Nonlinear Fluorescence Reabsorption in Excimer-Forming Crystals by Electronically Excited Molecules

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Anomalous slowing down of fluorescence decay at high excitation density has been observed in pyrene and α-perylene crystals, and attributed to nonlinear fluorescence reabsorption by electronically excited molecules. This phenomenon may have various implications in studies of condensed phases at high levels of optical exciation.

Excitons in molecular crystals at high levels of excitation interact and may either annihilate,[1] show induced fluorescence,[2] or, as predicted for some systems, form polyexcitons.[3] A value often measured in kinetic studies of exciton-exciton annihilation is the fluorescence flux $F(t)$, which is generally assumed to be proportional to the exciton density $n(t)$. It is clear that irrespective of the specific mechanism of exciton-exciton interaction the annihilation process will *speed up* the rate of fluorescence decay and decrease the fluorescence quantum yield. We report here an apparent *slowing down* of the fluorescence decay which shows up at high levels of optical excitation. The effect has been observed in excimer-forming molecular crystals (pyrene, α-perylene) at temperatures sufficiently low ($T < 100$ K) that the excimers (electronically excited dimers) are practically immobile.[4] Our measurements reveal that the magnitude of the slowing down depends on (1) the absorption coefficient, k_λ, of the crystal at the wavelength, λ, of excitation; (2) the wavelength at which the fluorescence is detected; and (3) the time lapse between the excitation pulse and detection. We attribute the slowing-down effect to nonlinear fluorescence reabsorption (NFR) by the excimers. We show that at high excimer density NFR can seriously mask the contribution of excimer-excimer annihilation to the observable variable $F(t)$.

Crystals of pyrene and α-perylene were used whose high purity was verified by their room-temperature fluorescence lifetimes and by the invariance of the low-temperature lifetimes to wavelength of excitation. The generation of high exciton density was performed via a pulsed DL 200 Molectron dye laser pumped by a 400-kW Molectron nitrogen laser. The exciting dye-laser

pulse (~ 6 nsec) was focused to a spot of about 100 μm diam on a crystal surface, with a maximal flux of photons of about 10^{27} cm^{-2} sec^{-1}. The fluorescence was isolated by cutoff filters and a grating monochromator, and detected by a fast photomultiplier followed by a Tektronix R7912 transient digitizer. The number of photons reaching the photomultiplier was kept constant within its linear range by means of a variable optical attenuator.

Figure 1 shows typical low-temperature fluorescence decay curves of perylene at low and high excitation intensities. Similar results were obtained for pyrene crystals. At low excitation intensity the single exponential decay (with a time constant of 90 nsec for perylene and 150 nsec for pyrene) was invariant to wavelength of observa-
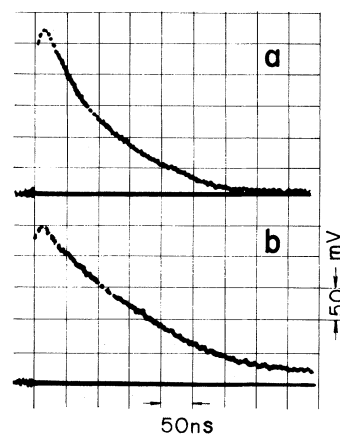

FIG. 1. Fluorescence decay of an α-perylene crystal at tail-absorption excitation (476 nm); wavelength of detection 610 nm and temperature 77 K. (a) $\sim 10^{22}$ photons cm^{-2} sec^{-1} (low intensity); (b) $\sim 10^{26}$ photons cm^{-2} sec^{-1} (high intensity).

tion as well as to wavelength of excitation from 337 nm to tail absorption. However, at high intensity two extreme types of behavior are observed for pyrene crystals which depend on the absorption coefficient, k_λ: (1) In the region of $k \gtrsim 10^4$ cm^{-1} with increasing intensity a regular speeding up of the decay, as well as an increase in the fluorescence quenching due to excimer-excimer annihilation, was observed. (2) In the tail absorption region (10^3–10^2 cm^{-1}) no speeding up was observed; on the contrary, the rate of fluorescence decay is apparently slowed down, especially at the beginning of the process. This effect is, however, accompanied by a substantial reduction in fluorescence quantum yield. There is no sharp boundary between "speeding-up" and "slowing-down" regimes; by varying the wavelength of excitation one passes smoothly from one type of behavior to the other. In the intermediate region a decrease in fluorescence quantum yield was not accompanied by corresponding speeding up in fluorescence decay time. Similar behavior to that presented above was observed for α-perylene crystals. However, the magnitude of the slowing

down was more sensitive to wavelength of fluorescence detection in α-perylene crystals than in pyrene.

All our observations are simply explained as resulting from the photon-exciton interaction: There is a finite probability of the excimer fluorescence being reabsorbed by other excimers. The upper electronically excited excimer states thus formed decay radiationlessly, restoring the excimers to their lowest excited state.[5] Since relaxation times of higher excited states are of the order of picoseconds,[6] the reabsorption process does not alter the number of excimers and its time evolution (on the time scale of our experiment), but it certainly affects the fluorecence flux. The quantum yield of fluorescence due to reabsorption has a lowest value immediately after the excitation pulse. However, the following excimer decay gradually increases the fluorescence quantum yield which shows up as a slowing down of the fluorescence decay. The fluorescence flux obviously depends on the density of excimers, their spatial distribution, and excimer absorption. In the wavelength interval $\lambda \to \lambda + \Delta\lambda$ the flux is described by the following equation:

$$F_\lambda(t) = \frac{q(\lambda)\Delta\lambda}{4\pi\tau} \int_V n(x,y,z,t)\,dx\,dy\,dz \oint \exp\{[-\sigma(\lambda)n(x,y,z,t)]L_\Omega(x,y,z)\}\,d\Omega. \tag{1}$$

Here x,y,z are the coordinates of a point where a photon is to be born; $n(x,y,z,t)$ is the excimer density at this point at time t; L_Ω is the distance traveled by the photon in a certain direction, Ω, before escaping from the excitation volume V; $\sigma(\lambda)$ is the cross section of the excimer-photon interaction; τ is the excimer radiative decay time; and $q(\lambda)$ is the low-intensity fluorescence spectrum normalized so that $\int q(\lambda)\,d\lambda = 1$.

Figure 2 presents the results of numerical integration of Eq. (1) at any given time t after excitation for a disk-shaped excitation and the assumption of uniform excimer density.[7] We take the disk radius r as equal to that of the laser focus spot, and the disk to be of height $h = k_\lambda^{-1}$. It is convenient to express both lengths in dimensionless form by referring them to a characteristic reabsorption length, $(\sigma n)^{-1}$. If we take a typical excimer density $n = 10^{19}$ cm^{-3} and a cross section $\sigma = 10^{-17}$ cm^2, as measured for pyrene excimers in solution,[8] we get $(\sigma n)^{-1} = 10^{-2}$ cm. Then, for example, a laser focus spot of 200 μm diam defines an excitation region having a dimensionless radius $r = 1$. Figure 2 shows that the reabsorption in pyrene crystals may be measurable for $h \gtrsim 0.1$ or $k \lesssim 10\sigma n = 10^3$ cm^{-1}. Such conditions

are achieved for pyrene tail-absorption excitation ($\lambda \gtrsim 370$ nm). At still smaller values of $k (\lesssim 10^2$ cm^{-1}) the fraction of fluorescence flux reabsorbed can reach 50%, or more, of the maximum value; the experimental data for the corresponding wavelengths indeed agree with this expectation. The absolute value of σ for perylene excimers is not known, but judged from the magnitude of the reabsorption in these crystals, it must be of the same order of magnitude as that of pyrene excimers.
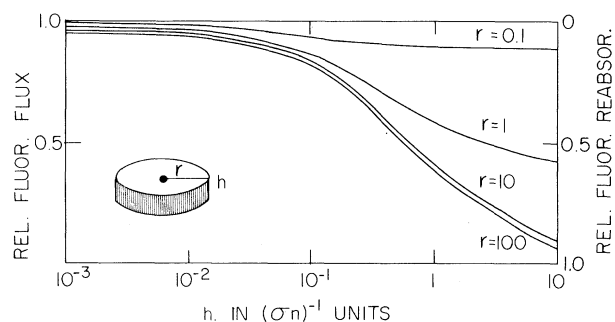

FIG. 2. Nonlinear fluorescence reabsorption as calculated from Eq. (1) as a function of the dimensionless radius (r) and depth (h) of the excitation region.

The room-temperature excimer absorption spectra of pyrene and α-perylene crystals[5] as measured by means of two pulsed dye lasers are presented in Fig. 3. As follows from this figure, the maximum excimer absorption is near 480–510 nm for pyrene and 610–640 nm for α-perylene. These spectral regions are also those of maximal slowing down of the flurescence decay at high intensities. However, the magnitude of the effect was observed to fall off more rapidly with changing fluorescence detection wavelength than expected from Fig. 3. In fact, for α-perylene at 700 nm there is no slowing down at all, in contradiction to the data of this figure. We attribute this discrepancy to the fact that the excimer absorption spectra were measured at room temperature whereas the fluorescence reabsorption was observed at low temperatures. On this basis it appears that in our systems the width of the excimer absorption band, especially on the low-energy side, is much narrower at low temperatures than at room temperature.

The final test of our model involves a quantitative study of the time evolution of excimer fluorescence. According to this model, in crystals at high exciton densities the numbers of photons escaping the excitation volume can be diminished not only by exciton-exciton annihilation but also by fluorescence reabsorption. The time evolution of the resulting photon flux is described by Eq. (1). Figure 4 compares the experimental fluorescence decay of pyrene at low temperature when excited at tail absorption (curve 2) with the decay characteristics expected on the basis of computer simulation of Eq. (1). The excimer density $n(t)$ necessary for this calculation was taken from another experimental decay curve, measured following main-band excitation ($h \simeq 10^{-3}$, $r \simeq 10$). The latter decay (curve 1) shows excimer annihilation

but with $F(t) \propto n(t)$ which is achieved when reabsorption is small (~ 3%, see Fig. 3). Since $n(t)$ is not influenced by the reabsorption one can use the data for $n(t)$ obtained from curve 1 for the computer simulation of the decay when reabsorption is important, provided the same $n(0)$ is valid for the two cases. The absolute value of $n(0)$ is known within a factor of 2. A value selected within this range to best fit the simulation to the experimental decay results. The excellent fit so obtained (Fig. 4) over the whole range of the decay strongly supports our interpretation of NFR as an additional and important nonlinear fluorescence quenching mechanism.

In summary, we emphasize that the phenomena of NFR by electronically excited species reported in this Letter need not be specific to excimer-forming molecular crystals, but may be operative in any system with sufficiently high exciton density and with an overlap between the absorption spectra of electronically excited species present and their emission spectra. Therefore, in studies of exciton-exciton annihilation it may be incorrect to assume that the fluorescence flux $F(t)$ is proportional to the exciton density $n(t)$, and a reabsorption term has to be introduced. For conditions where $\sigma \sim 10^{-17}$ cm^2, the exciton density $\sim 10^{20}$ cm^{-3}, and the excitation volume is $\sim 1 \times 1 \times 1$ mm^3, the reabsorption of luminescence photons may be close to 100% at some stage of the decay. Under such conditions the excitation region appears in a certain sense as a "black hole," trapping practically all the luminescence photons
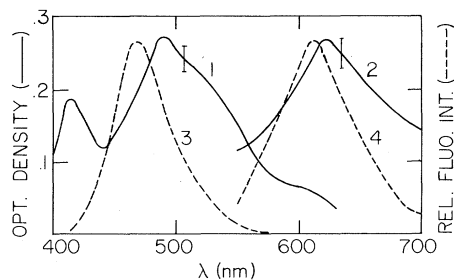

FIG. 3. Room-temperature excimer absorption spectrum of pyrene (curve 1) and α-perylene (curve 2) single crystals; curves 3 and 4 show the corresponding excimer emission spectra at 77 K.
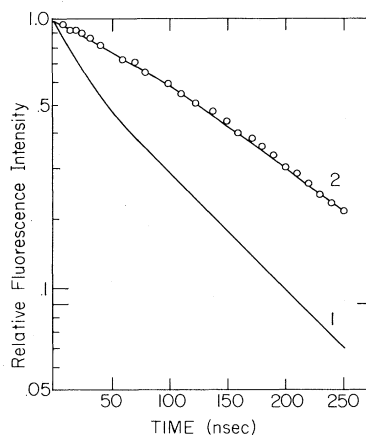

FIG. 4. Fluorescence decay of pyrene as calculated from Eq. (1) (circles) and experimentally observed without (curve 1) and with (curve 2) reabsorption. The excimer density $n(0)$ in both cases was about 10^{19} cm^{-3}.

and transforming them into heat. The nonlinearity of the fluorescence reabsorption is of a somewhat unusual nature: It grows exponentially with exciton density but to a first approximation does not alter the exciton dynamics. We have shown that such a nonlinear reabsorption affects the fluorescence decay as well as the shape of the fluorescence spectrum. One should be careful not to confuse these effects with the possible formation of polyexcitons or other excited species in the crystals at high excitation levels. NFR may be useful for experimental determination of the absorption coefficients of electronically excited species.

[1]A. Bergman, M. Levine, and J. Jortner, Phys. Rev. Lett. 18, 593 (1967); N. A. Tolstoy and A. P. Abramov, Fiz. Tverd. Tela (Leningrad) 9, 340 (1967) [Sov. Phys. Solid State 9, 255 (1967)].

[2]A. Benderskii, V. Kh. Brikenshtein, V. L. Broude, L. I. Korshunov, A. G. Lavrushko, and I. I. Tartakovskii, Opt. Spektrosk. 39, 75 (1975) [Opt. Spectrosc. USSR 39, 43 (1975)], and references cited therein.

[3]C. Mavroyannis, Phys. Rev. B 16, 2871 (1977); D. Fox, Mol. Cryst. Liq. Cryst. 57, 39 (1980).

[4]V. Yakhot, M. D. Cohen, and Z. Ludmer, Adv. Photochem. 11, 489 (1979).

[5]Z. Ludmer and L. Z. Zeiri, to be published.

[6]J. Covey and M. Malley, Opt. Commun. 18, 150 (1976).

[7]As follows from our direct measurements, the dye-laser intensity distribution is uniform over ~ 90% of the focal plane. In the incident direction the $n(x,y,z)$ distribution is uniform, to a good approximation, at tail absorption excitation where the penetration depth is of the order of magnitude of the crystal thickness.

[8]M. F. M. Post, J. Langelaar, and J. D. W. Van-Voorts, Chem. Phys. Lett. 10, 468 (1971).

Scaling Studies of Highly Disordered Spin-$\frac{1}{2}$ Antiferromagnetic Systems

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A numerical method is developed to study the scaling of distribution of couplings of highly random antiferromagnetic Ising and quantum Heisenberg spin-$\frac{1}{2}$ systems. The method shows how freezing into inert local singlets prevents ordering down to temperatures well below the median nearest-neighbor coupling or bare exchange percolation threshold in positionally disordered systems with Heisenberg exchange varying exponentially with distance (e.g., doped semiconductors, quasi one-dimensional salts). This is contrasted with the Ising system.

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Considerable effort has gone into the search for magnetic order, possibly of the spin-glass type,[1] in doped semiconductors (e.g., Si:P, CdS:In)[2,3] at donor concentrations (n) below the insulator-metal transition (n_{MI}). However, no anomaly is seen in the magnetic susceptibility[3] or Faraday rotation,[2] attributable to magnetic ordering caused by the antiferromagnetic (af) exchange coupling between donor electrons down to temperatures well below the median nearest-neighbor exchange or the coupling percolation threshold. Because the radius a of the donor electron (much greater than the host lattice spacing) sets the range of the exchange coupling, J, doped semiconductors constitute a three-dimensional (3D) system of spin $\frac{1}{2}$ distributed randomly in

space *in essentially a continuum way*, whose magnetic properties are characterized by the Heisenberg Hamiltonian

$$H = \tfrac{1}{2}\sum_{i \neq j} J(\vec{r}_i - \vec{r}_j)\vec{S}_i \cdot \vec{S}_j, \tag{1}$$

where $J(r)$ falls off exponentially[3] with r. (We use $J > 0$ for af exchange.)

The lack of ordering has been attributed in varying degrees to (i) the broad distribution of exchange couplings [typically varying by 10^4–10^8, Fig. 1(a)]; (ii) the short-range nature of $J(r)$; and (iii) the quantum character of spin $\frac{1}{2}$, all of which distinguish this system from conventional spin-glasses.[1] Because of (i), cluster calculations[2-5] have proved to be quite successful in pro-