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Excitation Spectrum of Crystalline Tetracene Fluorescence: A Probe for Optically-Induced Singlet–Exciton Fission†

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Abstract—The intrinsic fluorescence efficiency of crystalline tetracene depends on the energy of the exciting light. It decreases for $E_{\text{exc}} > 2.48$ eV displaying a minimum at $E_{\text{exc}} = 2.51$ eV which is identical with the energy of the triplet pair state. It is suggested that an optically populated, vibronically excited S_1^v-state which is iso-energetic with the triplet pair state can undergo fission into two triplet states. However the effect is at least one order of magnitude smaller than theoretically predicted, strongly temperature dependent and only noticeable with light polarized perpendicular to the crystallographic **b**-axis (weak Davydov component). It is therefore concluded that thermally induced singlet exciton fission must proceed via a different vibrationally excited intermediate state, which is optically inactive.

1. Introduction

Delayed fluorescence resulting from mutual annihilation of two triplet excitons is a well-known phenomena in molecular crystals.(1,2) Neglecting details the process can be described by

$$T + T \xrightarrow{\gamma} S_1 + S_0 \rightarrow 2S_0 + h\nu.$$

From thermodynamic reasons also the reverse process must be possible, i.e. fission of a singlet exciton into a pair of triplet excitons. Swenberg and Stacy(3) have postulated that this process is the dominant

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channel for radiationless decay of the first excited singlet state of crystalline tetracene and both Geacintov, Pope and Vogel⁽⁴⁾ and Merrifield, Avakian and Groff⁽⁵⁾ have confirmed this hypothesis experimentally. Since in tetracene crystals the energy of the triplet-pair state ($E(2T)$) is above the energy $E(S)$ of the first excited singlet state the rate constant for exciton fission is temperature dependent according to

$$k = k_0 \exp\left(-\frac{E(2T) - E(S)}{kT}\right). \tag{1}$$

The temperature dependence of the fluorescence efficiency yields $\Delta E_f = E(2T) - E(S) = 0.15 \cdots 0.24$ eV⁽⁶⁻⁸⁾ and $k_0 = 10^{13}\,\mathrm{s}^{-1}$.⁽⁷⁾ Below 200 °K the fission process is frozen in and genuine monomolecular decay of the S_1-state prevails.

It may be that thermally stimulated exciton fission proceeds via a vibronically excited S_1 state—in the following denoted by S_1^{v}—as a thermally populated intermediate which is isoenergetic to the triplet pair state. Then singlet exciton fission should also occur after *optical* excitation of the S_1^{v} state and may consequently be observable also at low temperatures when the " thermal " channel is effectively closed. This effect should manifest itself in a drop of the fluorescence efficiency if the excitation energy E_{exc} exceeds $E(2T)$. The present paper reports on an investigation of this effect.

2. Theory

Usually the fluorescence quantum yield of a molecular crystal with a pure surface does not depend on the excitation energy as long as neither photoionization⁽⁹⁾ nor photoreactions⁽¹⁰⁾ occur. If, however, an additional radiationless decay channel is opened when a certain vibronic level of the S_1 state is excited, the fluorescence quantum yield must be lower if exciton fission proceeds directly from that level before a radiationless transition to S_1^0 can occur. The fluorescence quantum yield will then be lower upon excitation of the S_1^{v} level (fluorescence yield ϕ^*) instead of the S_1^0 level (fluorescence yield ϕ). In this section the result of a calculation of the ratio ϕ^*/ϕ is presented based on the kinetic scheme shown in Fig. 1. Excimer formation⁽¹¹⁾ is neglected herein. This is justified by the

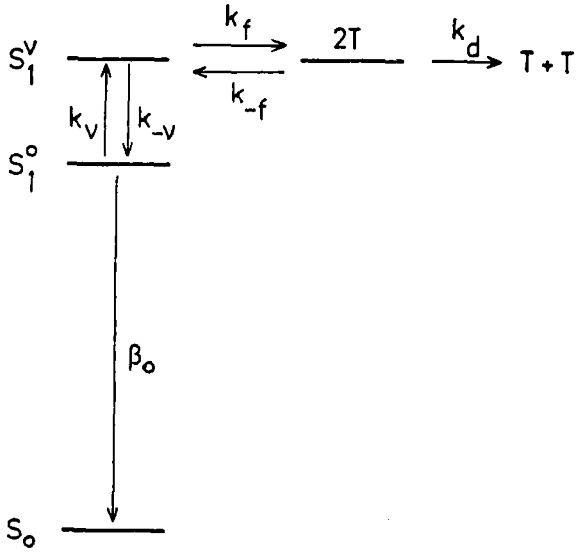

Figure 1. Level diagram for the kinetic analysis. Optically excited is either the S_1^0 or the S_1^v-state. k_f and k_{-f} determine the rate of fission of the S_1^v-state and fusion of the triplet pair state respectively. k_d is the rate constant for dissociation of the triplet pair state. k_v determines thermal population of the vibronically excited S_1^v-state, k_{-v} determines its deactivation to the S_1^0-state.

observation that singlet excitons in crystalline tetracene are essentially free, at least at temperatures above 160 °K.⁽¹²⁾ However, introduction of a hypothetical excimer state as an intermediate does not change the result. The basic assumption of the model employed is that thermally and optically induced exciton fission involves *the same* vibronically excited S_1^v state as an intermediate. Application of steady state conditions leads to the following expressions for the steady state population of S_1^0 which is the emitting state, depending on whether S_1^0 or S_1^v is optically excited. The latter case is characterized by $[S_1^0]^*$.

$$[S_1^0] = N\left(\beta_0 + k_v \frac{1}{1+(k_{-v}/k_f)\cdot(1/\kappa)}\right)^{-1} \tag{2a}$$

$$[S_1^0]^* = \frac{N}{\beta_0[1+(k_f/k_{-v})\cdot\kappa]+k_v(k_f/k_{-v})\cdot\kappa} \tag{2b}$$

$$\frac{[S_1^0]^*}{[S_1^0]} = \left(1+\kappa\cdot\frac{k_f}{k_{-v}}\right)^{-1} \tag{3}$$

κ stands for $k_d/(k_d+k_{-f})$ and denotes the fraction of fission events leading to separated triplet excitons, N is the number of absorbed quanta per second. The rate constants β_0, k_v, k_{-v}, k_f, k_{-f} and k_d are defined in Fig. 1. It further holds

$$\frac{\phi^*}{\phi} = \frac{[S_1^0]^*}{S_1^0} \tag{4}$$

Equation (3) predicts a lower fluorescence efficiency if S_1^v is excited instead of S_1^0. The magnitude of the effect can be estimated from the data derived from thermally stimulated exciton fission. From the temperature dependence of the fluorescence quantum yield the empirical relation follows

$$[S_1^0] = N(\beta_0+k) = N\left[\beta_0+k_0\exp\left(-\frac{\Delta E_f}{kT}\right)\right] \tag{5}$$

where k is the rate constant for thermally induced exciton fission. Comparing Eqs. (2) and (5) and setting $k_v = \nu_0 \exp(-\Delta E_f/kT)$ where ν_0 is a lattice frequency factor of the order $10^{13}\,\mathrm{s}^{-1}$, gives

$$k_0 = \nu_0\left[1+\frac{1}{\kappa}\frac{k_{-v}}{k_f}\right]^{-1} \tag{6}$$

Combining Eqs. (3), (4) and (6) finally yields

$$\frac{\phi^*}{\phi} = 1-\frac{k_0}{\nu_0} \tag{7}$$

With $\nu = 10^{13}\,\mathrm{s}^{-1}$, $k_0 = 10^{13}\,\mathrm{s}^{-1}$ Eq. (7) predicts $\phi^*/\phi = 0$.

The fluorescence efficiency of crystalline tetracene should be completely quenched if the energy E_{exc} of the exciting quanta exceeds $E(S)+\Delta E_f$. It is difficult to estimate the accuracy of the theoretical estimate for ϕ^*/ϕ. However in view of the fact that the Debye frequency of molecular crystals like tetracene is not much higher than 100 °K.(13) $\nu = 10^{13}\,\mathrm{s}^{-1}$ seems to be an upper limit. The error of k_0 stems from the uncertainty of both the value for the energy gap ΔE_f between singlet and triplet-pair state and the magnitude of the fluorescence increase upon cooling the crystal from 293 °K to 77 °K. Both values seem to depend on the " history " of the sample. We have therefore determined both quantities for the crystals used in the present experiments and have found $\Delta E_f = 0.18 \pm 0.01$ eV and a 30-fold increase of the fluorescence yield upon cooling from 293 °K to 160 °K. Using Pope *et al.*'s(7) values for the low temperature singlet lifetime $k_0 = 5 \cdot 10^{12}\,\mathrm{s}^{-1}$ is obtained. Thus we estimate an upper limit of 0.5 for ϕ^*/ϕ.

A second important consequence of the kinetic analysis is that ϕ^*/ϕ does not depend on temperature, i.e. the drop of the fluorescence efficiency for $E_{\mathrm{exc}} > E(S) + \Delta E_f$ should also occur at room temperature—in striking contrast to the results of Geacintov *et al.*⁽⁹⁾ We therefore decided to reinvestigate this effect, taking exciton diffusion and quenching into account and thus look for more subtle changes in $(\phi^*/\phi)(\lambda)$ than can be gleaned from the data in Ref. 9, which are obtained with unpolarized light.

3. Experimental and Results

The excitation spectrum of the relative fluorescence efficiency of crystalline tetracene was measured with polarized light in the temperature range 293 to 160 °K. For a description of the experimental setup the reader is referred to a previous paper on singlet exciton diffusion in tetracene crystals.⁽¹²⁾

Figure 2 shows the experimental spectrum for $\perp$ **b**-polarized light. The main problem in the interpretation of the fluorescence excitation spectrum is to distinguish between a dependence of the fluorescence yield on the energy of the exciting light as a result of surface quenching of singlet excitons and as a result of optically induced exciton fission. The " diffusional " quenching effect can be described by

$$1 - I_f = \Delta I_f = g\,\frac{l_d}{\alpha^{-1} + l_d} \tag{8}$$

l_d is the diffusion length of singlet excitons, α the absorption coefficient, i.e. α^{-1} the penetration depth of the exciting light, $l_d/(\alpha^{-1} + l_d)$ denotes the fraction of excitons reaching the surface and g is the probability that these excitons do no longer contribute to ordinary crystal fluorescence. For crystals containing an oxidized surface layer $g = 1$ has been found.⁽¹²⁾ In Eq. 8 I_f is the relative fluorescence efficiency at an arbitrary wavelength normalized to the incident photon flux in such a way that $I_f = 1$ for $d \gg \alpha^{-1} \gg l_d$ (d is the crystal thickness); ΔI_f is the fluorescence " decrement " resulting from surface quenching. Equation (8) can be rewritten to give

$$(\Delta I_f)^{-1} = 1 + (\alpha \cdot l_d)^{-1} \tag{9}$$

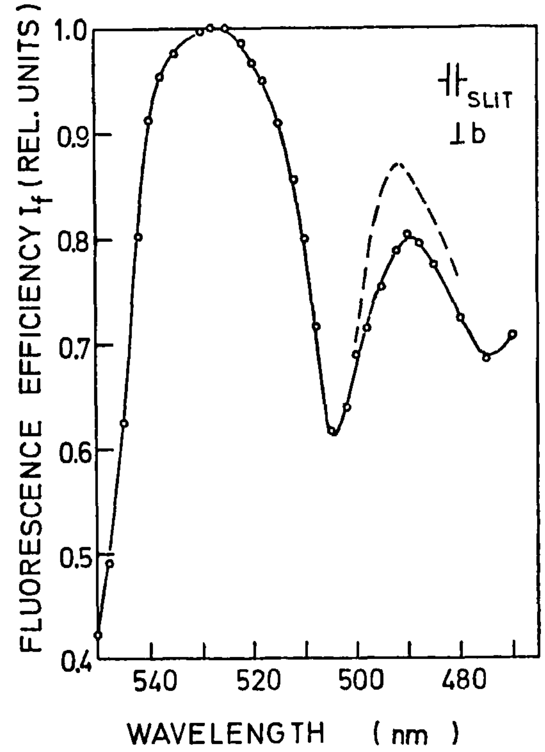

Figure 2. Relative fluorescence efficiency I_f of crystalline tetracene as a function of excitation wavelength for light polarized ⊥**b**. T = 183 °K. The decrease of I_f at the long wavelength-side is due to the fact that the penetration depth α^{-1} becomes comparable to the crystal thickness. The dashed curve is calculated under the assumption that $I_f(\lambda)$ is exclusively determined by surface quenching of singlet excitons.

In Ref. 12 it has been shown that with **b**-polarized light the fluorescence excitation spectrum in the temperature range 293 to 160 °K can solely be understood in terms of Eq. (9). Thus no additional decrease of I_f at an excitation energy $E_{\text{exc}} \approx E(S) + \Delta E_f$ indicative of optically stimulated fission was noticeable. The limit of detectability for a reduction $1-(\phi^*/\phi)$ of the relative fluorescence yield is $\lesssim 0.05$ owing to the neglect of change in the crystal reflection coefficient with temperature.

According to Eq. (9) the data for **b**-polarized light yielded certain values for l_d. Since transitions between both Davydov levels are fast, the same l_d values must apply to excitation into the upper

Davydov band. Indeed, analysis of the data for excitation energies near the absorption maximum for $\perp$ **b**-polarized light ($\lambda_{\text{exc}} = 502 \cdots 505$ nm respectively $E_{\text{exc}} = 2.465 \cdots 2.455$ eV depending on temperature) gives identical l_d values using the absorption data of Bree and Lyons.(14) In order to detect a decrease of the fluorescence efficiency resulting from optically stimulated singlet exciton fission one has to carefully analyse the excitation spectrum in the range 550 to 450 nm. This requires knowledge of the crystal reflection spectrum which is not known for tetracene. In order to overcome this difficulty we proceeded as follows: Transposing the reflection data from anthracene(15) to tetracene presents evidence that at room temperature the fluorescence decrement $1-(\phi^*/\phi)$ originating from optically induced fission cannot exceed 0.02 which is close to the experimental error. Therefore we assumed $[1-(\phi^*/\phi)]_{T=293^\circ\text{K}} = 0$. Then the experimental $I_f(\alpha)$-curve was normalized in such a way that Eq. (9) which considers only surface exciton quenching was fulfilled taking those values for the singlet exciton diffusion length which were obtained with **b**-polarized light at the same crystal. This gave an empirical wavelength dependent normalization factor which subsequently was applied to the excitation spectra taken at lower temperatures. The result is that upon lowering the temperature an *additional* decrease δI_f of the fluorescence efficiency is observed for $E_{\text{exc}} > 2.50$ eV, which cannot be explained in terms of exciton quenching (see Fig. 1): $I_f = 1-(\Delta I_f + \delta I_f)$. The maximum additional fluorescence decrement δI_f which equals $1-(\phi^*/\phi)$ increases from $\leqslant 0.02$ at room temperature to 0.07 ± 0.02 below 200 °K (Fig. 3). The ratio $\delta I_f/\Delta I_f$ is 0.4 at maximum effect. It should be noted that the δI_f-values represent minimum values because they are based on the assumptions that $\delta I_f = 0$ in the whole temperature range for **b**-polarized light and $\delta I_f = 0$ at room temperature for $\perp$ **b**-polarized light.

We propose that the spectral dependence of I_f is due to the action spectrum of the optically stimulated fission process for singlet excitons (Fig. 4). It has a peak at 2.51 ± 0.01 eV which is identical with the sum of the energies of two triplet excitons.(16) This agreement confirms the interpretation of the experimental result within the framework of singlet exciton fission. At lower temperatures the center of the lowest Davydov component of the crystal absorption

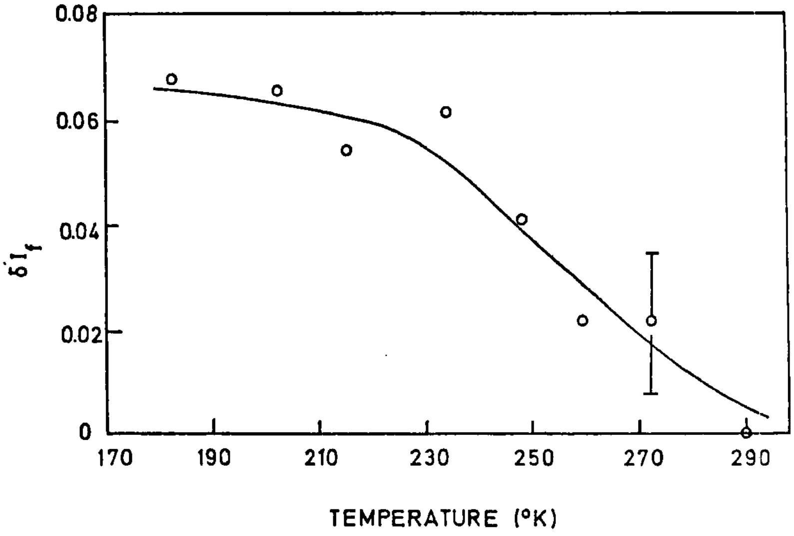

Figure 3. Temperature dependence of the fluorescence decrement δI_f caused by fission of the optically excited S_1^{v}-state which is isoenergetic with the triplet pair state.

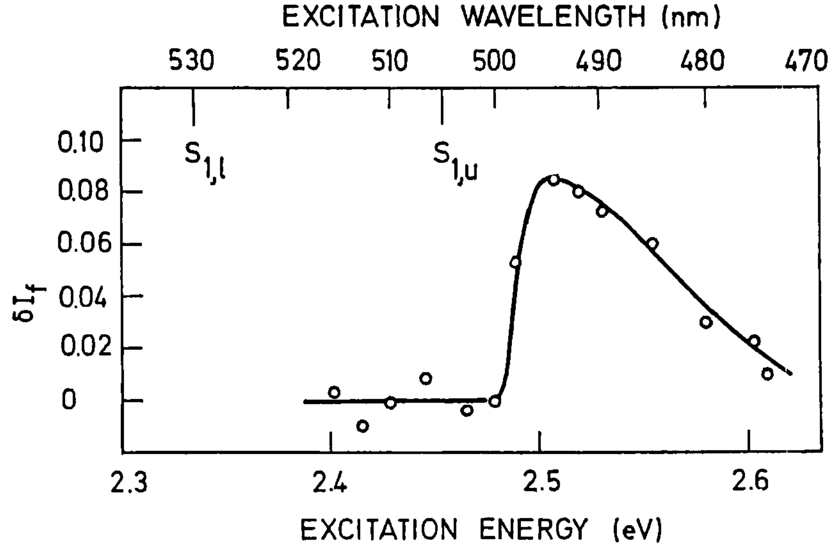

Figure 4. Action spectrum for fission of the optically excited S_1^{v}-state. $S_{1,l}$ and $S_{1,u}$ denote the position of the absorption maxima for transitions to the lower and upper Davydov branches of the exciton band. Temperature: 183 °K.

spectrum peaks at 2.335 eV.(17) Thus the fission process is most effective at an energy $\Delta E_f = 0.175 \pm 0.01$ eV above the lowest excited singlet level. The same value for ΔE_f was obtained from the temperature dependence of the fluorescence efficiency upon excitation of the zero-vibronic S_1-level.

The experimental results can be condensed into the following:

(1) With $\perp$ **b**-polarized light there is a drop δI_f of the relative fluorescence efficiency at a photon energy identical to the energy of the triplet pair state, indicative of an additional radiationless decay channel for the vibrationally excited S_1^{v} state into a pair of triplet states.

(2) δI_f is strongly temperature dependent. It approaches a maximum value of less than 10% below 200 °K. At room temperature the effect is within the limits of the experimental error.

(3) With **b**-polarized light no effect is noticeable. This however could be an artifact due to the neglect of changes in the shape of the crystal reflexion spectrum.

4. Discussion

The experimental result contradicts the theoretical prediction in two points. (1) The observed fluorescence decrease for excitation energies $E_{\mathrm{exc}} \geqslant E(S) + \Delta E_f$ is about one order of magnitude too small. (2) It strongly depends on temperature, at room temperature the effect is within the experimental uncertainty i.e. $1 - (\phi^*/\phi) \lesssim 0.02$. We must therefore assume that the basic assumption of the kinetic model namely the identity of the vibrationally excited intermediate state from which thermally and optically induced singlet exciton fission starts, is wrong.

Instead, it is suggested that the intermediate state for thermally induced fission is optically inactive and at least 10 times as effective in producing exciton fission than the optically active intermediate. It can either be a S_1 state coupled to a non-totally symmetric molecular vibration or to a lattice phonon cloud. Since the resonance interaction between neighboring molecules critically depends on molecular orientation, it is likely that those molecular or lattice modes are most effective which lead to a favorable molecular position.

A second possibility is that the thermally fissioning state is a trapped exciton state. Since above 180 °K the tetracene lattice seems to be unstable(17) a high concentration of shallow traps can be expected. This, however, contradicts the observation that above 160 °K singlet excitons are essentially free, or one has to assume that the fission rate of an almost free exciton at a defect site is extremely high.

According to Eq. (3) the rate constant for fissioning of the optically excited S_1^v state is $k_f = (k_{-v}/\kappa)[(\phi/\phi^*) - 1]$. Inserting $(\phi/\phi^*) - 1 = 8 \cdot 10^{-2}$ at $T < 200$ °K and an estimated value $k_{-v} = 10^{12}\,\mathrm{s}^{-1}$ for vibronic relaxation yields $k_f = 10^{11}\,\mathrm{s}^{-1}$. This is within the limits calculated by Swenberg and Stacy.(3) The decrease towards higher temperatures can be explained in terms of changes in the molecular arrangement which are evidenced by a continuous decrease in the Davydov splitting.(17)

At present no definite explanation can be given for the observation that optically induced fission is much more effective with $\perp$ **b**-polarized light. There are several possibilities:

(1) The singlet → triplet-pair transition is subject to selection rules based on symmetry relations.

(2) Intersection of the potential surfaces of triplet-pair state and both Davydov components of the S_1-state occurs at different energies.

(3) Since for the lower and upper Davydov component the vibrational energies amount to 0.175 ± 0.01 eV and 0.055 ± 0.01 eV respectively, the vibronic state involved in S_1^v is different for both Davydov components. Therefore the lifetime k_{-v}^{-1} might also be different.

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REFERENCES

1. Avakian, P. and Merrifield, R. E., *Mol. Cryst.* **5**, 37 (1968).
2. Swenberg, C. E., *J. Chem. Phys.* **51**, 1753 (1969).
3. Swenberg, C. E. and Stacy, W. T., *Chem. Phys. Letters* **2**, 327 (1968).
4. Geacintov, N., Pope, M. and Vogel, F., *Phys. Rev. Letters* **22**, 593 (1969).
5. Merrifield, R. E., Avakian, P. and Groff, R. P., *Chem. Phys. Letters* **3**, 155 (1969).
6. Kazzaz, A. A. and Zahlan, A. B., *J. Chem. Phys.* **48**, 1242 (1968).
7. Pope, M., Geacintov, N. E. and Vogel, F., *Mol. Cryst and Liq. Cryst.* **6**, 83 (1970).
8. Groff, R. P., Avakian, P. and Merrifield, R. E., *Phys. Rev.* **B1**, 815 (1970).
9. Geacintov, N., Pope, M. and Kallmann, H., *J. Chem. Phys.* **45**, 2639 (1966).
10. Braun, C. L., Kato, S. and Lipsky, S., *J. Chem. Phys.* **39**, 1645 (1963).
11. Katul, J. A. and Zahlan, A. B., *J. Chem. Phys.* **47**, 1012 (1967).
12. Vaubel, G. and Baessler, H., *Mol. Cryst. and Liq. Cryst.*, **12**, 47 (1970).
13. Friedman, L., *Phys. Rev.* **140**, A 1649 (1965).
14. Bree, A. and Lyons, L. E., *J. Chem. Soc.* 2662 (1956).
15. Bree, A. and Lyons, L. E., *J. Chem. Soc.* 5206 (1960).
16. Private communication by the Dupont group.
17. Vaubel, G. and Baessler, H., *Mol. Cryst. and Liq. Cryst.*, **12**, 39 (1970).