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Diffusion of Singlet Excitons in Tetracene Crystals†

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Abstract—The diffusion length l_s of singlet excitons in crystalline tetracene was measured in the temperature range 293 to 160 °K utilizing the quenching effect exerted on the crystal fluorescence by exciton traps located at the crystal surface. It is found that $l_s = 120 \pm 10 \text{ Å}$ at room temperature. It increases exponentially with decreasing temperature until it approaches a constant value of $580 \pm 50 \text{ Å}$ below 190 °K. The temperature dependence of the singlet exciton lifetime determined by exciton fission can fully account for the observed temperature dependence of the diffusion length. Therefore energy localization, like excimer formation, cannot be an effective process. The exciton diffusion coefficient is by a factor of 4 higher than in anthracene crystals. This can be explained in terms of the increase in the Davydov-splitting.

Introduction

Singlet exciton diffusion is a well-known phenomena in organic molecular crystals.^(1,2) In crystalline anthracene a diffusion length l_s of about 400 Å in a direction perpendicular to the *ab*-plane has been measured.⁽³⁾ Since the Davydov splitting of the first excited singlet state increases from 170 cm^{-1} ⁽⁴⁾ to 700 cm^{-1} ⁽⁵⁾ when going from anthracene to tetracene crystals one might also expect an increase in the diffusion length. On the other hand, there are two processes which should lead to a reduction of l_s : 1. Fission of a singlet exciton into a pair of triplet excitons effectively reduces the

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singlet lifetime at room temperature.^(6,7) τ becomes equal to $1/(\beta_0 + k_f)$, where β_0 is the sum of the monomolecular radiative and radiationless decay constants of the first excited singlet state of the molecule and $k_f = k_{f,0} \exp[-(\Delta E_f/kT)]$ is the rate constant for singlet exciton fission. Numerically $k_f \approx 5 \times 10^9 \text{ s}^{-1}$ at 300 °K.⁽⁸⁾ This effect suggests an increase of the diffusion length of singlet excitons with decreasing temperature as the fission process is suppressed. (2) Katul and Zahlan⁽⁹⁾ have interpreted the fluorescence spectrum of crystalline tetracene in terms of dimer emission. Since, however, tetracene crystallizes in the triclinic system with only two molecules in the unit cell, no ground state dimers like in pyrene crystals can exist. Therefore it seems to be more appropriate to speak in terms of excimer emission. Excimer formation, however, must involve some molecular reorientation. Such a process is equivalent to trapping of a singlet exciton, the trap depth being equal to the energy difference between excited monomer and excimer state. Consequently the exciton diffusion coefficient should be much lower than for free excitons, in particular at low temperatures where thermal release of the localized excitation becomes unlikely.

These arguments lead to the conclusion that the singlet exciton diffusion length in crystalline tetracene should be reduced significantly compared with anthracene. However, Geacintov, Pope and Kallmann⁽¹⁰⁾ have calculated a value $l_s \approx 2000 \text{ Å}$ based on measurements of extrinsic photoconduction. This value has been questioned by Mulder. Meanwhile investigations about risetime and electrode effects have shown that the reported photocurrents were essentially caused by interaction of *triplet* excitons with the electrode.^(11,12) Consequently the l_s -value reported in Ref. (10) must refer to triplet exciton diffusion. It compares well with $l_T = 4000 \pm 2000 \text{ Å}$ reported for triplet excitons in tetracene.⁽¹²⁾ A reinvestigation of singlet exciton diffusion in tetracene crystals seemed therefore to be necessary.

Experimentally the technique of measuring the fluorescence efficiency of tetracene crystals as a function of the penetration depth of the exciting light was employed utilizing the effect of exciton quenching at a surface containing acceptor molecules. The reliability of this method with respect to determination of the singlet exciton diffusion length has recently been checked using anthracene crystals.⁽¹³⁾

Experimental

Tetracene single crystals were grown by sublimation under an inert atmosphere from three times resublimed tetracene powder. The crystal-fluorescence spectrum was identical with the spectrum reported in the literature^(5,9) indicating the absence of impurity emission. The thickness of the crystals varied between 50 and about 100 μ . Monocrystallinity was checked microscopically. The crystal was exposed to air prior to performance of the measurements so that a layer of tetraquinon could develop at the surface acting as a sink for excitons. In one series of experiments this layer was removed by rinsing the crystal in benzene. Subsequently an about 50 Å thick layer of capriblue providing exciton surface traps was deposited by evaporation of a solution of capriblue in methanol. (Capriblue has an absorption maximum coinciding with the tetracene emission maximum.) Crystals treated in this way gave identical results concerning exciton diffusion as "oxidized" crystals did. The crystals were mounted strain free in an optical cell provided with a N_2 -gas cooling unit operating between room temperature and 140 °K with a temperature stability of $\pm 0.1^\circ$. In all cases cooling occurred at a maximum speed of about 30 degrees per hour.

The optical excitation unit consisted of a 1600 W Xenon lamp, a Beckman grating monochromator operated at 2 nm spectral band width and a polarizer with a wavelength-independent polarization degree $\geq 99\%$. (Use of two polarizers did not change the results.) The incident photon flux was below 10^{13} quants $\text{cm}^{-2} \text{s}^{-1}$. No bimolecular effects⁽⁸⁾ could therefore play a role. It was desirable to vary the excitation wavelength up to 550 nm. Since the crystal emission spectrum peaks near 565 nm great care had to be spent on selecting appropriate filter combinations. The following combinations gave no background effect with an excitation wavelength up to 550 nm: Excitation side: Solution of capriblue in methanol to cut down straylight and 5 mm Schott BG18 bandfilter to remove dye-stuff emission. Emission side: Interference filter 599 nm (band width 20 nm), 2 mm OG 570 and 4 mm OG 590 Schott cutoff filters. Fluorescence emission emerging from the crystal backside was fed through a light guide to the cathode of a RCA 7265 photomultiplier connected to a Hewlett Packard μ ammeter and a servotrace recorder

(Sefram, Paris). In order to achieve high accuracy the fluorescence spectrum was not recorded continuously but in a stepwise manner in wavelength intervals of 2 or 3 nm. At minimum emission intensity (room temperature, $\lambda_{\text{exc}} = 550$ nm) the signal to noise ratio was about 30. The incident photon flux was calibrated independently for both polarization directions by replacing the crystal by a solution of phenosafranin in methanol which has absorption and emission properties very similar to crystalline tetracene. A semiquantitative correction for the wavelength dependence of reflexion losses at the crystal surface was made by transposing the literature values for crystalline anthracene⁽¹⁴⁾ to tetracene, which seems to be a reasonable approximation in view of the similarity of the absorption spectra. Not making this correction means that one has to confine the analysis of the fluorescence excitation spectrum leading to Fig. 2, as will be shown below, to a wavelength region in which the reflectivity is expected not to vary drastically. This does not change the numerical results significantly but causes the estimated relative uncertainty for the value of the diffusion length to increase from about 15 to 30%.

The method of effect modulation was employed for adjustment of the proper polarization directions of the incident beam: For light polarized parallel to the crystallographic *b*-axis the $^1A_g \rightarrow ^1B_{2u}$ transition has a peak at 521 nm. Therefore the polarizer was rotated until a maximum net effect at 521 nm was recorded, i.e. maximum fluorescence decrease.

Results

1. Fluorescence Measurements

Figure 1 shows the relative fluorescence yield $I_f(\lambda)$ normalized to the incident photon flux in such a way that at any temperature $I_{f,0} = 1$ in a wavelength region where $d \gg \alpha^{-1} \gg l_s$. Here d denotes the crystal thickness, α the crystal absorption coefficient measured in cm^{-1} and l_s the diffusion coefficient for singlet states. This normalization procedure enables separation of the temperature dependence of the fluorescence excitation spectrum from the temperature dependence of the overall fluorescence efficiency caused by singlet exciton fission. The fact that the room temperature curve $I_f(\lambda)$ for light polarized $\parallel \mathbf{b}$ shows minima at $\lambda = 521 \pm 1$ nm, 480 ± 2 and (not shown) 440 ± 2 nm which

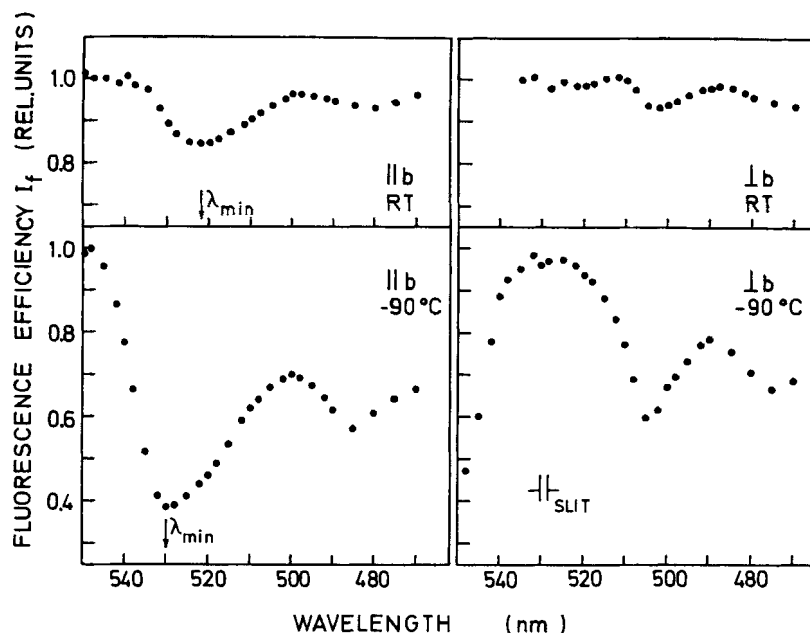


Figure 1. Relative fluorescence efficiency I_f as a function of excitation wavelength (RT = room temperature).

exactly coincide with the minima of the penetration depth α^{-1} strongly suggests that the quantity $1 - I_f(\lambda)$ denotes the fraction of singlet excitons being quenched after diffusion to the surface and which therefore can no longer contribute to ordinary crystal fluorescence. Diffusion theory predicts that this fraction is given by

$$\Delta I_f(\lambda) = 1 - I_f(\lambda) = g \frac{l_s}{1/\alpha(\lambda) + l_s} \quad (1)$$

g is the probability that an exciton is lost for crystal fluorescence after reaching the surface. Figure 2 shows plots of $(\Delta I_f)^{-1}$ versus α^{-1} for b -polarized light at different temperatures. The α -values are taken from Bree and Lyons⁽¹⁵⁾ taking into account the redshift of the absorption spectrum upon lowering the temperature.⁽¹⁶⁾

Several conclusions can be drawn from these plots: (1) In the whole spectral range under investigation (550 to 425 nm) a single straight line can be fitted to the experimental points. This means that within the experimental accuracy the dependence of the fluorescence yield on the wavelength of exciting (b -polarized) light

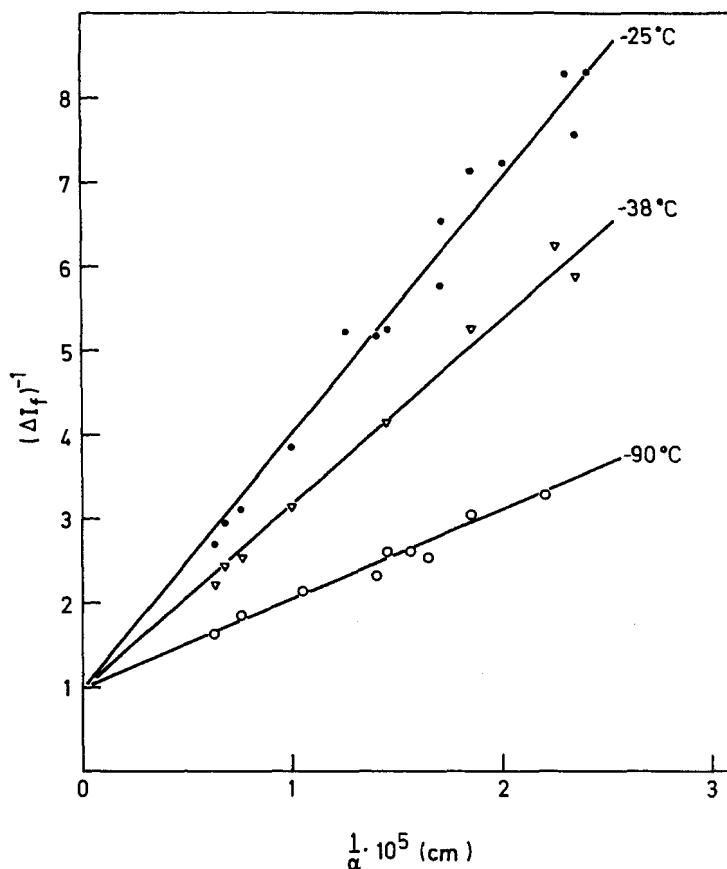


Figure 2. $(\Delta I_f)^{-1}$ versus the penetration depth of the exciting light. ΔI_f is the fluorescence reduction caused by surface quenching of singlet excitons.

can be solely understood by assuming surface quenching of singlet excitons. (2) The ordinate intercept of the straight lines equals g^{-1} yielding $g = 1.0 \pm 0.1$, i.e. every singlet exciton reaching the crystal surface gets quenched or trapped and can no longer contribute to ordinary crystal fluorescence. This also provides experimental evidence that emission from the quenching layer—most likely tetraquinone—as a result of excitation by crystal excitons does not contribute to the recorded luminescence intensity. Tetraquinone either acts as an ideal quencher for singlet excitons or emits at longer wavelengths. (3) The exciton diffusion length l_s can be calculated

from $l_s = [d(1/\Delta I_s)/d(1/\alpha)]^{-1}$. It is strongly temperature dependent (see dashed curve in Fig. 3). At room temperature $l_s = 120 \pm 20 \text{ \AA}$ is obtained.

It is necessary to comment here on a possible error caused by light absorption within the quenching layer. The thickness of the oxidized layer is not known. It might, however, comprise a few molecular layers. If the absorption coefficient of the layer were the same as that of the undisturbed crystal, the thickness of the layer had to be subtracted from the l_s values evaluated from the slope of the ΔI_s^{-1} versus α^{-1} curves in order to obtain correct values for the diffusion length. It can, however, be anticipated that the absorption spectra of tetraquinone and tetracene are similarly related as those of anthraquinone and anthracene: The quinone absorption is red-shifted, but in the spectral range of strong $S_0 - S_1$ absorption of anthracene the quinone absorption coefficient is two orders of magnitude lower. Therefore we conclude that in the present experiments the error in l_s introduced by surface layer absorption does not exceed 10 \AA .

According to our knowledge no systematic investigation of the

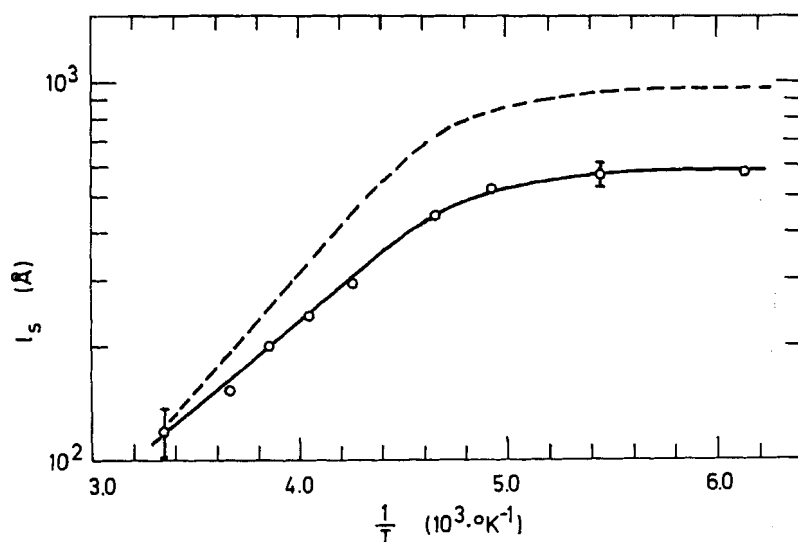


Figure 3. Temperature dependence of the diffusion length of singlet excitons in tetracene crystals. The dashed curve is obtained if the temperature dependence of the magnitude of the absorption coefficient is neglected.

temperature effect on the absorption spectrum of crystalline tetracene has been conducted. Upon evaluation of the temperature dependence of the diffusion length from the temperature dependence of the fluorescence excitation spectra (Fig. 2) it has therefore implicitly been assumed that the only temperature effect is a redshift of the absorption spectrum. This, however, is certainly not justified. Upon lowering the temperature a reduction of the width of the zero-vibronic $S_0 - S_1$ absorption line is observed. Since the integral over an absorption line must be temperature-independent, one can to a first order approximation assume that the peak value α_{\max} of the crystal absorption coefficient increases in the same fashion as the full linewidth at half maximum (fwhm) decreases, i.e. $\alpha_{\max}(T)/\alpha_{\max}(300^\circ\text{K}) = \text{fwhm}(300^\circ\text{K})/\text{fwhm}(T)$. Taking the data from Ref. 16 one finds that $\alpha_{\max}(T)$ should approach the value $2.3 \times 10^5 \text{ cm}^{-1}$ which agrees with a value reported recently⁽¹⁷⁾ for $T = 112^\circ\text{K}$. Adopting the above temperature correction for α the experimental values for the singlet exciton diffusion length below room temperature are reduced. (See full curve in Fig. 3.) l_s increases proportional to $\exp(0.09 \pm 0.005 \text{ eV}/kT)$ until it approaches a saturation value $l_{s,\max} = 580 \pm 50 \text{ \AA}$ below 190°K . Analysis of the data obtained with light polarized $\perp \mathbf{b}$ yields quantitatively the same result with respect to singlet exciton diffusion. There is, however, some additional reduction of the fluorescence yield at photon energies above 2.50 eV which is indicative of optically stimulated singlet exciton fission. This will be discussed in a subsequent paper.

Discussion

Diffusion coefficient D and diffusion length l_s of the excitons are related by $l_s = (D\tau)^{1/2}$ where τ is the exciton lifetime. In crystalline tetracene τ can be expressed by $\tau = 1/(k_f + \beta_0)$, where $k_f = k_{f,0} \exp[-(\Delta E_f/kT)]$ is the rate constant for thermally induced fission of a singlet exciton into a pair of triplet excitons and β_0 is the monomolecular decay constant of the S_1 -state of a molecule in the crystal. According to Pope *et al.*⁽⁸⁾ $\beta_0 \approx 10^8 \text{ s}^{-1}$ and $k_f(300^\circ\text{K}) = 5 \times 10^9 \text{ s}^{-1}$. ΔE_f is the energy difference between triplet pair state ($2T$) and the lowest excited singlet state. Measurements of the temperature dependence of the fluorescence quantum yield gave ΔE_f values

ranging from 0.15 to 0.24 eV^(8,18,19) depending on experimental conditions.⁽¹⁶⁾ In the present series of experiments ΔE_f was found to be 0.175 ± 0.01 eV. It was inferred from the threshold energy for optically induced singlet exciton fission. Upon cooling from room temperature to 140 °K the total fluorescence yield increased by a factor of 20. Using $\beta_0 = 10^8 \text{ s}^{-1}$ the temperature dependence of τ in our experiments can thus be described by

$$\tau = \frac{1}{10^8 \{1 + 2.5 \times 10^4 \exp[-(0.175/kT)]\}} \text{ (sec)}.$$

On the other hand the dependence of the square of the diffusion length on temperature determined herein can be expressed by

$$l_s^2 = \frac{1}{3 \times 10^{10} \{1 + 2.84 \times 10^4 \exp[-(0.18/kT)]\}} \text{ (cm}^2\text{)}$$

i.e. the activation energy associated with l_s^2 is identical with ΔE_f . Thus, within the limits of experimental accuracy the exciton diffusion coefficient perpendicular to the crystallographic *ab*-plane is $D_c = l_s^2/\tau = 3.3 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$, *independent of temperature*. This means that singlet exciton fission alone can account for the observed temperature dependence of the diffusion length. If trapping of singlet excitons as a result of excimer formation were an effective process compared with fission and monomolecular decay, the diffusion coefficient should be affected with an activation energy approximately equal to ΔE_{ex} where ΔE_{ex} is the excimer binding energy. Consequently a net decrease of the diffusion coefficient with temperature had to be expected. We must therefore conclude that either excimer formation does not take place at all or that the binding energy of the excimers is so small that thermal release is a very efficient process above 140 °K, i.e. ΔE_{ex} cannot be much larger than 10^{-2} eV, which would be typical for the binding energy of an exciton in a shallow trap rather than for the binding energy of an excimer. This is confirmed by the fact that inspection of the emission spectra of crystalline tetracene reported by Prikhotko and Skorobogatko⁽⁵⁾ and by Kazzaz and Zahlan⁽¹⁸⁾ (except their Fig. 1 which however is in disagreement with their Fig. 5) does *not* lend unambiguous support for an energy gap between absorption and emission in crystalline tetracene and hence for the existence of excimers.

Furthermore the absolute values for l_s and D at low temperatures are typical for free excitons ruling out the possibility of excimer motion. Comparison with anthracene yields $D_{T_{et}}/D_A = (l_s^2\tau)_{T_{et}}/(l_s^2\tau)_A = 2$ assuming $l_{s,A} = 400 \text{ \AA}$ and $\tau_A = 10 \text{ nsec.}^{(20)}$ Such an increase might qualitatively be expected from the increase in the Davydov splitting of the first excited singlet state observed with light vibrating in the ab -plane if one assumes a similar enhancement of the molecular resonance interaction also along the c -axis.

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