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Temperature dependence of the triplet exciton yield in fission and fusion in tetracene

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The increase in quantum efficiency for luminescence with increasing excitation intensity is measured as a function of temperature in tetracene. The results indicate that the quantum efficiency for the production of triplets from an excited singlets decreases markedly below 300 °K. This decrease is accounted for by a process which competes with exciton fission with a rate $K = (1.3 \pm 0.2) \times 10^8 \text{ sec}^{-1}$. This value is shown to be inconsistent with a singlet trapping interpretation for the nonexponential decays found by others in the prompt fluorescence. The results are consistent with a nearly temperature independent value for the fraction of exciton fusion events which lead to excited singlets f . The relative constancy of f above 300 °K implies that fusion resulting in a triplet proceeds via the first excited triplet. This in turn provides a qualitative explanation for the apparent lack of a relationship between the measured value of f and the rudimentary value inferred from spin statistics.

I. INTRODUCTION

A great deal of work has shown that exciton fission in tetracene occurs in $\sim 200 \text{ psec}$ at room temperature.¹⁻³ Other processes competing for singlet excitons have been found to have various rates from one third of the fission rate¹ ("fast competing rate") to a rate one fiftieth that of fission⁶ ("slow competing rate"). The slow competing rate is the result of a theory by Klein⁴ in which the nonexponential character of the fluorescence decay curves is interpreted in terms of a collective motion of the geminate triplet pair. The experiments interpreted in this way were carried out under conditions of weak pulse excitation³ from a synchrotron. The fast competing rate is the result of a trapping model which is used in interpreting nonexponential decays which are produced by relatively intense pulse excitation from a frequency doubled Nd-YAG laser.¹ Each of these models involves a multiparameter fit to the decay curves. Clearly, an independent determination of the rate of competing processes is important in understanding the mechanism for the nonexponential decays. The present work presents the results of a steady-state measurement in which the ratio of the competing rate to the fission rate is isolated and determined in a manner which is relatively independent of other factors.

Since fission increases with temperature, competing rates should be swamped by fission at elevated temperatures. Where other rates compete the average number of triplets produced for each singlet which decays will be less than 2. Therefore, a measurement of the quantum yield for triplet production g^* at various temperatures allows one to estimate the extent to which other processes are important. An accurate measurement can be made by utilizing the increase in the fluorescence quantum efficiency with increasing excitation intensity. Such a technique has previously been used by Ern *et al.*⁵ for determining the fraction of exciton fusion events which lead to singlet excitons f .

The concentration of singlet excitons n_s and triplet

excitons n_t in tetracene under constant illumination I is given by the solution to the following equations:

$$0 = \frac{\partial n_s}{\partial t} = \epsilon I e^{-\epsilon x} + \frac{1}{2} f \gamma_{tt} n_t^2 - (K + K_F) n_s, \quad (1)$$

$$0 = \frac{\partial n_t}{\partial t} = 2K_F n_s - \beta_t n_t - \gamma_{tt} n_t^2, \quad (2)$$

where ϵ is the absorption coefficient, x is the depth from the crystal surface, γ_{tt} is the net bimolecular fusion rate constant, f is the fraction of fusion events leading to singlet excitations, β_t is the monomolecular decay rate for triplets, K_F is the fission rate, and K is the rate of loss of singlets by processes other than fission. If the light is strongly penetrating so that ϵ^{-1} is considerably smaller than the thickness of the sample but larger than the triplet diffusion length perpendicular to the surface, then the quantum yield Y at all intensities to the yield Y_0 at low intensity [i.e., $\gamma_{tt} n_t^2$ can be neglected in both Eqs. (1) and (2)] can be shown from Eqs. (1) and (2) to be

$$\frac{Y}{Y_0} = \left(1 - \frac{fg^*}{2}\right)^{-1} (1 - 2fg^*(\mu^*)^{-1} \{(1 + \mu^*)^{1/2} - \ln[\frac{1}{2} + \frac{1}{2}(1 + \mu^*)^{1/2}] - 1\}),$$

where

$$g^* = \frac{2K_F}{K_F + K} \quad (3)$$

and

$$\mu^* = 4g^*\epsilon(1 - \frac{1}{2}fg^*)\gamma_{tt}/\beta_t^2.$$

The function described by Eq. (3) has a value of 1 at intensities for which $\mu^* I \ll 1$ and a value of $(1 - \frac{1}{2}fg^*)^{-1}$ at high intensities ($\mu^* I \gg 1$).⁵ The high intensity value of Y/Y_0 therefore gives fg^* . g^* is expected to be temperature dependent due to the dependence of the fission rate $K_F = K_{F\infty} \exp(-\Delta E/KT)$. Combining this with the definition of g^* from Eq. (3) gives

$$g^* = \frac{2}{1 + (K/K_{F\infty}) e^{-\Delta E/KT}}, \quad (4)$$

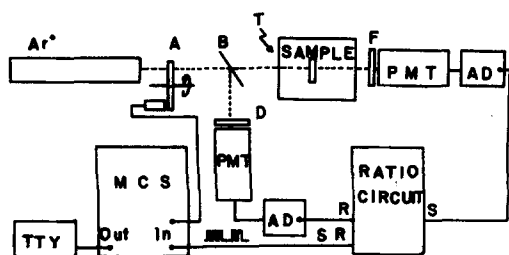


FIG. 1. Experimental setup: A is a variable circular neutral density wedge, T is a constant temperature cell, and F is the fluorescence isolation filter.

where ΔE is the activation energy for fission ($\Delta E \approx 2400^\circ \text{K}^5$) and K_F is the fission rate at infinite temperature. Since f is not expected to be temperature dependent *a priori* (more will be said about this assumption in Sec. III), a measurement of fg^* gives information concerning the competition of other processes with fission (i.e., one can evaluate K/K_F). In addition, since previous evaluations of f involved the assumption that $g^* = 2$ at room temperature, the temperature dependence of g^* is necessary in order to insure the reliability of f .

II. EXPERIMENT

Tetracene powder was subjected to two successive vapor gradient zone purifications and single flakes 10 to 20 μ in thickness were grown in a N_2 atmosphere.

In order to record the intensity dependence of the quantum efficiency as a function of temperature the set-up in Fig. 1 was used. Light from an Ar^* laser provided the excitation which was directed perpendicular to the crystal *ab* plane. The combined lines in the ultraviolet at 3511 and 3638 \AA were used. The light was attenuated with a series of neutral density filters for a total range of five orders or by a circular neutral density filter having a logarithmic profile and a range of

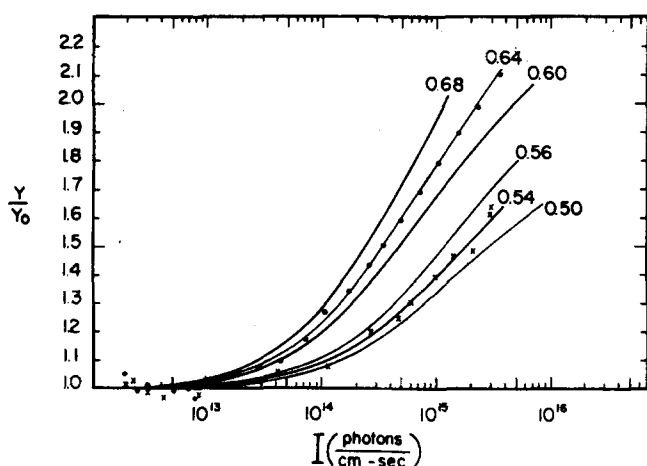


FIG. 2. Experiment and theory for luminescence quantum efficiency (Y/Y_0) vs intensity I at 300°K (—) and 243°K (---). The computer fitted values of $fg^*/2$ and μ^* at 300°K are 0.638 ± 0.05 and $2.1 \times 10^{-14} \text{ cm}^2 \text{ s}$, respectively. The corresponding values at 243°K are 0.545 ± 0.009 and $0.8 \times 10^{-14} \text{ cm}^2 \text{ s}$. Shown also on the same graph for comparison are theoretical curves for $fg^*/2 = 0.68$ and 0.60 with $\mu^* = 2.1 \times 10^{-14} \text{ cm}^2 \text{ s}$ and $fg^*/2 = 0.56$ and 0.50 with $\mu^* = 0.8 \times 10^{-14} \text{ cm}^2 \text{ s}$.

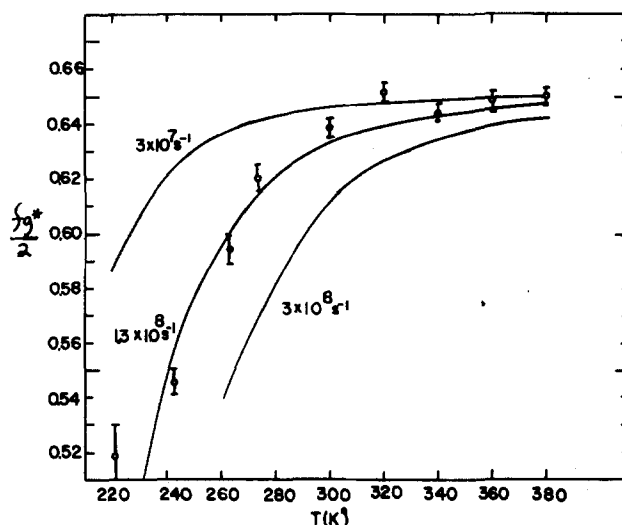


FIG. 3. Measurements of $fg^*/2$ vs temperature. Curves generated from Eq. (5) are represented by the solid lines annotated with their respective value of K .

three orders of magnitude. Although a complete attenuation of five orders was carried out at room temperature in order to check the results in Ref. 5, the temperature measurements were only carried out over three orders of magnitude (by the automated technique shown in Fig. 1). A multichannel scalar MCS was started as the attenuation fell from its highest value. This MCS was used to store the record of a frequency proportional to the ratio of the sample luminescence to the excitation intensity.

The reference optoelectronic circuit consisted of a beam splitter B followed by attenuator D, a 1P21 photomultiplier, and a photon counting amplifier discriminator (A-D). The sample circuit was of similar construction although the attenuator D was replaced by a filter F (CS 3-67). A digital ratio circuit with a six-order linearity range⁷ produced an output frequency proportional to the ratio of the signal frequency to the reference frequency. The data accumulated on the MCS were taken for about 10 sweeps of the circular neutral density filter.

III. RESULTS

Figure 2 shows typical data of Y/Y_0 vs intensity for tetracene. The value for $fg^*/2$ at room temperature (0.64) obtained from a two-variable χ^2 fit of Eq. (3) is slightly smaller than the value of 0.66 obtained with 3250 \AA excitation.⁵ As one can see, the effect of lowering the temperature from 300 to 243°K is to make μ^* less than half of its value at room temperature and to decrease f from 0.64 to about 0.54. The mechanism by which μ^* is lowered is complicated by all the factors which enter in determining its value [see Eq. (3)]. Since the change in g^* is only 20%, it clearly cannot account for the change in μ^* . A more likely reason probably lies in an increase in β_i caused by exciton trapping.⁸ Further discussion will revolve around changes in $fg^*/2$. With the assumption that f does not change, fg^* vs temperature is rich in explicit information about processes which compete with fission. Figure 3 shows the way in which $fg^*/2$ changes with temperature.

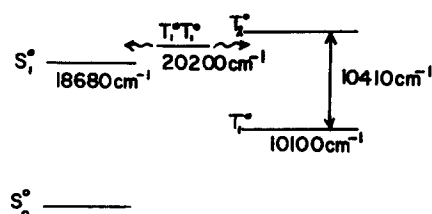


FIG. 4. Electronic energy levels S_1^0 , T_1^0 , and $2T_1^0$ measured in the crystal.⁶ The separation between T_2^0 and T_1^0 is taken from measurements in solution.¹⁰

Although $fg^*/2$ varies by no more than 2% from 300 to 380 °K, below room temperature $fg^*/2$ decreases so that its value at 220 °K is almost 20% below that at room temperature.

IV. CONCLUSION

It is clear from Fig. 4 that $fg^*/2$ remains fairly constant above 340 °K with the value at room temperature lowered from the maximum value by $\leq 2\%$. With K_F taken to be $5 \times 10^9 \text{ sec}^{-1}$ we find that $K \sim 10^8 \text{ sec}^{-1}$. A similar result is arrived at by attempting to fit all the data in Fig. 4. Using Eq. (4), $\Delta E/k = 2400 \text{ °K}$,⁶ $f = 0.65$, and the fact that the fission rate at room temperature is $5 \times 10^9 \text{ sec}^{-1}$, $fg^*/2$ may be written as

$$\frac{fg^*}{2} = \frac{0.64}{1 + 6.7 \times 10^{-14} K e^{-2400/T}}. \quad (5)$$

The solid lines in Fig. 4 are a graph of Eq. (5) for various values of K . As one can see, $K = (1.3 \pm 0.2) \times 10^8 \text{ sec}^{-1}$. This rate is a typical rate for radiative decay but is ten times smaller than the competing rate reported by Smith and Weisz.¹

In the work of Smith and Weisz¹ the rate K is $K = K_{NR2} + K_{R2} + K_{21} [1 - K_{12}/(K_{12} + K_{RT1} + K_{NR T1})]$, where K_{NR2} and K_{R2} are the rates of nonradiative and radiative decay from the first excited singlet, K_{RT1} and $K_{NR T1}$ are the corresponding rates from a trap, and K_{21} and K_{12} are the fill and emptying rates of the trap, respectively. Although K_{12} is temperature dependent, the limits over which K can range are from $K_{NR2} + K_{R2} + K_{21}$ at low temperature to $K_{NR2} + K_{R2}$ at high temperature. Therefore, K will be greater than $K_{NR2} + K_{R2}$ which from Ref. 4 is $1 \times 10^9 \text{ sec}^{-1}$. This result is clearly inconsistent with our measurements. The present results support the explanation given by Klein⁴ for the fast nonexponential decays found by Lopez-Delgado *et al.*³ It appears that these³ nonexponential decays³ in the prompt fluorescence are due to collective motion of the triplet pair itself and not a consequence of singlet trapping.

The assumption that f is constant over the temperature range studied is not a trivial one. The value of f in tetracene is considerably larger than is expected on the basis of spin statistics (as will be shown) and its temperature independence may be used in ruling out several hypotheses which could account for this disparity.

f is a measure of singlet production in a fusion reac-

tion. If we neglect the rate of intersystem crossing, then $f^{-1} = (\gamma_3/2\gamma_1) + 1$, where γ_3 and γ_1 are true rates of production of triplets and singlets, respectively. For $f = 0.65$, $\gamma_3/\gamma_1 = 1.1$ (i.e., triplets and singlets are produced at almost the same rates). This number is far from the value of 3 which would be expected from spin statistics alone.⁹ The introduction of intersystem crossing would be to further lower γ_3/γ_1 . If spin separation can be affected in the matrix elements in fusion, and we expect this to be the case, then the lack of agreement with spin statistics of γ_3/γ_1 is certainly contained in the vibroelectronic parts of the interaction. In the particular case of tetracene the fusing state is positioned relatively close to the excited singlet state S_1 (18 680 cm^{-1}) compared with its energetic distance from the first excited triplet state T_1 (10 100 cm^{-1} , see Fig. 4).⁸ The position of T_2^0 has not been measured in the crystal. However, triplet-triplet absorption measurements in solution¹⁰ place it at 300 cm^{-1} (465 °K) above $2T_1^0$. Inasmuch as the Franck-Condon overlap factors 10 080 cm^{-1} from an excited state origin are small, we expect the possibility of fusion into T_2 with the aid of thermal activation. As Fig. 3 shows, f changes less than +2% from 300 to 380 °K whereas $\exp(-465/T)$ changes by -47%. If the position of T_2^0 is to be believed, then the lack of temperature dependence in f indicates that fusion produces triplets in the T_1 state. The small Franck-Condon factors associated with the large separation of $2T_1^0$ from T_1^0 may well be the major factor contributing to the small value of γ_3/γ_1 .

Further evidence for the role which excess vibrational energy differences play in the value of γ_3/γ_1 comes from examining the energetic situation in anthracene. The value of f for anthracene is in close accord with spin statistics ($\gamma_3/\gamma_1 = 3.5 \pm 0.2$)¹⁰ in comparison with tetracene. In addition, the triplet pair state in anthracene is almost the same energetic distance above T_2 (3805 cm^{-1}) as it is above the singlet state S_1^0 (3520 cm^{-1}). Naphthalene also shows a correlation between the relative excess vibrational energy of the triplet pair state with respect to triplet and singlet channels and the experimental value of f .

It appears that the major influence in reducing the value γ_3/γ_1 in tetracene is vibronic in the case of large energetic differences. A more complete theory for f will be presented in the near future.¹¹

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