EFFECT OF MAGNETIC FIELD ON THE FLUORESCENCE OF TETRACENE CRYSTALS: EXCITON FISSION*

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The fluorescence efficiency of tetracene single crystals may be enhanced by as much as 38 % in a magnetic field $H > 2000$ G. The enhancement is anisotropic with respect to the orientation of H in the ab plane. It is shown that a magnetically sensitive coupling of singlet states to a double–triplet-exciton state (T_1T_1) at ~2.40 eV is an important channel for radiationless decay in crystalline tetracene above 160°K.

The nature of radiationless transitions in organic molecular solids and molecules is currently a subject of intensive investigation.[1] A striking example of radiationless processes occurs in tetracene, which is a homolog of anthracene in the linear polyacene aromatic hydrocarbon series. Solid anthracene has a fluorescence efficiency φ of 0.95,[2] whereas for tetracene[3] $\varphi \sim 0.002$ at 298°K. In solution, however, the isolated tetracene molecule exhibits a fluorescence efficiency of 0.21.[4]

A theoretical explanation of the low φ in tetracene crystals was advanced by Swenberg and Stacy[5]; it was suggested that a predominant quenching channel is a decay of a singlet into two triplet excitons. Energetically, this mechanism is feasible in tetracene, but not in anthracene. This would constitute a process of singlet-exciton fission, which is the reverse of the mutual annihilation of two triplet excitons to produce one singlet (exciton fusion). The latter mechanism has been investigated extensively in anthracene[6] and it was observed that the constant representing the radiative bimolecular annihilation rate is magnetic field sensitive.[7]

Recently it was reported[8] that φ for crystalline tetracene increases by 6% in a magnetic field of 2000 G. An analogous effect with anthracene was not observed. These observations were interpreted in terms of an effect of H on the mixing of singlet- and triplet-type Wannier excitons in tetracene.[8]

The present paper reports on the effect of H on the fluorescence of tetracene single crystals as a function of temperature, orientation of H with respect to the crystal axes, excitation intensity, and photon energy. The first two aspects of this work are stressed in this note. The results are interpreted in terms of the level-crossing resonances of Merrifield[9,10] which in turn provide strong support for the Swenberg-Stacy hypothesis as an important quenching channel of the excitation energy in tetracene above 160°K.

Tetracene powder was subjected to four successive vapor-gradient zone purifications and single crystals (~10 μ thick) were grown in an atmosphere of argon. The fluorescence was viewed by means of a fiber optics instrument and an end-on photomultiplier (the latter was carefully shielded to prevent any stray magnetic field effects). A 1000-W mercury-xenon source and a monochromator were used in conjunction with appropriate filter combinations to eliminate stray light. The crystal axes were determined by means of a polarizing microscope.

We obtained the following results: (1) At 298°K the fractional increase in the fluorescence intensity

$$\eta(H) = \frac{\varphi(H)-\varphi(0)}{\varphi(0)},$$

varied from 0.28 to 0.37 at saturation field strengt of ~2000 G (as compared with 0.06 reported previously).[8] The letter H and the zero in parentheses refer to experiments with and without magnetic field, respectively. It was noted that the lower values of $\eta(H)$ were observed with crystals of poorer quality. (2) $\eta(H)$ was the same for a given crystal in air at 1 atm and at 10^{-5} Torr. (3) As the temperature was decreased, $\varphi(0)$ increased and $\eta(H)$ decreased (see Fig. 1). The former effect in tetracene is well known.[11,12] (4) When H was rotated in the ab plane, $\eta(H)$ fluctuated periodically, exhibiting two maxima (Fig. 2). Each peak repeated itself every 180°. On the basis of experiments with six different single crystals, and full 360° rotations for each, it was found that the two peaks were an average of 53° ± 1° apart. The error in locating the b axis is at most ±1°. The peaks were thus located at average values of +23° and −30° with respect to the b axis. (5) $\eta(H)$ was independent of excitation wavelength in the photon energy range 2.6-4.6 eV. (6) The fluorescence efficiency $\varphi(0)$ at 298°K

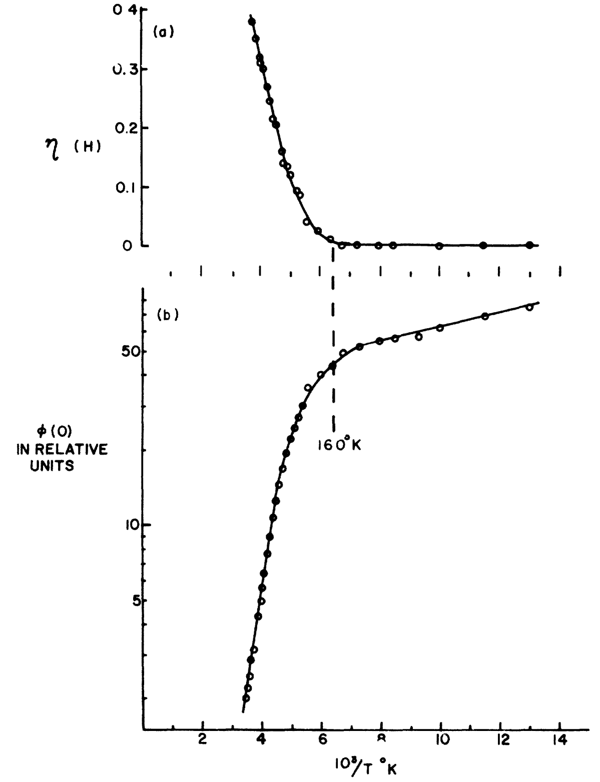

FIG. 1. (a) Temperature dependence of the fluorescence enhancement $\eta(H)$ of the fluorescence of crystalline tetracene in a magnetic field (4000 G). (b) Temperature dependence of the fluorescence $\varphi(0)$ in the absence of a magnetic field; activation energies calculated from the two slopes are 0.16 and 0.006 eV, respectively.

exhibits two constant values depending on the light intensity, being about 1.4 times greater in the intensity region $I \gtrsim 10^{15}$-10^{17} quanta cm^{-2} sec^{-1} (photon energy 3.4 eV) than for $I < 10^{15}$ quanta cm^{-2} sec^{-1}. A concomitant decrease in $\eta(H)$ was noted in the higher intensity region as compared with the value of $\eta(H)$ at $I < 10^{15}$ quanta cm^{-2} sec^{-1}. At 77°K no change in $\varphi(0)$ as a function of I was observed for intensities up to 10^{17} quanta cm^{-2} sec^{-1} and $\eta(H)$ is zero at this temperature (Fig. 1).

The existence of a Wannier-type charge-transfer exciton at 2.9 eV in tetracene has been proposed by one of us.[13] Since $\eta(H)$ is independent of photon energy in the wavelength range 2.6-4.6 eV, we conclude that these excitons do not play a significant role in the observed magnetic field effects.

The emission spectrum of tetracene crystals is broad and exhibits only one shoulder. The peak is at 2.24 eV with the high-energy edge at ~2.3 eV. There is evidence that the fluorescence-emitting state in crystalline tetracene is a dimer.[12]

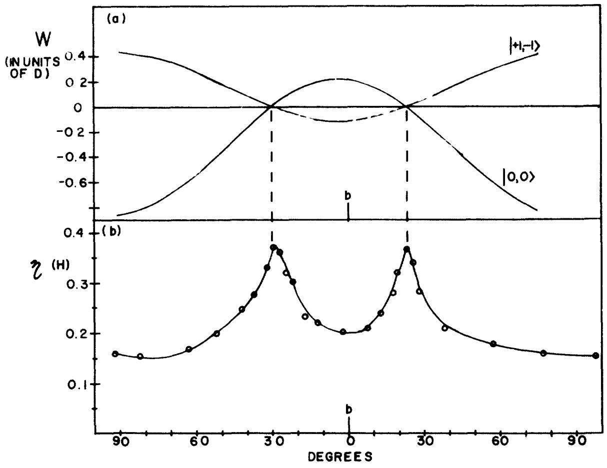

FIG. 2. The dependence of the magnetic field enhancement $\eta(H)$ as a function of orientation of the magnetic field vector (4000 G) in the ab plane (the b axis is at 0°). (a) Calculation of the triplet-pair-state energies $W_{0,0}$ and $W_{+1,-1}$ according to Eqs. (3) and (4). (b) Experimental determination of $\eta(H)$.

The fluorescence increases exponentially with decreasing temperature; in the temperature range 160-298°K, the activation energy is 0.16 eV. For temperatures <160°K, the activation energy is 0.006 eV. $\eta(H)$ decreases with decreasing temperature and becomes zero at $T \lesssim 160$°K. This is evident in Fig. 1. The correlation between the two curves in Fig. 1 is a strong indication that a singlet state at ~2.40 eV is strongly coupled to a magnetically sensitive radiationless decay channel which is thermally populated from the dimer state S. Our experiments support the proposal of Swenberg and Stacy[5] that there is a double-triplet-exciton energy state (T_1T_1) lying slightly above the singlet state S. If this is the case, the triplet-exciton energy in tetracene can be estimated at ~1.20 eV. The solution value is 1.26 eV,[14] which indicates that the crystal value obtained in this way is reasonable.

Our results can be explained completely on this basis and Merrifield's theory.[8-10] We assume that the (T_1T_1) state and excited vibrational states of T_1 (and perhaps T_2) are in resonance with the fluorescence-emitting dimer, where T_1 and T_2 are the first- and second-excited triplet states, respectively. Merrifield has analyzed the effect of H on the bimolecular triplet-exciton recombination to form a fluorescence-emitting singlet in anthracene:

$$T_1+T_1 \rightleftharpoons (T_1T_1) \rightleftharpoons S \rightarrow \text{fluorescence}. \tag{1}$$

In the high-field limit there are certain orientations of H with respect to the crystal axes of anthracene for which the fluorescence intensity resulting in (1) exhibits minima. These effects are explained in terms of level-crossing resonances.[9,10] These dips in the fluorescence intensity occur for orientations for which the $|0,0\rangle$ and $|-1,+1\rangle$ triplet pair states (T_1T_1) are degenerate. These are the only kinds of pair states which have singlet character. At the field orientations at which these degeneracies occur the coupling between the triplet and singlet manifold of states is reduced.[9] When the fluorescence is generated indirectly as in (1) via the (T_1T_1) pair states, the fluorescence intensity is decreased at the orientations at which these degeneracies occur, which is indeed observed in anthracene in the high-field limit.[8] In tetracene, the coupling of the singlet state to (T_1T_1) represents a radiationless decay channel and the fluorescence should be maximum for orientations at which the $|0,0\rangle$ and $|-1,+1\rangle$ degeneracies occur. These orientations were calculated by first-order perturbation theory as follows: The triplet-exciton energies of a single molecule were calculated from the Hamiltonian[15]

$$\mathcal{H}=g\beta\vec{H}\cdot\hat{S}+D(S_z^{\,2}-\tfrac{1}{3}S^2)+E(S_x^{\,2}-S_y^{\,2}). \tag{2}$$

In the high-field limit the zero-field splitting terms comprising D and E in (2) can be treated as a perturbation. The zero-order energies of the magnetic field quantized states $|0\rangle$ and $|\pm1\rangle$ are then $W=0$ and $\pm g\beta H$, respectively. When the perturbation is included, the zero-field splitting terms manifest themselves as an anisotropy of the energies with respect to the direction of H.[15] Crystalline tetracene is triclinic, space group $P\bar{1}$, with two molecules per unit cell. The single-molecule triplet energies therefore have to be averaged over the two sites and the energies of the pair states $|0,0\rangle$ and $|-1,+1\rangle$ are assumed to be equal to the sums of the two triplet-exciton energies.[7,10] The D and E parameters for the tetracene molecule have not been determined experimentally because of the short triplet lifetime. Calculated values of D and E, however, are available. These are 0.063[16] and -0.0046,[17] respectively. Since the calculated values of these parameters are usually somewhat higher[16] than the experimental values, we used a ratio of $D/E=-13$ in our calculations rather than the absolute values. The energies W are then expressed in units of D. The energies were calculated using the known orientations[18] of the two tetracene molecules in the crystal according to the equations

$$W_{0,0}=D\{\tfrac{2}{3}-(\cos^2\gamma_1+\cos^2\gamma_2)+(1/13)[(\cos^2\alpha_1+\cos^2\alpha_2)-(\cos^2\beta_1+\cos^2\beta_2)]\}, \tag{3}$$

$$W_{+1,1}=-\tfrac{1}{2}W_{0,0}, \tag{4}$$

where $\cos\alpha=\cos(L,H)$, $\cos\beta=\cos(M,H)$, and $\cos\gamma=\cos(N,H)$, where L, M, and N refer to the orientations of the long, short, and normal axes of the tetracene molecule.[18] The subscripts 1 and 2 in (3) refer to the two different sites in the crystal. The results are plotted in Fig. 2(a). The level crossings occur at 30° and 23.5° on either side of the b axis, in excellent agreement with the experimental results. It should be pointed out that the assumption made above regarding the ratio of D and E is not a critical one. For example, assuming a ratio of -0.1 for these values (the observed ratio for anthracene) displaces each resonance point by only 1° closer to the b axis.[19]

The excellent agreement between theory and experiment exhibited in Fig. 2 indicates that the theory proposed by Merrifield will have wide application in organic solids whenever bimolecular processes involving triplet states are involved. The Swenberg-Stacy hypothesis is in complete accord with the experimental facts, with one important qualification: The (T_1T_1) state does not necessarily split up only into two triplet excitons as was suggested.[5] This state also decays into one triplet exciton (plus lattice energy). Evidence for these processes can be obtained from a detailed analysis of the intensity, temperature, and H dependence of φ [see result (6)]; these data are consistent with the assumption that at high light intensities triplet-triplet fusion to form the (T_1T_1) state becomes applicable. As in anthracene, the formation of these states leads to an additional radiative decay channel, thus increasing the fluorescence efficiency. Since this radiative channel, however, is adversely affected by

H, the overall $\eta(H)$ decreases at high light intensities. At low temperatures these effects are inhibited because the rate of formation of triplet excitons via the (T_1T_1) state is low. These and other results will be described in detail in a forthcoming publication.

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QUANTUM MECHANICAL TUNNELING OF DISLOCATIONS*

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Measurements of the temperature dependence of the yield stress in tungsten crystals show a temperature-independent region, which is consistent with Gilman's theory of quantum mechanical tunneling of dislocations.

Dislocation motion[1] is normally considered to occur by thermally activated processes, with the barrier height depending upon the imposed shear stress σ, i.e., the strain rate $\dot{\epsilon}$ at which a crystal deforms varies as $\dot{\epsilon} \sim e^{-W(\sigma, \cdots)/kT}$, where W is the potential barrier, T the temperature at which the process occurs, and k is Boltzmann's constant. For most metals in the range of temperatures studied, plastic deformation is interpreted as a classical process. On the other hand, many bcc crystals exhibit a sharp temperature dependence of the critical resolved shear stress, and the work done by the external stress raises the dislocation up the potential barrier which opposes the motion of the dislocation. If the stress raises the dislocation high enough, then thermal activation over the barrier is not required; instead the dislocation can tunnel through the barrier. We wish to report on some observations of plastic deformation of tungsten crystals, which are consistent with the general requirements for dislocations tunneling through potential barriers.[2]

The observations were made on relatively pure crystals of tungsten (99.99+% pure), grown by standard electron-beam zone-refining techniques. Tensile specimens were obtained by chemical polishing of the as-grown crystals, so that no extraneous plastic deformation was introduced by such operation as grinding or spark erosion. This was essential, since such processes are known to introduce extraneous dislocations and thereby mask the true temperature dependence of the critical resolved shear stress.[3] Tensile deformation was carried out in a tensile machine,