

## Coexistence of Exciton Fission and Fusion in Tetracene Crystals

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Triplet exciton fusion and singlet exciton fission have been observed in tetracene crystals, and the magnetic field dependence and the rate constants for these processes have been measured. At 0°C the singlet fission rate constant and the triplet-triplet fusion rate constant (leading to excited singlets) are  $(6.3 \pm 0.7) \times 10^8 \text{ sec}^{-1}$  and  $9 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$  (within an order of magnitude), respectively.

**T**RIPLET excitons in tetracene crystals have been generated with near-infrared light, and the magnetic field dependence of delayed fluorescence resulting from radiative decay of singlet excitons produced by the fusion of triplet pairs (triplet-triplet annihilation) has been measured. In the same crystals we have investigated the magnetic field dependence of prompt fluorescence (excited with blue or ultraviolet light). The existence of exciton fission in tetracene, previously inferred<sup>1,2</sup> from measurements of the magnetic field dependence of prompt fluorescence alone, is confirmed by our measurements. We have measured the rate constants for the exciton fission and fusion reactions.

## I. INTRODUCTION

In organic molecular crystals the lowest electronic excited states are triplet (*T*) and singlet (*S*) exciton states<sup>3-5</sup> as shown schematically in Fig. 1. Both types of excitons can be generated with light, although the absorption coefficient leading to the generation of triplet excitons is very small ( $\sim 10^{-4} \text{ cm}^{-1}$  in anthracene) because the transition occurs between states of different multiplicity.<sup>4,5</sup>

It is well known that, in aromatic hydrocarbons, as two diffusing triplet excitons enter into each other's range of interaction, they can undergo pairwise annihilation (or fusion),<sup>6</sup> giving rise to singlet excitons. The luminescence from radiative decay of these singlet excitons resulting from triplet-triplet fusion is called delayed fluorescence. Previous experimental and theoretical work has shown that the triplet-triplet annihilation rate constant, and, therefore, the delayed fluorescence intensity, can be influenced by an external magnetic field.<sup>7-9</sup>

The possibility of observing fission or splitting of a singlet exciton into two triplet excitons (i.e., the inverse of triplet-triplet annihilation) in tetracene crystals was proposed recently by Swenberg and Stacy.<sup>10</sup> In order to explain the anomalously low quantum yield (0.002 at room temperature<sup>11</sup>) for fluorescence from tetracene crystals, they suggested fission as the dominant loss mechanism for the singlets. Furthermore, they explained the thermal quenching of the quantum yield on the assumption that the singlet-exciton fission reaction is endothermic, and that an activation energy  $\Delta E$  ( $\equiv 2E_T - E_S$ ) is required (see Fig. 1).

Observations of the magnetic field dependence of prompt fluorescence in tetracene have been interpreted on the basis of this model.<sup>1,2</sup>

We have observed a weak delayed fluorescence in tetracene crystals, and we report here on the investigation of the exciton reaction

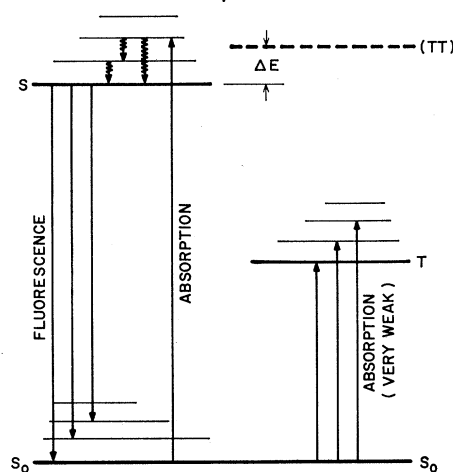
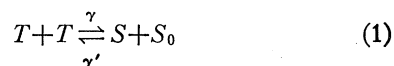


FIG. 1. Schematic energy-level diagram for a tetracene crystal showing the lowest exciton states. The light horizontal lines represent molecular vibrational levels, and the zigzag arrows, radiationless transitions. The dashed horizontal line above the line *S* represents the sum of the energy of two triplet excitons.

<sup>8</sup> R. C. Johnson and R. E. Merrifield, *Phys. Rev.* (to be published).

<sup>9</sup> R. E. Merrifield, *J. Chem. Phys.* **48**, 4318 (1968).

<sup>10</sup> C. E. Swenberg and W. T. Stacy, *Chem. Phys. Letters* **2**, 327 (1968).

<sup>11</sup> E. J. Bowen, E. Mikiewicz, and F. W. Smith, *Proc. Phys. Soc. (London)* **A62**, 26 (1949).

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<sup>1</sup> N. Geacintov, M. Pope, and F. Vogel, *Phys. Rev. Letters* **22**, 593 (1969).

<sup>2</sup> R. E. Merrifield, P. Avakian, and R. P. Groff, *Chem. Phys. Letters* **3**, 155 (1969).

<sup>3</sup> H. C. Wolf, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. 8, p. 1.

<sup>4</sup> S. A. Rice and J. Jortner, in *Physics and Chemistry of the Organic Solid State*, edited by D. Fox, M. M. Labes, and A. Weissberger (Wiley-Interscience, Inc., New York, 1967), Vol. 3, p. 201.

<sup>5</sup> P. Avakian and R. E. Merrifield, *Mol. Cryst.* **5**, 37 (1968).

<sup>6</sup> See, e.g., Ref. 5 and references cited therein.

<sup>7</sup> R. C. Johnson, R. E. Merrifield, P. Avakian, and R. B. Flippin, *Phys. Rev. Letters* **19**, 285 (1967).

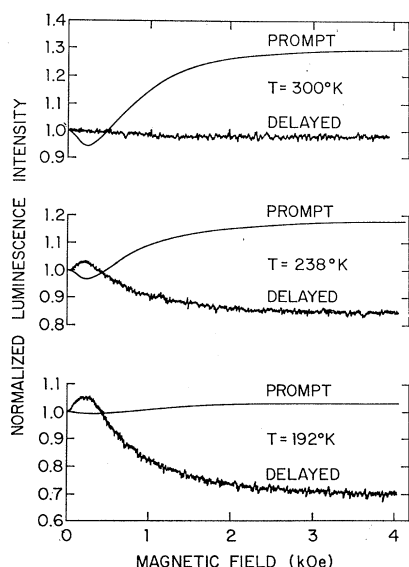


FIG. 2. Experimental curves of magnetic field dependence of prompt and delayed fluorescence intensities in a tetracene crystal. The field was oriented at  $-20^\circ$  with respect to the  $b$  axis in the  $ab$  plane of the crystal.

in both directions in the same system. In studies of exciton fusion, triplet excitons were generated with near-infrared light, and the yellowish *delayed* fluorescence  $\phi$  was observed from the radiative decay of singlet excitons formed by triplet-triplet annihilation or fusion with bimolecular rate constant  $\gamma$ . The dependence of  $\phi$  on magnetic field  $H$  was investigated. In studies of the reverse reaction (exciton fission) with rate constant  $\gamma'$ , singlet excitons were generated directly from the ground state  $S_0$  via absorption of blue or near-ultraviolet light, and the *prompt* fluorescence  $F$  was investigated as a function of  $H$  and of temperature.

## II. THEORY

The fission and fusion rate constants in Eq. (1) are related by<sup>2</sup>

$$\gamma'/\gamma = \frac{3}{2}e^{-(2E_T - E_S)/kT} \equiv c(T), \quad (2)$$

where  $E_T$  is the energy of a triplet exciton,<sup>12</sup>  $E_S$  the energy of a singlet exciton,  $k$  Boltzmann's constant, and  $T$  the absolute temperature.

Under the assumption of uniform excitation of the crystal,<sup>13</sup> the rate equations for concentration of singlet and triplet excitons are

$$d[S]/dt = \alpha_S i_S - (\beta_S + \beta')[S] + \frac{1}{2}\gamma[T]^2 \quad (3)$$

and

$$d[T]/dt = \alpha_T i_T - \beta_T(T) - \gamma_{\text{tot}}[T]^2 + (a\beta_S + 2\beta')[S]. \quad (4)$$

<sup>12</sup> We assume external magnetic fields are sufficiently small such that the Zeeman splitting of the triplet is negligible compared to  $kT$ .

<sup>13</sup> Extinction depth for the absorbed light is much greater than exciton diffusion length.

In these equations  $\alpha_S$  and  $\alpha_T$  are the absorption coefficients for blue light and for infrared light of intensity  $i_S$  and  $i_T$ , respectively;  $\beta_S$  and  $\beta_T$  are the monomolecular decay rate constants for singlets (exclusive of the fission process) and for triplets;  $\beta'$  ( $=[S_0]c\gamma$ ) is the singlet fission rate constant;  $\gamma_{\text{tot}}$  and  $\gamma$  are the total bimolecular annihilation rate constant for triplets and the bimolecular annihilation rate constant leading to excited singlets, respectively; and  $a$  is the fraction of singlets leading to triplets via intersystem crossing (not involving fission). Under steady-state conditions, with *low* exciton concentrations, the solutions of the rate equations are as follows. For prompt fluorescence experiments,  $i_T = 0$  and

$$F = \beta_1[S] = \frac{\beta_1 \alpha_S i_S}{\beta_S + [S_0]c\gamma}, \quad (5)$$

where  $\beta_1$  is the radiative singlet decay rate constant; for delayed fluorescence experiments,  $i_S = 0$ , and

$$\phi = \beta_1[S] = \frac{\beta_1(\frac{1}{2}\gamma\alpha_T^2 i_T^2 / \beta_T^2)}{\beta_S + [S_0]c\gamma}. \quad (6)$$

In accordance with experimental and theoretical work on anthracene,<sup>7-9</sup>  $\gamma$  is the only parameter that is expected to be magnetic-field-dependent in the above equations. Changes in  $F$  and  $\phi$  due to changes in  $\gamma$  (e.g., induced by a magnetic field) are expected to be opposite in sense. Since the triplet-triplet fusion process is adding to the reservoir of singlets, an increase in  $\gamma$  should result in an increase in  $\phi$ . Conversely, singlet fission is reducing the singlet concentration, and an increase in  $\gamma$  (and hence  $\gamma'$ ) should result in a decrease in  $F$ .

Using Eqs. (5) and (6), the singlet fission rate constant at zero field can be related to experimentally measurable quantities as follows:

$$\beta' = \beta_{\text{eff}}x/(1+x), \quad (7)$$

where  $\beta_{\text{eff}} = \beta_S + \beta'$  is the total decay rate constant and

$$x = -\frac{[F(H) - F(0)]/F(0)}{[\phi(H) - \phi(0)]/\phi(0)}.$$

## III. EXPERIMENTAL

Vapor-grown tetracene single crystals were placed between the poles of an electromagnet with the field in the  $ab$  plane<sup>14</sup> of the crystal. In the delayed fluorescence measurements the crystal was excited with near-infrared light ( $0.7\text{--}1.0\ \mu$ ) obtained by filtering (Corning C.S. 2-64+7-59) the output of a 1000-W xenon arc (Hanovia 976C-1). The emitted luminescence at  $5700\ \text{\AA}$  passed through a light guide and was detected by a

<sup>14</sup> R. B. Campbell and J. M. Robertson, *Acta Cryst.* **15**, 289 (1962); J. M. Robertson, V. C. Sinclair, and J. Trotter, *ibid.* **14**, 697 (1961).

photomultiplier (E.M.I. 6255S) through appropriate filters (Baird-Atomic B-5-5700+2 Schott BG-18). The expected square dependence of emission intensity on excitation intensity was verified. In the prompt fluorescence measurements, the excitation source was blue light (4358-Å line) from a 75-W mercury lamp (General Electric H35A3). A small fused-silica cryostat was employed for the low-temperature measurements. A phase-shift  $\tau$  meter, built at this laboratory, was used for measuring the singlet-exciton lifetime.

#### IV. RESULTS AND DISCUSSION

The dependence of delayed and prompt fluorescence intensity with steady-state excitation of the crystal on the magnitude of a static magnetic field at 192, 238, and 300°K is shown in Fig. 2. The magnetic field was in the *ab* plane of the crystal at  $-20^\circ$  from the *b* axis (one of the resonance directions in Fig. 3).

The shape of the field-dependence curves in delayed fluorescence is very similar to that in anthracene.<sup>7,9</sup> In view of the similarity of the crystal structures of anthracene and tetracene,<sup>15</sup> this is as one would expect. The decrease in the effect of a magnetic field at higher temperatures is consistent with an increase of  $c(T)$  [see Eq. (2)] because of the manner in which  $c$  appears in the expression for  $\phi$  [Eq. (6)]. As expected from Eqs. (5) and (6), the field-dependence curves for prompt fluorescence are the inverse of those obtained for delayed fluorescence.

The dependence of the delayed and of the prompt fluorescence intensity on the orientation of a 4-kOe field at 192, 238, and 300°K is shown in Fig. 3. Level-crossing resonances similar to those in anthracene<sup>7,9</sup> are found both in delayed and in prompt fluorescence. Within experimental error, the orientations of the magnetic field where resonances occur in prompt fluorescence coincide with those in delayed fluorescence.

The observed inverse magnetic field dependence in prompt and in delayed fluorescence, together with the observed coincidence in the level-crossing resonances, provides very strong support for the singlet-exciton-fission model. The experimentally found positions of the resonances are consistent with the theoretical prediction<sup>1,2</sup> that is based on the existing theoretical values for the zero-field splitting parameters  $D$  and  $E$  for tetracene molecules and the known crystal structure.

From Eq. (7), the singlet fission rate constant can be determined by measuring the singlet lifetime  $\tau = \beta_{\text{eff}}^{-1}$  and the ratio  $x$  of the normalized effect of a magnetic field on prompt and on delayed fluorescence.

At  $T = 273^\circ\text{K}$ , for a typical crystal, we obtained  $\tau = (1.45 \pm 0.15) \times 10^{-9}$  sec and  $x = 8 \pm 1$ . Taking the concentration of tetracene molecules  $[S_0] = 3.37 \times 10^{21}$

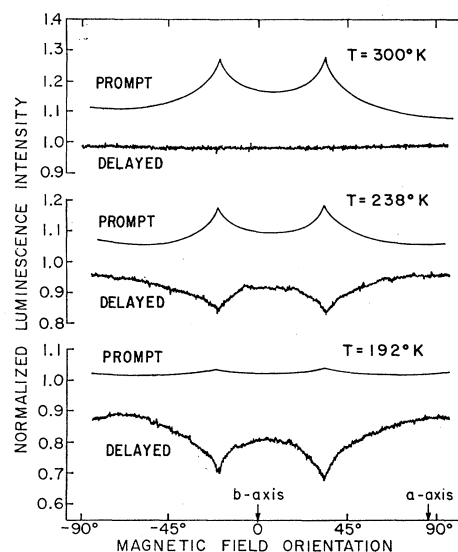


FIG. 3. Dependence of prompt and delayed fluorescence intensity on the orientation of a 4-kOe magnetic field in the *ab* plane of a tetracene crystal.

$\text{cm}^{-3}$ ,<sup>14</sup> we obtain

$$\begin{aligned}\beta' &= (6.3 \pm 0.7) \times 10^8 \text{ sec}^{-1}, \\ \gamma' &= (1.9 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}.\end{aligned}$$

Assuming that  $c$  is the only temperature-dependent quantity in Eq. (5), the activation energy  $\Delta E (= 2E_T - E_S)$  for singlet fluorescence quenching for the above crystal was found to be  $1900 \pm 200 \text{ cm}^{-1}$ . Thus the value of  $\gamma$ , the triplet-triplet fusion rate constant leading to excited singlets, becomes

$$\gamma = 9 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}.$$

Because of the above assumption, as well as problems associated with measurement of  $\Delta E$ ,<sup>16,17</sup> the present value of  $\gamma$  should only be regarded as correct to within an order of magnitude. As expected, we found the value of the quantity  $x$  to be independent of the value of  $H$ .

The above value of  $\gamma$  is somewhat larger than that for anthracene.<sup>5</sup> It is  $10^6$  times larger than the theoretical estimate of  $3 \times 10^{-16} \text{ cm}^3 \text{ sec}^{-1}$  for tetracene.<sup>18</sup> This estimate, however, depends critically on the exact position of the lowest charge-transfer exciton state, which is not well known. The same problem arises in the theoretical estimate of  $\beta'$  ( $0.04$ – $1 \times 10^{12} \text{ sec}^{-1}$ ).<sup>10</sup>

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<sup>16</sup> The value of  $\Delta E$  (and the fluorescence emission spectrum) appears to depend, in an unexplained way, on the history of the crystal. Values of 1200 (Ref. 17), 1300 (Ref. 1), and 1660  $\text{cm}^{-1}$  [N. Geacintov (private communication)] have been reported.

<sup>17</sup> A. A. Kazzaz and A. B. Zahlan, J. Chem. Phys. 48, 1242 (1968).

<sup>18</sup> C. E. Swenberg, J. Chem. Phys. 51, 1753 (1969).

<sup>15</sup> Although the crystal structure of tetracene is triclinic, it departs only slightly from that of anthracene (monoclinic) (Ref. 14).