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Delayed Fluorescence Wave Form from Free-Deep Trapped Triplet Exciton Annihilation

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Delayed Fluorescence Wave Form from Free-Deep Trapped Triplet Exciton Annihilation

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Abstract—Free-deep trapped triplet exciton annihilation leads to an asymmetric behavior in the buildup and decay of the delayed fluorescence wave form excited with low-intensity light in the first triplet exciton band. The kinetic analysis for the case of a single trap shows that the study of the temperature-and frequency-dependence of the complete delayed fluorescence wave form can yield the lifetimes of the free and the trapped triplets, the trapping rate, and the trap depth. Experimental results on the delayed fluorescence wave form from crystalline phenanthrene containing trapping levels at 0.6 eV below the triplet band show the behavior predicted by the kinetics.

1. Introduction

Free-trapped triplet exciton annihilation in molecular crystals has been extensively studied in recent years.(1–15) Conclusive evidence now exists that, after excitation in the first triplet exciton band of the host crystal, trapping of the " free " triplets can occur at structural defects or chemical impurities in the lattice. Delayed fluorescence emission can now arise from free-free or free-trapped triplet excitons annihilations.(16) The trapped excitation can be thermally released from the traps leading to strong temperature dependence of the delayed emission. Hence, also a direct excitation of the guest triplet (e.g. via intersystem crossing from the guest-singlet manifold) can lead to delayed fluorescence. The emission now originates from the interaction between the optically produced guest- and the

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thermally populated host-triplets. In principle, free-trapped triplet exciton annihilation can yield both host crystal- and guest molecule-delayed fluorescence and in many practical instances the steady-state emission due to free-trapped triplet exciton annihilation at a given temperature cannot be distinguished from free-free annihilation on the basis of spectroscopic data alone.

Free-free and free-trapped triplet exciton annihilations on the other hand should lead to different behaviors in the time-dependence of delayed fluorescence excited with chopped light. Several studies of the time-dependence of delayed fluorescence from free-trapped triplet exciton annihilation have been reported in the literature.(4,7–12) The more detailed experiments, however, were performed using strongly absorbed light to generate the triplets by intersystem crossing from the singlet manifold. This requires typically the use of a phosphoroscope arrangement to separate the weak delayed emission from the, directly excited, prompt fluorescence part. Thus, only a *fraction* of the delayed fluorescence wave form, the slowly decaying thermally activated part of delayed emission, is detected.

In this paper, we wish to point out that free-deep trapped triplet exciton annihilation can lead to a strongly asymmetric behavior in the buildup and decay portions of the delayed fluorescence wave form and that an experimental study of the time-dependence of the complete wave form observed under *direct* excitation of triplets with low-intensity light can yield several parameters of the trapping process. For the case of a single deep triplet exciton trap a simple time-dependence of delayed fluorescence can be obtained which is readily distinguishable from the one due to a free-free annihilation. The lifetimes of the free and trapped triplets, the trapping rate, and the trap depth can be deduced from an analysis of the temperature and frequency-dependence of the complete delayed fluorescence wave form. The method has been applied to commercial phenanthrene containing a trapping level at 4,700 cm^{-1} below the triplet exciton band.

2. Kinetic Analysis and Delayed Flourescence Wave Form

Figure 1 shows schematically the relevant rates in the simple case of trapping levels at depth ΔE below the triplet exciton band. The coupled rate equations giving the concentrations x and y of the free and trapped excitons, respectively, under excitation with light in the first triplet band can be simply written as(6)

$$\begin{aligned} \mathrm{d}x/\mathrm{d}t &= \alpha i + qy - ax \\ \mathrm{d}y/\mathrm{d}t &= k_t x - by, \end{aligned} \tag{1}$$

where α is the $S_0 \rightarrow T_1$ absorption coefficient of the crystal, i the

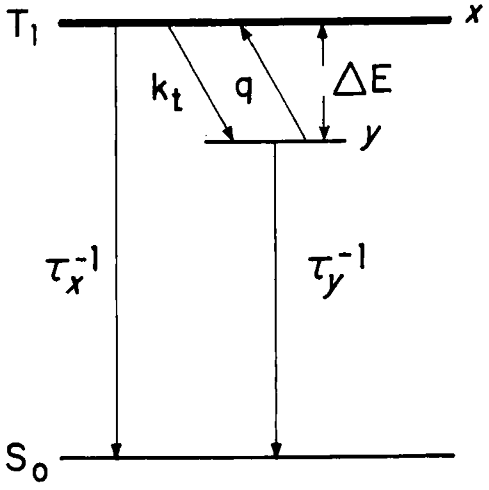

Figure 1. Schematic energy level diagram and definition of relevant rates for trapping at a level (y) at depth ΔE below the triplet exciton band (x).

exciting intensity, k_t the trapping rate, $q \equiv q(T) \propto \exp\{-\Delta E/kT\}$ the rate of detrapping by thermal activation,(17) and

$$\begin{aligned} a &\equiv \tau_x^{-1} + k_t \\ b &\equiv \tau_y^{-1} + q \end{aligned} \tag{2}$$

are the total monomolecular decay rate constants for the free and trapped excitons whose lifetimes are τ_x and τ_y, respectively. It has been assumed that the exciting intensity i is sufficiently low so as to insure a negligible depletion of the populations by the bimolecular processes x^2 and xy, respectively, and that no saturation of the trap levels occurs, that is, $y \ll N_y$, where N_y is the concentration of the trapping sites, e.g. of an impurity in the lattice. The total delayed fluorescence flux per unit volume of crystal due to triplet exciton interactions will be given by

$$F(t) = \tfrac{1}{2}\gamma x^2 + \tfrac{1}{2}\gamma' xy \tag{3}$$

where γ and γ' are respectively, the effective rate constants for the free-free and free-trapped triplet exciton annihilations leading to radiative singlets. The outcome of the free-trapped annihilation could be either the crystal- or the guest molecule-fluorescence.

For chopped light providing a square-wave modulation of the exciting intensity with a period T one has, $i = i_0$ for $0 \leqslant t \leqslant T/2$, and $i = 0$ for $T/2 \leqslant t \leqslant T$. If the frequency of modulation ω is sufficiently small with respect to the smaller of the two relevant rates a and b, ω/a, $\omega/b \ll 1$, one obtains from (1) that the buildup of the two exciton populations will be given by

$$\begin{aligned} y(t) &= C\{A^+(1 - e^{\lambda^+ t}) + A^-(1 - e^{\lambda^- t})\} \\ x(t) &= C\{B^+(1 - e^{\lambda^+ t}) + B^-(1 - e^{\lambda^- t})\}, \end{aligned} \tag{4}$$

where

$$\begin{aligned} C &= \alpha i_0[(\lambda^+ - \lambda^-)(ab - qk_t)]^{-1} \\ A^+ &= -k_t\lambda^-, \quad A^- = k_t\lambda^+, \\ B^+ &= -\lambda^-(\lambda^+ + b), \quad B^- = \lambda^+(\lambda^- + b), \end{aligned}$$

and where the two effective decay rates are given by

$$\lambda^{\pm} = -\tfrac{1}{2}\{a + b \mp [(a-b)^2 + 4qk_t]^{1/2}\}. \tag{5}$$

The steady-state concentrations of the free and trapped excitons are $x_0 = \alpha i_0 b/(ab - qk_t)$ and $y_0 = \alpha i_0 k_t/(ab - qk_t)$, respectively, having the expected ratio $x_0/y_0 = b/k_t$ of the free to the trapped populations.(18)

The general form of the time-dependence of the *buildup* $F_b(t)$ of the total delayed fluorescence flux from the crystal [Eq. (3)] can be then written as

$$F_b(t) = \tfrac{1}{2}C^2\{\phi_1(1 - e^{\lambda^+ t})^2 + \phi_2(1 - e^{\lambda^- t})^2 + \phi_3(1 - e^{\lambda^+ t})(1 - e^{\lambda^- t})\} \tag{6}$$

where the coefficients of the different exponentials are defined as

$$\begin{aligned} \phi_1 &= \gamma(B^+)^2 + \gamma' \mathrm{A}^+\mathrm{B}^+ \\ \phi_2 &= \gamma(B^-)^2 + \gamma' A^- B^- \\ \phi_3 &= 2\gamma B^+ B^- + \gamma'(A^+B^- + A^-B^+) \end{aligned}$$

with the first terms on the right-hand side giving the contribution of the free-free triplet exciton annihilation to the total delayed fluorescence signal. In a similar way, one can derive the time dependence of the *decay* portion $F_d(t)$ of the delayed fluorescence wave form as

$$F_d(t) = \tfrac{1}{2}C^2\{\phi_1 e^{2\lambda^+ t} + \phi_2 e^{2\lambda^- t} + \phi_3 e^{(\lambda^+ + \lambda^-)t}\}, \tag{7}$$

where the coefficients ϕ_i are the same as defined above.

A situation realized readily in practice is one of a deep ($\Delta E \gg kT$) trappling level due to the presence of a chemical impurity having its triplet level considerably lower than the first triplet band of the host crystal. In this case the trapping rate of the free triplet excitons can be several orders of magnitude faster than the rate of the emptying of the traps by either the direct or the thermally activated processes, that is, k_t/τ_y^{-1} and $k_t/q \gg 1$.(19) One has $b \ll a$ and the two rates [Eq. (5)] in the process can then be approximated by $\lambda^+ \approx -a$, and $\lambda^- \approx -a^{-1}(ab - qk_t)$. Since $\lambda^-/\lambda^+ \ll 1$ the coefficients ϕ_i determining the time dependence of the delayed fluorescence wave form [Eqs. (6) and (7)] can also be considerably simplified. Assuming that γ and γ' have similar orders of magnitude(20) and neglecting terms of the order of $b/k_t \ll 1$, one obtains

$$F_b(t) = K\{(1 - e^{-at})(1 - e^{-\beta t}) + \rho(1 - e^{-\beta t})^2\}, \tag{8}$$

$$F_d(t) = K\{e^{-at} + \rho e^{-2\beta t}\}, \tag{9}$$

where

$$K = \tfrac{1}{2}\gamma'\alpha^2 i_0^2 k_t/a(ab - qk_t), \tag{10}$$

$$\rho = k_t q(\tau_y^{-1}a + \tau_x^{-1}q)^{-1}, \tag{11}$$

and

$$\beta = \tau_y^{-1} + (a\tau_x)^{-1}q. \tag{12}$$

The delayed fluorescence signal is entirely due to free-trapped triplet exciton annihilation since the concentration of free triplets is several orders of magnitude smaller than the trapped population.

Figure 2 illustrates the strong asymmetry in the behavior of the buildup and decay portions of the wave form as predicted by Eqs. (8) and (9). The buildup of delayed fluorescence is slow, having two components with temporal behaviors $(1 - e^{-\beta t})$ and $(1 - e^{-\beta t})^2$, respectively. The last of these is the same as for mutual annihilation of free excitons with an hypothetical decay rate β. Since $a/\beta \gg 1$,

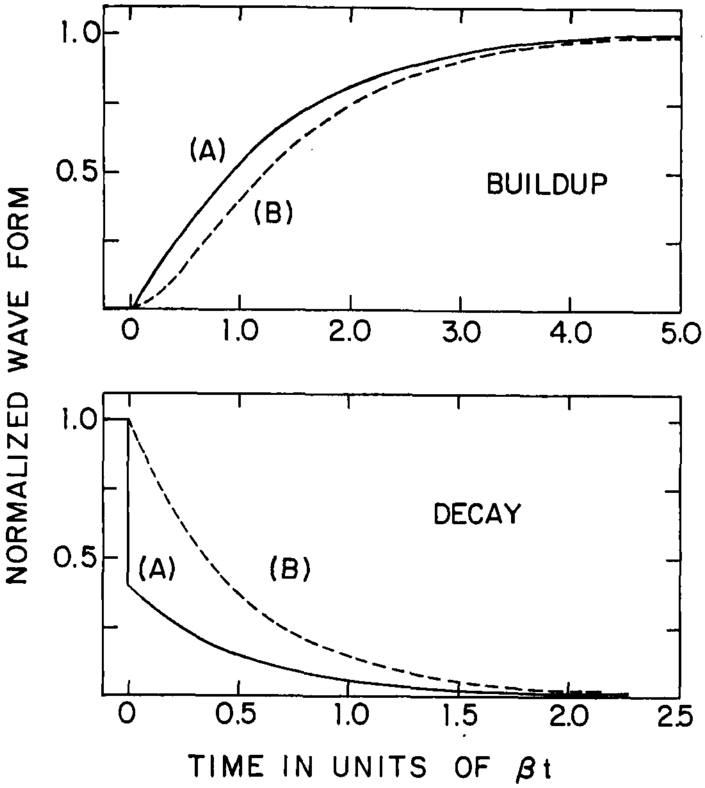

Figure 2. Normalized delayed fluorescence waveform (curves A) due to free- deep trapped triplet exciton annihilation as predicted by Eqs. (8) and (9) for $\rho = 2/3$ and $a = 10^3\beta$. For comparison, the usual delayed fluorescence waveform for free-free triplet exciton annihilation $(1 - e^{-\beta t})^2$ for buildup and $e^{-2\beta t}$ for decay, respectively) is also shown (curves B).

the coefficient of $(1 - e^{-\beta t})$ is unity on the time scale of the wave form and the proportion of the two components is given by ρ. The decay portion of the wave form clearly shows two components, also in the proportion given by ρ. The fast component e^{-at} appears to follow the shutoff of the exciting light on the time scale of the observations while the slow component, the only one that can be observed in a phosphoroscope arrangement, has a decay time given by $(2\beta)^{-1}$. Clearly, both components are proportional to the square of the exciting intensity.$^{(21)}$ At low temperatures β^{-1} approaches τ_y, the lifetime of the trapped triplets. The quantity $\Delta \equiv \beta - \tau_y^{-1}$ is proportional to q(Eq. (12)) and should yield ΔE, the depth of the trap.[22] At high temperatures the main route for trap depopulation is via the thermal activation and τ_y^{-1} becomes negligible with respect to q. If a and τ_x^{-1} have similar orders of magnitude Eq. (11) will then predict that ρ, the relative ratio of the slow to the fast component in the wave form, will increase with temperature to a finite value given by k_t/τ_x^{-1}, that is, to a value given by the ratio of the trapping to the direct decay rates of the free triplets. At low temperatures ρ becomes proportional to q and should decrease with decreasing temperature as $\exp\{-\Delta E/kT\}$.

An independent measurement of $a = \tau_x^{-1} + k_t$ can be obtained from the behavior of the delayed fluorescence wave form under excitation with light modulated at a frequency $\omega\beta \gg 1$ and $\omega \approx a$. For a general periodic excitation of the form

$$i(t) = \sum_{l=-\infty}^{\infty} I_l e^{jl\omega t}$$

one gets from (1) that the two exciton populations will be given by

$$x(t) = \sum_{l=-\infty}^{\infty} X_l e^{jl\omega t},$$

and

$$y(t) = \sum_{l=-\infty}^{\infty} Y_l e^{jl\omega t}, \tag{13}$$

where the complex coefficients are given by

$$\begin{aligned} Y_l &= \alpha I_l k_t[a + jl\omega)(b + jl\omega) - qk_t]^{-1}, \\ X_l &= \alpha I_l(b + jl\omega)[a + jl\omega)(b + jl\omega) - qk_t]^{-1}. \end{aligned} \tag{14}$$

The delayed fluorescence (Eq. (3)) wave form can be written as

$$F = \tfrac{1}{2} \sum_{n=-\infty}^{\infty} F_n e^{jn\omega t}$$

with the complex harmonic amplitudes given by

$$F_n = \sum_{l,l'=-\infty}^{\infty} \{2\gamma X_l X_{l'} + \gamma' X_l Y_{l'} + \gamma' X_{l'} Y_l\}, \tag{15}$$

being the sum restricted to terms such that $l + l' = n$.

For $b/k_t \ll 1$ and for frequencies such that $\omega \gg b$ one obtains for the fundamental harmonic F_1 of delayed fluorescence under excitation with a square wave modulation ($l = 0, \pm 1, \pm 3, \ldots$) the simple expression

$$F_1 \propto (1 + \omega^2 a^{-2})^{-\frac{1}{2}} \sin(\omega t - \theta_1), \tag{16}$$

where $\theta_1 = \arctan(a\omega^{-1})$. The total decay rate constant, $a = \tau_x^{-1} + k_t$, for the free triplets can thus be obtained from a study of the frequency dependence of the phase-angle or of the amplitude of the first harmonic of the delayed fluorescence wave form excited with a sufficiently high-frequency of modulation. This, and knowledge of the ratio k_t/τ_x^{-1} obtained from the behavior of ρ (Eq. (11)) in the low frequency limit allows thus the determination of the lifetime τ_x and the trapping rate k_t of the free triplets.(23)

3. Experimental Example

The asymmetric behavior of buildup and decay of the wave form shown in Fig. 2 (curve A) has been observed in the delayed fluorescence from high-purity commercially available (from Princeton Organics, Princeton, New Jersey, Prinz quality, 99.999% mol. purity) phenanthrene. Similar effects were found for the as purchased powders and for single crystal ingots grown from the melt of the material. Whitten *et al.*(12) have recently reported that indeed extensively purified, anthracene-free, phenanthrene can still contain a small concentration (~1 ppm) of residual impurities, notably fluoranthene and pyrene, which can act as efficient triplet exciton traps. The material, when excited with strongly absorbed light in a phosphoroscope arrangement, was found to exhibit a delayed emission in the phenanthrene fluorescence region with a thermally activated behavior of the slow decay characteristic of an emission due to free-trapped, triplet exciton annihilation.(12) An analogous conclusion has been also reached by Tschampa(10) in similar studies on samples from polycrystalline phenanthrene ingots after photochemical removal of anthracene as the main impurity and subsequent zone-refining. An extensive study of the steady-state delayed emission from phenanthrene containing anthracene as guest has been recently reported by Yee and El-Sayed.(14)

Figure 3 shows the delayed fluorescence wave form from the commercial material. Both the " fast " and the " slow " com-

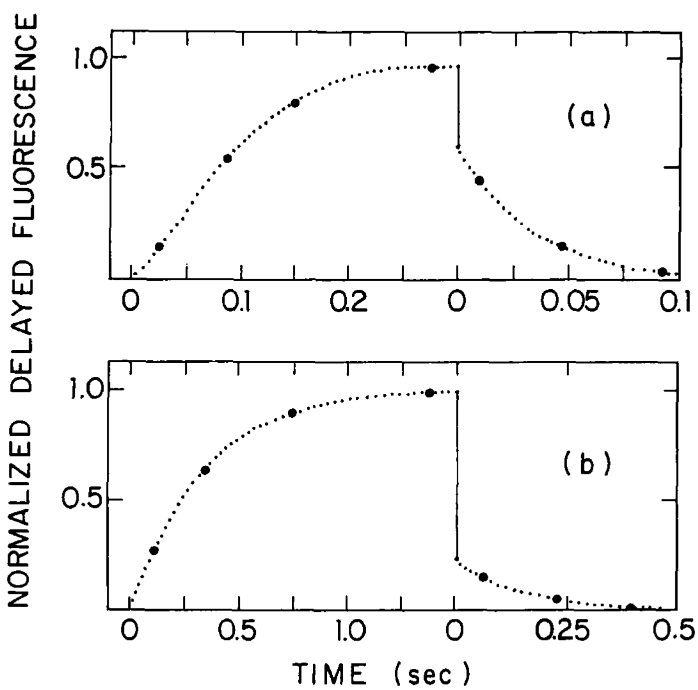

Figure 3. Normalized delayed fluorescence waveforms due to free-deep trapped triplet exciton annihilation in crystalline phenanthrene at two typical temperatures (a) 343 °K and (b) 300 °K. The light dots are contents of CAT 400 channels after accumulations with (a) 1.25×10^{-3} and (b) 5.0×10^{-3} sec per channel. The contents of every 4th and 5th channel are shown. The heavier dots are calculated from Eqs. (8) and (9) in text with $\alpha = 10^3\beta$ and with (a) $\rho = 1.6, \beta^{-1} = 71$ msec and (b) $\rho = 0.29, \beta^{-1} = 310$ msec.

ponent in the wave form were proportional to the square of the intensity of the exciting light. The phenanthrene samples were excited with the chopped beam of an He-Cd laser (Spectra Physics Model 185) operating at 4416 Å. The beam was recollimated to ~5 mm. diameter after the focusing on the chopper blade. A combination of Corning C.S. 5–58 and 3–73 filters was used to eliminate stray laser light. The intensity of the chopped beam was controlled with two Glan prisms to insure a negligible contribution of the bimolecular processes to the decay. The delayed fluorescence was detected with an EMI 9634QB photomultiplier through a stack of one C.S. 4–72 and two C.S. 7–60 Corning filters. The output of the photomultiplier was fed to an operational amplifier (Tektronix Type O) and either displayed on an oscilloscope or, for enhancement of the signal-to-noise ratio, was accumulated in a computer of average transients (CAT Model 400, Technical Measurement Corp.). Delayed fluorescence was excited in the $S_0 \rightarrow T_1$ absorption band also with a 150 W Xe arc lamp via a *B* and *L* high-intensity monochromator through a filter stack consisting of one C.S. 4–72 and two C.S. 3–73 filters. The excitation spectra for the fast and the slow components in the delayed fluorescence wave form were found to be the same within 80 Å resolution. A separate observation of each temporal component was obtained by using either a sufficiently high-frequency of chopping(23) (200–500 Hz) or a phosphoroscope arrangement and accumulating the signals via a lock-in amplifier in the CAT 400 for the repetitive wavelength scans of the monochromator. The position of the first band of excitation was at $21{,}500 \pm 100$ cm^{-1}. The reported positions of the 0, 0 band of phenanthrene phosphorescence in solid solution are in the range 21,600 to 21,730 cm^{-1}(24,25) and from crystals at 4.2 °K, 21,033 cm^{-1}.(26) Also no difference in wavelength of emission (λmax $\approx$ 380 mμ) for the two components was detected with similar low-resolution techniques.

The temperature of the samples (typically 2–4 mm thick *ab*-plane cleaved platelets) was varied between -50 °C and 85 °C by standard techniques in an optical cryostat under N_2 atmosphere. The effective lifetime β^{-1} and the ratio of the slow to fast components in the wave form, ρ, were obtained as a function of temperature from an analysis of the digital printout of CAT's 400 data. Typical results are shown in Figs.4 and 5. Both quantities, and hence the appearance of the waveform, show a strong temperature dependence in the vicinity of room temperature. No anomalous behavior was detected in going through the reported electrical-conductivity transition in phenanthrene in the vicinity of 72 °C.(27,28) The observed temperature-dependence of β^{-1} and ρ conforms to the behavior predicted by Eqs. (11) and (12) with q proportional to $\exp\{-\Delta E/kT\}$. For the results shown in Fig. 5 one obtains for the lifetime of the trapped triplets $\tau_y = 410$ msec and for the ratio of the trapping to the direct decay rates of the free excitons $k_t/\tau_x^{-1} \approx 1.8$.(29) The total decay rate $a = \tau_x^{-1} + k_t$ was obtained from the frequency-dependence of the amplitude of the first harmonic of delayed fluorescence excited in

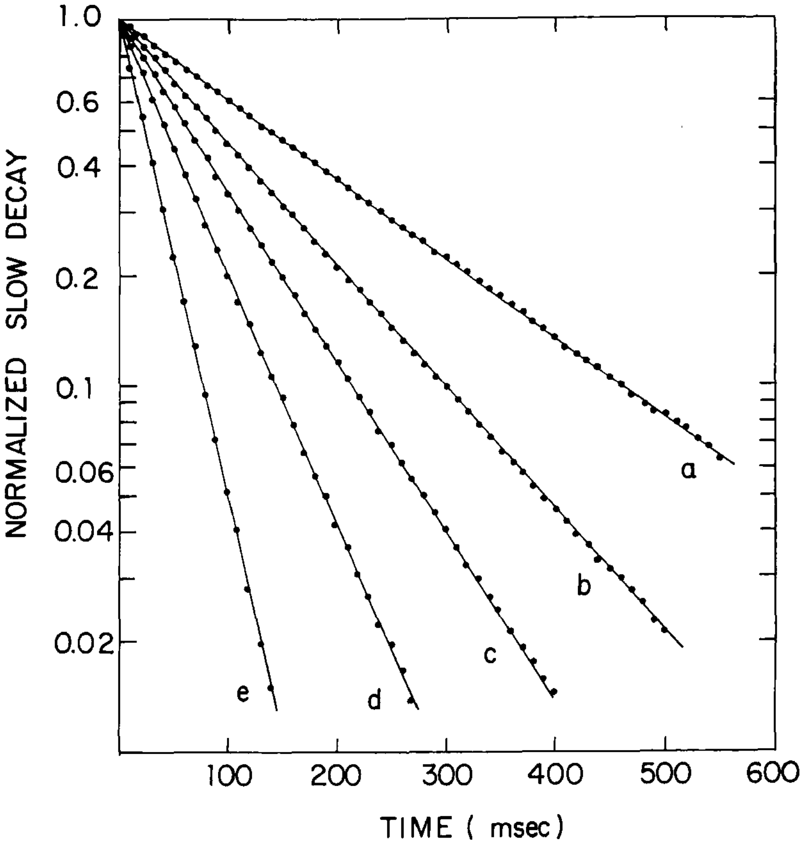

Figure 4. Time-dependence of the slow component of the decay in the delayed fluorescence waveform from crystalline phenanthrene at several temperatures (a) 280, (b) 308, (c) 320, (d) 330, and (e) 343 °K. The points are from accumulations in the CAT 400 with appropriate channel resolutions and chopping frequencies. The effective decay rates β are obtained by fitting to the exponential behaviour $\exp\{-2\beta t\}$.

the $5 \times 10^3 - 1.5 \times 10^5$ Hz frequency-range by modulating the laser beam with an electro-optic modulator (Isomet TFM Model 502). The results, showing the dependence of the inverse of the square of the first harmonic amplitude of delayed fluorescence on the square of the exciting frequency, are displayed in Fig. 6. A least-squares fit of the data to the behavior predicted by Eq. (16) gives $\alpha = 3.1 \times 10^5$ sec^{-1}. Measurements of the phase angle of the first harmonic using a tracking-filter technique reported elsewhere[(30)] were in good agreement

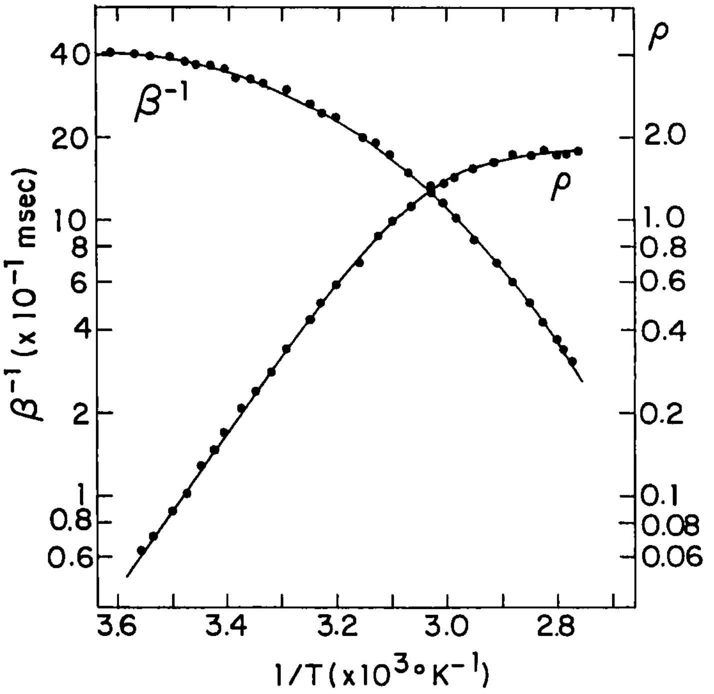

Figure 5. Typical temperature dependence of the effective life-time (β^{-1}) and of the ratio of the slow to fast components (ρ) in the waveform from crystalline phenanthrene. The data are from analysis of the waveforms after accumulations in the CAT 400.

(± 10%) with this value. One obtains $\tau_x = 9 \times 10^{-6}$ sec and $k_t = 2.0 \times 10^5$ sec^{-1}.(31) The triplet exciton trapping observed via the delayed fluorescence accounts therefore for about $\frac{2}{3}$ of the total monomolecular decay rate constant of the free triplets in this system. The density of the trapped population at room temperature is larger by a factor of about 5×10^4 than that of the free triplets.

Figure 7 shows a semilogarithmic plot of the quantity $\Delta \equiv \beta - \tau_y^{-1}$ as a function of the inverse of the temperature. A good agreement with the thermally activated behavior is obtained. The deduced depth of the triplet traps is $\Delta E = 4{,}700 \pm 200$ cm^{-1}. The difference between the position of the 0, 0 band observed for excitation of the triplets and that of the pyrene triplet in solution (16,900 cm^{-1})(24) is $\approx 4{,}600$ cm^{-1}.(32) The close agreement between these two values

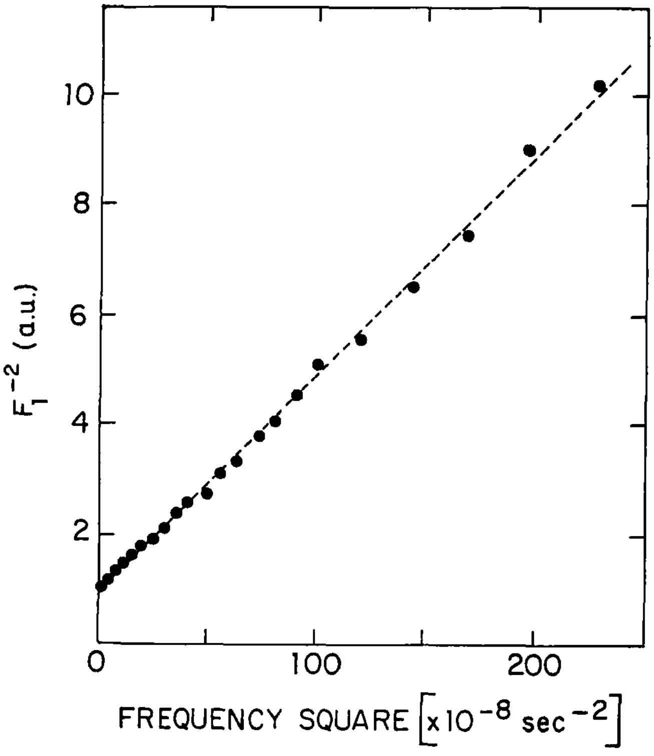

Figure 6. Plot of the inverse of the square of the observed amplitude (points) of the first harmonic in the delayed fluorescence waveform ($T = 298$ °K as a function of the square of the exciting frequency. The line is from a least-squares fit of the data to expression (16) in text. Deduced total decay rate for the free triplets $a = 3.1 \times 10^5\ \mathrm{sec}^{-1}$.

gives a strong support to the earlier suggestion by Whitten *et al.*$^{(12)}$ that small concentrations of pyrene can act as efficient triplet exciton traps in nominally pure phenanthrene crystals.

4. Concluding Remarks

Free-trapped triplet exciton annihilation can result in a strongly asymmetric behavior in the time-dependence of the buildup and decay portions of the delayed fluorescence waveform. A simple time dependence is obtained in the case of a deep triplet exciton trap and when the trapping rate of the free triplets is much faster than the

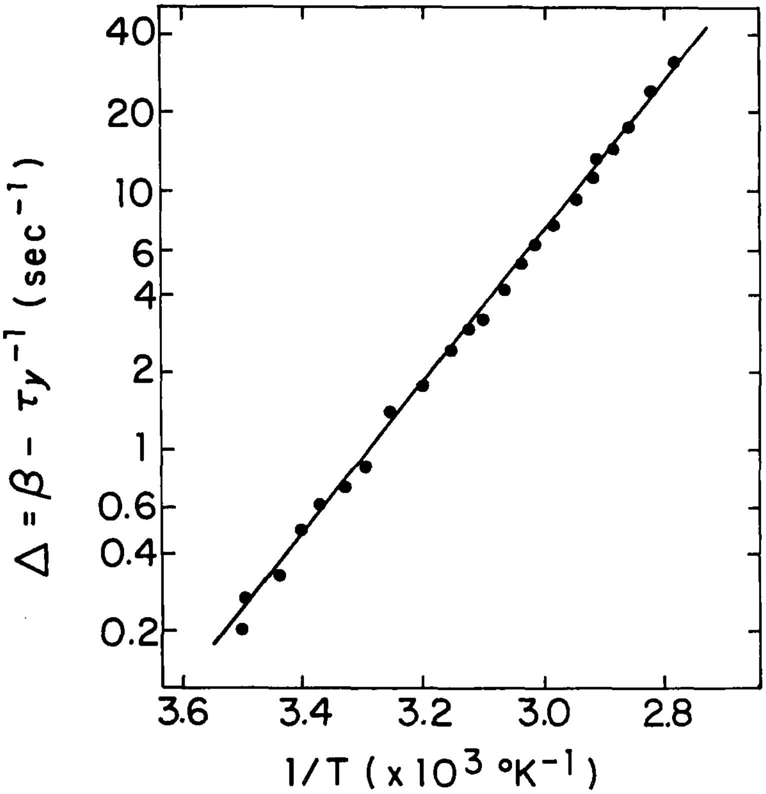

Figure 7. Semilogarithimic plot of the quantity $\Delta = \beta - \tau_y^{-1}$ (points) as a function of the inverse of the temperature, $\tau_y = 410$ msec. The deduced depth of the traps is $\Delta E = 4{,}700 \pm 200\ \mathrm{cm}^{-1}$.

rate of decay of the trapped excitation. The resulting waveform is readily distinguishable from that due to free-free triplet exciton annihilation when observed under excitation with low intensity light absorbed in the first triplet band. The most pronounced asymmetry in the appearance of the waveform occurs when a small amount of the slowly varying component is present in the decay (e.g., if the depth of the traps is sufficiently large with respect to kT). The waveform has then a slow buildup and a fast decay which is solely determined by the lifetime of the free population. The use of a slow phosphoroscope arrangement in this case could prevent the detection of the annihilation process. A simple analysis of the frequency- and temperature-dependence of the complete waveform can yield several parameters of the trapping process. The method could find useful applications in future studies of triplet kinetics in mixed organic crystals.

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16. For a recent review see, for instance, Birks, J. B., *Photophysics of Aromatic Molecules*, Wiley-Interscience, London, 1970, Ch. 11.
17. The trapping and release rates could be written as $k_t = \gamma_t N_y$ and $q = \gamma_t N \exp\{-\Delta E/kT\}$, respectively. N_y and N are the number of traps and molecules in the crystal, and γ_t the rate constant for the interaction which leads to the trapping, being mainly determined by the transport properties of the triplet excitons (Ref. 6).
8. The steady-state solutions of Eqs. (1) for the general case of several

trapping levels have been obtained and elegantly applied by Siebrand (Ref. 6) to interpret the anomalous temperature-dependence of delayed fluorescence intensity observed by Singh and Lipsett in anthracene (Singh, S. and Lipsett, F. R., *J. Chem. Phys.* **41,** 1163 (1964)).

19. One expects $k_t/q \approx C_y \exp\{\Delta E/kT\}$ where C_y is the concentration of trapping sites (Ref. 6). For a typical trap concentration of ~ 1 ppm, the condition $k_t/q \gg 1$ will be amply satisfied at room temperature for trapping depths $\Delta E \geqslant 0.5$ eV.
20. This is a reasonable assumption since the diffusion of the free triplets is, more likely, the limiting step for both types of annihilation.
21. The steady-state fluorescence intensity is given by $F_0 = K(1+\rho)$. If the temperature dependence is entirely due to the thermal activation of the traps one has $F_0 = K'\Phi(T)$, where $K' = \frac{1}{2}\gamma'\alpha^2 i_0^2 k_t$ and $\Phi(T) = b(ab - qk_t)^{-2}$ is the temperature-dependant part. The steady-state signal is maximum at a temperature where the effective lifetime measured on the waveform is $\beta^{-1} = \frac{1}{2}\tau_y[1 + 1/k_t\tau_x]$, that is, close to one-half of the intrinsic lifetime of the trapped triplets if $k_t\tau_x \gg 1$.
22. A reliable value of ΔE can be only obtained if k_t and τ_x have, at most, a weak temperature-dependence in the relevant temperature range.
23. At intermediate frequencies such that $\omega \approx \beta$ and $\omega \leqslant a$ the low-frequency waveform (curve A of Fig. 1) develops an initial " step " also in the buildup region since, now, some trapped population is still present at the beginning of each cycle. The relative proportion of this step in the waveform grows with increasing frequencies and for $a \gg \omega \gg \beta$ the delayed fluorescence waveform has the appearance of a square-wave which follows closely that of the exciting light on the time scale of the chopping.
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29. This ratio was found to vary between 1.5 and 2.5 for the samples studied. This is to be expected since k_t should be proportional to the trap concentration (Ref. 17) while τ_x is determined by the presence of other impurities in the crystal. The relative concentration of both can vary from sample to sample, e.g., along the length of the melt-grown ingot.
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31. This value would imply a concentration of traps of ~ 1 ppm assuming a reasonable value, $\sim 10^{-10}$ cm^3 sec^{-1}, for the rate constant of the interaction leading to the trapping of the triplets.
32. The pyrene singlet is nearly coincident with that of phenanthrene. The observed delayed fluorescence can be then either a host or a guest emission.