Fluorescence of anthracene crystals at high exciton concentrations

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It is shown that in an anthracene crystal with high exciton concentration, an additional glow, with distinctive kinetics, appears in the fluorescence spectrum on the long-wave edge of the vibronic band (VB) 23692 cm^{-1}.

In earlier investigations,[1] the onset of light generation in the vibronic band (VB) stabilized the exciton concentration at the level 10^{16}–10^{17} cm^{-3}. In this study we used very small light-spot diameters (not larger than 0.02 cm), thus guaranteeing the absence of generation and allowing us to attain a concentration $\sim 2 \times 10^{18}$ cm^{-3}. The optical pumping (OP) was by a pulsed nitrogen laser (3371 Å) and corresponded, at an absorption coefficient 2×10^4 cm^{-1}, to a volume rate of exciton generation $\sim 6 \times 10^{27}$ cm^{-3} sec^{-1}. The time variation of the fluorescence spectra was recorded stroboscopically, and each measured point corresponded to averaging over $\sim 10^3$ readings.

At the employed optical pumping level, the fluorescence intensity integrated over the spectrum depends sublinearly on the pump intensity, owing to the nonlinear fluorescence quenching.[3] The quenching factor
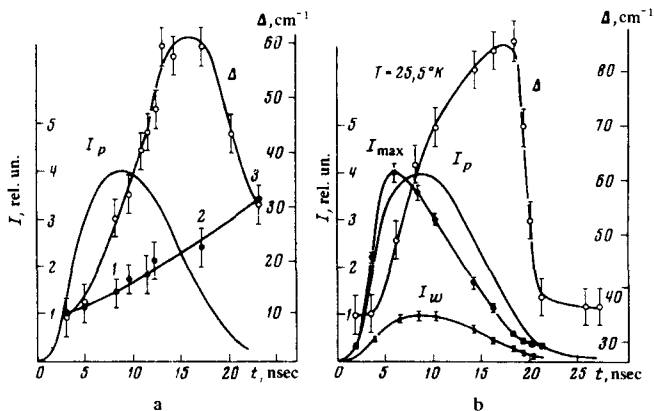
I_p—dependence of the optical-pump pulse amplitude on the time. Points 1, 2, and 3 correspond to temperatures 15, 22, and 25.5°K, respectively. The remaining notation is explained in the text.

was about 10–12, corresponding to a decrease in the exciton lifetime from the usual 4 nsec to ~0.4 nsec.

During the time of action of the optical pumping (~11 nsec), the samples become heated. To monitor the heating, we used the value of the Debye-Waller factor in the spectrum of tetracene introduced as an impurity (~10^{15} cm^{-3}) in individual crystal samples. [2] Owing to the high rate of heat transfer in perfect anthracene crystals, [2] the sample was heated almost uniformly over its thickness within 10^{-3} cm.

Figure a shows the dependence of the half-width Δ of the 23692 cm^{-1} VB on the time during the OP pulse. If it is assumed that the "tetracene thermometer" reads the equilibrium lattice temperature, then the separately measured temperature dependence of the VB half-width under ordinary conditions (see, e.g., [4]) can yield the expected value of Δ_0, which is shown for comparison in the same figure.

It follows from Fig. a that during the OP pulse there is observed an anomalous broadening of the VB, which then vanishes rapidly. When the OP intensity is decreased by one order of magnitude, this effect disappears and there is no difference between the time variations of Δ and Δ_0. Measurements of the contour have shown that the broadening is due mainly to the appearance of an appreciable long-wave wing in the VB. The specific nonmonotonic dependence of Δ on the time is observed even more pronouncedly if the same lattice temperature, 25.5°K, is maintained in the sample by controlling the temperature of the thermostat and by monitoring it against the tetracene spectrum at all points of the OP (Fig. b). [2] We measured the time dependences of the luminescence amplitudes at the VB maximum (I_{max}) and at one of the points of its long-wave wing (23630 cm^{-1}-I_w) (Fig. b). It is seen from these measurements that the intensity I_{max} begins to decrease 4–5 nsec before the OP reaches its maximum value. On the other hand, the long-wave wing flares up in the spectrum only near the maximum of the OP pulse. It has turned out here that the total integrated luminescence in this region of the spectrum practically duplicates the shape of the OP pulse. At the start of the

pulse and at its end, the VB has the form usual for T = 25.5°K, whereas the broadened contour produced in the intermediate period cannot be set in correspondence with any of the spectra of the samples heated at equilibrium.

Thus, the observed phenomenon consists of a peculiar redistribution of the intensity from the maximum of the VB, 23692 cm^{-1}, into its long-wave wing, thus leading to an effective broadening of the band. It reaches its full development approximately 7–8 nsec after the maximum of the OP pulse, and at the end of the pulse (within ~1 nsec) the spectrum again resumes its ordinary (equilibrium) form.

The appearance of a long-wave in the 23692-cm^{-1} VB, corresponding to a transition from the bottom of the exciton band, can hardly be ascribed to a change in the energy distribution of the band excitons, since such a change would affect, in the main, its short-wave edge. It is difficult to set the observed picture in correspondence with the broadening of the spectrum as a result of exciton-exciton collisions, for in this case both wings of the band would become deformed, especially the short-wave wing, which corresponds to head-on collisions.

It might be assumed that the observed singularities are due to some degree to accumulation of nonequilibrium lattice phonons in the system. It is then necessary, however, to assume accumulation of high-frequency phonons (50–100 cm^{-1}) from the region of the high density of the phonon states. [5] Furthermore, accumulation of the nonequilibrium phonons should increase also the probabilities of the optical transition with participation of phonons, leading to a relative growth of both wings of the VB in the spectrum.

It can thus be assumed that the observed singularities are due to a new hitherto-unobserved phenomenon in a system of Frenkel excitons of high density.

One such phenomenon may be the formation of a new exciton phase of increased density. It is produced in the exciton system with a certain time delay necessitated by the need for awaiting the formation of the nuclei of the new phase. [3] It is this delay which can explain the inertial processes illustrated in Fig. b. If this treatment is correct, then we must assume values 50–100 cm^{-1} for the binding energy of the excitons in the new phase. From the very abrupt decay of the half-width Δ on the tail of the pulse (Fig. b) we can conclude that the lifetime of the exciton phase is short (~1 nsec).

[1] At low temperatures this VB corresponds to optical transitions from the bottom of the exciton band to a narrow band of the intramolecular crystal vibrations, $\hbar\omega$ = 1404 cm^{-1}.

[2] We recall that the stroboscopic procedure makes it possible to measure independently the response at each point of the OP pulse.

[3] A similar phenomenon seems to occur, for example, when an electron-hole plasma is produced in a CdS crystal following intense optical pumping. [6]

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