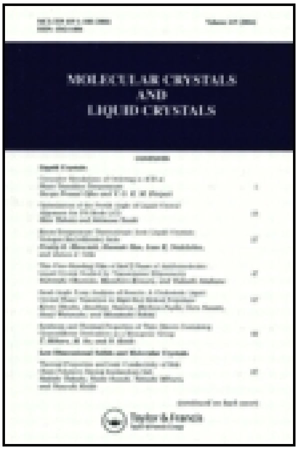

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Triplet Exciton Decay in Phenanthrene Single Crystals‡

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Abstract—Delayed fluorescence in single crystals of high purity phenanthrene has been studied. The lifetime of triplet excitons has been obtained as a function of temperature and estimates have been made of the rate constant for triplet–triplet annihilation and of the triplet diffusion constant. The results have been interpreted in terms of impurity trapping of the triplet excitons.

Introduction

Measurements of delayed fluorescence decay in organic crystals are of special interest because of the information which can be obtained about triplet exciton transport processes in the solid state. In the delayed fluorescence process a distribution of triplet excitons is generated in the crystal, either by direct absorption or by intersystem crossing from excited singlet states. When the source of excitation is removed, the singlet and triplet exciton populations decay by various mechanisms. The lifetimes of singlet excitons are generally of the order of nanoseconds and their decay usually produces the character-

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istic fluorescence of the material. The triplet excitons on the other hand have lifetimes of milliseconds and their decay in the crystalline state is usually non-radiative. When two triplet excitons come close enough, they may combine to form a singlet exciton which then decays radiatively to the ground state. The delayed fluorescence produced by this bimolecular decay can be observed long after most of the singlet excitons have decayed because of the much longer triplet lifetime. From a study of this delayed fluorescence one can determine the rate constants for various decay mechanisms and infer from these rate constants characteristics of the behavior of the triplet excitons in the crystal.

The properties of phenanthrene single crystals have not been studied as extensively as those of anthracene. Electrical measurements by Arndt and Damask[1] revealed an anomalous behavior of the dark conductivity of phenanthrene crystals in the vicinity of 72 °C as well as persistent polarization phenomena and a strongly temperature dependent photocurrent. Anomalous behavior of the resistivity of powder samples was reported previously by Matsumoto and Tsukada[2] and by Andrews *et al.*[3] A peak in the heat capacity is observed in the same temperature range.[4] In chrysene, another nonlinear molecule, similar behavior of the electrical conductivity and heat capacity has been observed.[5]

Most measurements of the delayed fluorescence of phenanthrene have been made on dilute solutions where the properties of the isolated molecule predominate. Recently Tschampa has reported measurements of delayed fluorescence and phosphorescence in polycrystalline phenanthrene.[6] These measurements showed that the delayed fluorescence was strongly affected by impurities or defects even though the material had undergone extensive purification. The present report is concerned with measurements of delayed fluorescence and triplet exciton diffusion in single crystals of high purity phenanthrene. The lifetime of triplet excitons has been obtained as a function of temperature and estimates have been made of the rate constant for bimolecular decay and of the triplet diffusion constant.

Theory

The kinetics of triplet exciton decay have been treated by several authors.[7,8,9] The analysis presented below closely follows the formulation of Singh *et al.*[8] for anthracene, although certain terms must be modified to take into consideration the large intersystem crossing rate constant and low fluorescence yield for phenanthrene.[9]

Triplet excitons are generated by intersystem crossing with rate constant K_{ST} from singlet states which are excited by ultraviolet light. After removal of the exciting radiation, the singlet and triplet densities, n_S and n_T, can be described by the following expressions,

$$\frac{dn_S}{dt} = -K_S n_S + \phi\gamma n_T^2 \tag{1}$$

and

$$\frac{dn_T}{dt} = K_{ST} n_S - \beta n_T - \gamma n_T^2 \tag{2}$$

with rate constants K_S for monomolecular singlet decay, β for monomolecular triplet decay, and γ for triplet–triplet annihilation. The efficiency factor, ϕ, is the ratio of singlet excitons produced to triplet excitons destroyed, and is therefore less than or equal to 0.5. When the excitation is removed at $t = 0$, the singlet and triplet densities are assumed to be n_{S0} and n_{T0}. The singlet population is assumed to decay rapidly to a steady state density so that for $t \gg K_S^{-1}$ we have

$$n_S = (\phi\gamma/K_S)n_T^2 \tag{3}$$

With this approximation Eq. (2) has the solution,

$$n_T = \beta n_{T0}[(\gamma' n_{T0} + \beta)\exp(\beta t) - \gamma' n_{T0}]^{-1} \tag{4}$$

where

$$\gamma' = \gamma(1 - K_{ST}\phi/K_S) \tag{5}$$

The delayed fluorescence intensity, I_B, is given by $I_B = K_F n_S$, where K_F is the rate constant for radiative singlet decay. At times long compared to β^{-1}, the delayed fluorescence decay is of the form,

$$I_B = \text{const} \times \exp[-2\beta t]. \tag{6}$$

At short times, i.e. for $K_S^{-1} \ll t \ll \beta^{-1}$, the delayed fluorescence can be expressed,

$$I_B = (I_{B0}^{-1/2} + St)^{-2}, \tag{7}$$

where I_{B0} is the value of I_B extrapolated to $t = 0$ and S is defined by

$S = \frac{d}{dt} I_B^{-1/2}$. By algebraic manipulation of Eqs. (3), (4), and (5), S can be expressed as

$$S = \gamma^{1/2}\left(\frac{K_S}{K_F\phi}\right)^{1/2}\left(1 - \frac{K_{ST}\phi}{K_S}\right) + \beta I_{B0}^{-1/2} \tag{8}$$

If S is plotted versus $I_{B0}^{-1/2}$, the slope gives a value for β while γ can be obtained from the intercept if certain assumptions, considered later, are made about the rate constants.

If, as has been demonstrated for anthracene,[10] the bimolecular decay is limited by the rate at which triplet excitons come together, the bimolecular rate constant can be expressed in terms of the diffusion constant,[11]

$$\gamma = \frac{8\pi}{9}\langle R\rangle D \tag{9}$$

where D is the diffusion constant and $\langle R\rangle$ a mean molecular spacing. Thus, a measure of triplet exciton diffusion can be obtained from the delayed fluorescence decay.

Experiment

The phenanthrene for this investigation was obtained from the K & K Chemical Company. Anthracene and fluorene, which have segregation coefficients close to unity and therefore are difficult to remove by zone refining, were removed chemically by treatment with maleic anhydride and KOH. The material was then chromatographed, sublimed, and zone refined for 40 passes. Concentrations of impurities which could be observed by gas chromatography were reduced to the limit of detectability (or better), ~1 ppm for impurities which elute before phenanthrene, somewhat higher for those coming after because of tailing of the phenanthrene peak. Three impurities which strongly influence the triplet behavior, as explained below, are anthracene, fluoranthene, and pyrene. Analysis by fluorescence spectroscopy indicated anthracene and fluoranthene concentrations of less than 0.1 and 1 ppm, respectively. The pyrene concentration was also probably less than 1 ppm, as the initial concentrations of fluoranthene and pyrene were about the same and the segregation coefficients for the two materials in phenanthrene are similar.[12] Crystals were grown from the purified phenanthrene by the Bridgeman technique at a rate of 1.2 cm/day. Single crystal specimens of about 1 cm^2 cross section and 0.2 thick were cleaved from the boules.

For measurements of the time dependence of the delayed fluorescence decay, singlet excitons were generated by strongly absorbed light from a 50 joule xenon flash lamp. An initial population of triplet excitons was obtained through intersystem crossing from these singlet states. A rotating shutter isolated the sample from the photomultiplier during the flash and isolated the xenon lamp from the sample during the delayed fluorescence decay. The specimen was contained in a small quartz-windowed chamber in which an inert atmosphere could be maintained for measurements at elevated temperatures.

Results

Delayed fluorescence could be observed at room temperature for several hundred milliseconds after the flash excitation. The values of the monomolecular decay constant, β, at several temperatures are shown in Fig. 1. As the decay at times long compared to β^{-1} is still not perfectly exponential, the value of the decay constant depends on the region of the decay curve from which it is calculated. The values shown in Fig. 1 were calculated from Eq. (6) at approximately two triplet lifetimes after the flash excitation.

When the temperature is increased, β increases rapidly. A plot of $In(\beta)$ versus T^{-1} gives an activation energy of 0.3 eV. At 300 °K the triplet lifetime is 140 msec, some 6 times longer than the triplet lifetime in high purity anthracene. In polycrystalline phenanthrene, Tschampa[6] observed a similar temperature dependence of β with an activation energy of 0.28 eV, but the triplet lifetimes were considerably smaller than our values. The difference in lifetime is probably due to different impurity concentrations.

For times short compared to the triplet lifetime and for high initial triplet populations, triplet–triplet annihilation may be the dominant mechanism in the fluorescence decay. In this case the delayed fluorescence intensity can be described by Eq. (7). A plot of $S = \frac{d}{dt} I_B^{-1/2}$ versus $I_{B0}^{-1/2}$ is shown in Fig. 2. According to Eq. (8),

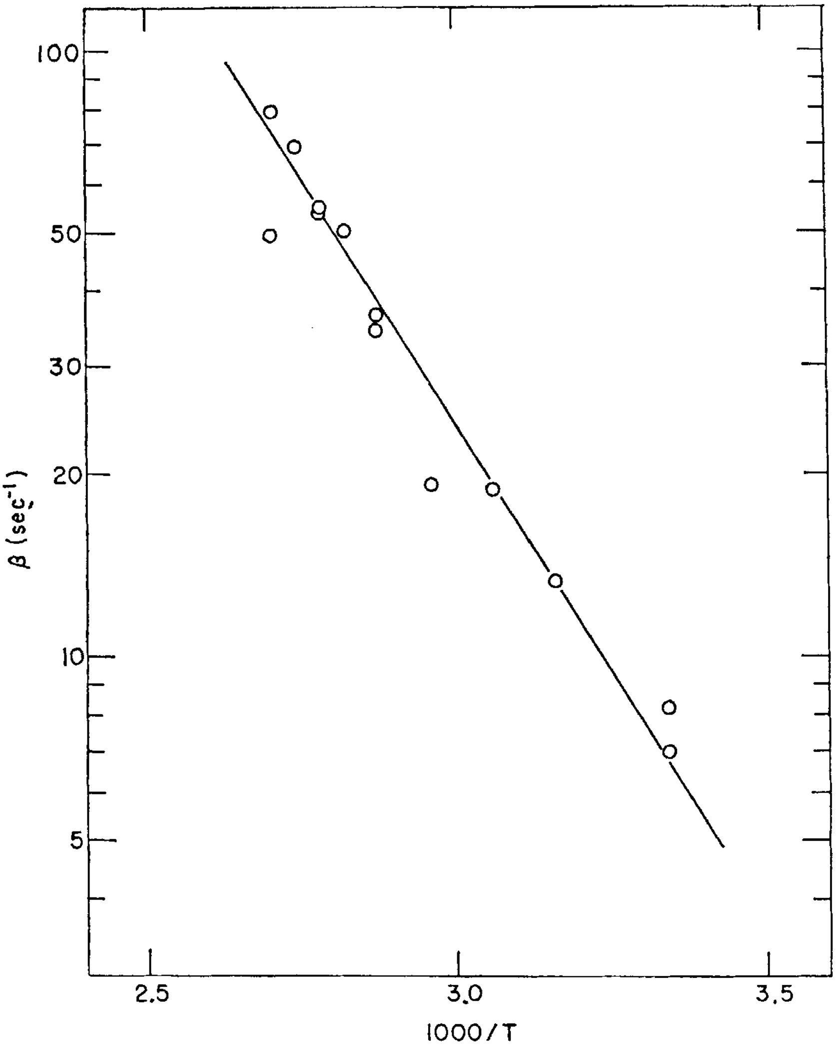

Figure 1. Triplet exciton decay constant, β, versus reciprocal temperatures.

the slope should be equal to β. However, the value obtained for β in this manner, 19 sec^{-1}, is about twice that obtained from the decay at longer times as described by Eq. (6) for the same crystal. Singh *et al.*[8] reported a similar effect with strongly absorbed excitation and attributed the discrepancy to surface effects which were not included in the kinetic formulations. The intercept of S versus $I_{B0}^{-1/2}$ should

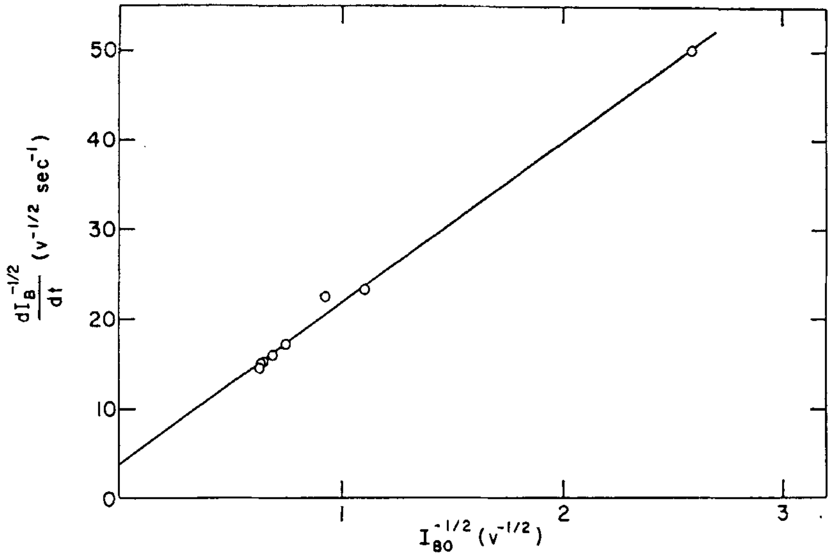

Figure 2. A plot of $\frac{dI_B^{-1/2}}{dt}$ versus $I_{B_0}^{-1/2}$. The units of intensity are volts of photomultiplier output.

be $\gamma^{1/2}$ times a numerical factor which depends upon the efficiencies of fluorescence, intersystem crossing, and singlet production from biomolecular triplet decay. In our calculations we have assumed that the values obtained by Powell[9] for phenanthrene vapor, $K_{ST}/K_S = 0.88$ and $K_F/K_S = 0.07$, are applicable as well to crystalline phenanthrene, and that ϕ is 0.5.

For an absolute evaluation of γ, the photomultiplier output which is expressed in volts in Fig. 2 must be converted into units of fluorescence intensity, photons/cm^3 sec. The largest uncertainty in this conversion is the thickness of the emissive region of the crystal. Because of this uncertainty, we are only able to obtain upper and lower limits for γ, and hence for the diffusion coefficient and diffusion length. The thickness of the active region of the crystal should be larger than one triplet diffusion length, $L = \sqrt{D\beta^{-1}}$, and must be less than or equal to the crystal thickness, which for this sample was 0.02 cm, the thinnest which could be obtained. For the former case, Eq. (9) can be used to express the diffusion length in terms of γ. From the two extreme cases we estimate that γ has a value from 10^{-15} to 10^{-13} cm^3/sec.

From Eq. (9) with $\langle R \rangle = 6$ Å, we estimate that D, the diffusion constant, lies between 10^{-9} and 10^{-7} cm^2/sec and that the diffusion length L is between 10^{-5} and 10^{-4} cm. When these values are compared with $D = 2 \times 10^{-4}$ cm^2/sec and $L = 10 \times 10^{-4}$ cm for anthracene,[10] it is evident that the triplet excitons in phenanthrene are much less mobile than they are in anthracene.

When the measurements of γ were extended to very high excitation intensities a saturation of the delayed fluorescence intensity was observed. In Fig. 3 are shown values of I_{B0} versus incident intensity.

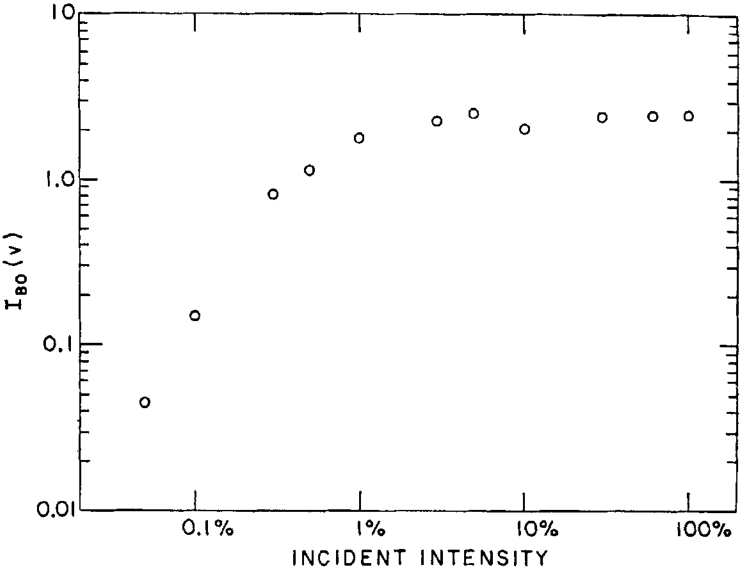

Figure 3. Delayed fluorescence intensity extrapolated to $t = 0$ as a function of the intensity of the flash excitation.

This curve was obtained with white radiation from the xenon flash attenuated with neutral density filters. Saturation was also observed when the incident light passed first through a Corning CS 7-54 filter which transmits principally in the ultraviolet. Although we have as yet no quantitative explanation for this effect, it is possibly due to an interaction of the incident light with the excited singlet or triplet populations which would become increasingly important at higher light intensities, or due to a nonlinearity in the absorption or other rate constants.

Discussion

The relatively small mobility of the triplet excitons in phenanthrene, the temperature dependence of β, and the only approximately exponential fluorescence decay suggest that the delayed fluorescence decay is largely determined by traps more than kT below the phenanthrene triplet exciton band. Impurity molecules with singlet and triplet energy levels appreciably below those of the singlet and triplet excitons in phenanthrene can act as traps or quenching centers depending on the relative probabilities for thermal release of the excitation and for decay to the ground state of the impurity. If the trapping time on the impurity is longer than the impurity triplet lifetime, we would expect the impurity to be a quenching center whereas if the trapping time is less than the impurity lifetime, the excitation will probably be released. In phenanthrene of the present purity, we propose that the triplet exciton lifetime is governed mainly by the time required for an exciton to reach a quenching center, most of this time being spent in traps.

Of the impurities known to be present in our crystals, anthracene, fluoranthene and pyrene have triplet levels below the phenanthrene triplet exciton level. If we assume a triplet exciton energy of 21,033 cm^{-1},[13] and that the impurity levels are shifted only slightly from their values measured in rigid glass solutions,[14] then the three impurities, fluoranthrene, pyrene, and anthracene, have triplet levels 0.3, 0.5, and 0.7 eV below the phenanthrene triplet energy.[14]

The triplet lifetimes for the isolated molecules are 850, 500, and 45 msec. respectively for fluoranthene, pyrene, and anthracene.[14] Although the lifetimes would probably be somewhat different when the molecules become substitutional impurities in the phenanthrene lattice, these values indicate that fluoranthene and pyrene are unlikely to be quenching centers in phenanthrene since a quenching center should have a shorter lifetime than the triplet lifetime of 150 msec at room temperature. The trapping times for the three impurities are difficult to estimate but they should decrease with increasing temperature and should be much shorter for the shallower traps. The activation energy of 0.3 eV from the temperature dependence of the phenanthrene triplet lifetime agrees very well with the trap-depth assumed for fluoranthene. We conclude that anthracene, with its short lifetime and deep trap depth is probably an important quenching center in phenanthrene, and that fluoranthene and probably pyrene act as traps. The presence of fluoranthene and pyrene as well as anthracene could account for the short wavelength impurity phosphorescence peaks observed by Tschampa in phenanthrene at low temperatures.[6]

No anomalous behavior in the triplet exciton decay was observed in the temperature region of the electrical and thermal anomalies. This is not surprising, however, if the exciton decay is governed by deep traps which are only slightly influenced by the surrounding lattice. The presence of these traps may explain the strong temperature dependence of the photoconductivity and its small value at room temperature[1] as the traps would both inhibit carrier production by free excitons and reduce the mobility of the electrical carriers.

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