescence (by a factor 2.5), indicating that the intensity is transferred from the entire spectrum to the enhanced band I. It should be noted that at constant bath temperature, meaning in the case of varying temperature of the illuminated region of the sample, all the thresholds become noticeably smeared out. The reason is the temperature broadening of the spontaneous-fluorescence bands, which leads to a radical change in the threshold I_p .

The data on Fig. 1 show that the amplification regime in this thin anthracene crystal sets in at an exciton concentration $n_p = (3 - 6) \times 10^{17} \text{ cm}^{-3}$ ($n_p = \Phi K I_p \tau$, where $\tau = 4 \times 10^{-9} \text{ sec}$ is the time of spontaneous fluorescence, $K = 2 \times 10^4 \text{ cm}^{-1}$ is the coefficient of absorption of the exciting light, and Φ is the integral-fluorescence quenching factor. An estimate of the gain yields then an approximate value 50 cm^{-1} , indicating that the amplification length is much larger than the crystal thickness.

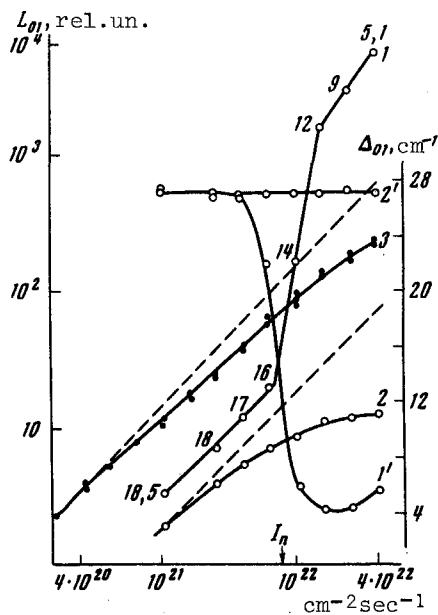


Fig. 1

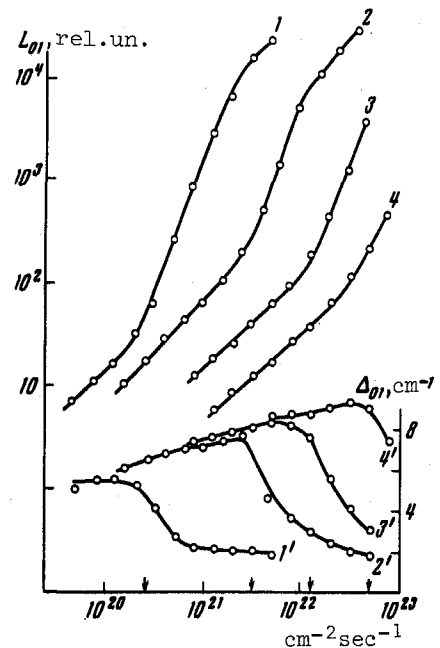


Fig. 2

Fig. 1. Intensities (curves 1, 1') and half-widths (curves 2, 2') of the bands 23.692 cm^{-1} (band I) and 24.705 cm^{-1} (band II), and integral fluorescence (curve 3) vs. the pump intensity for a sample 0.5μ thick. The temperature of the illuminated part of the crystal is 21°K . The numbers denote the bath temperatures.

Fig. 2. Intensities and half-widths of band I vs. the pump intensity at different diameters D of the illuminated region: 1 - 3.2 mm , 2 - 1.2 mm , 3 - 0.65 mm , 4 - 0.3 mm . Crystal thickness $\sim 1 \mu$, bath temperature 4.2°K .

The presence of sharp thresholds in the dependences of the half-width and the intensity of band I on the pump allow us to assume that a regime of light generation is realized in thin anthracene crystals. The nature of the generation is not quite clear. Its strong dependence on the crystal thickness, however, gives grounds for assuming that it develops on modes that experience total internal reflection and have amplification lengths L on the order of the diameter D of the illuminated region. It is precisely in this case, when $d > 1/K$, that the amplification length L should decrease with increasing thickness d . Although d/λ approaches unity in the investigated crystals, the noted decrease of L can be qualitatively confirmed within the framework of geometrical optics, when $L = 2D/kd \sin\alpha$ (α is the angle of total internal reflection). For crystals with $d > 2 \mu$, the self-excitation conditions may not be attained then because of the decrease of L . The induced-fluorescence light from the generating modes can be emitted as a result of intermode transfer due to the presence of defects and mechanical stresses in the sample [6].

Additional measurements of the dependence of the gain of band I on the value of D agree with the model considered here. Figure 2 shows plots of the peak intensity and of the half-width of band I against the pump for different values of D . With increasing D , the generation threshold decreases, since the amplification length L increases. At $D = 3 \text{ mm}$ we have $I_p = 4 \times 10^{28} \text{ cm}^{-2}$, i.e., generation sets in at arbitrarily low exciton concentrations ($3 \times 10^{16} \text{ cm}^{-3}$), when the quenching is small. Thus, by varying the bath temperature, the crystal thickness, and the diameter of the illuminated region, it is possible to observe generation under nonlinear-quenching conditions, as well as each of these phenomena separately.

As a result of the measurements it was found that the generation observed in the anthracene crystal is more readily of laser origin. This is particularly important because, besides the known generation on exciton-phonon transitions in crystals of the CdS type [7], this is the second observation of generation in which excitons take part, and is apparently the first for pure molecular crystals.

In addition, the measurements have shown that at equal values of the pump different samples are differently heated and hence their bands are differently broadened. The characteristics of the nonlinear quenching and the generation thresholds are therefore also different in such samples. This is evidence of the need for a more detailed study of the connection between the discussed phenomena and vibrational relaxation processes. Such investigations can be performed, in particular, by measuring the temporal characteristics with the apparatus described above.

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