CONSEQUENCES OF SYMMETRY BREAKING IN TRIPLET-EXCITON FUSION

R. P. Groff, R. E. Merrifield, P. Avakian, and Y. Tomkiewicz
Central Research Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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The magnetic field dependence of the fusion rate between *inequivalent* triplet excitons (free and trapped triplets in tetracene-doped anthracene crystals) is qualitatively different from that between equivalent excitons. Additional high-field level-crossing resonances and a new low-field dip appear in delayed fluorescence at room temperature.

We have investigated the magnetic field dependence of fusion between inequivalent triplet excitons (free and trapped triplets in a tetracene-doped anthracene crystal) and have found that both high-field anisotropy and field dependence are qualitatively different from that for equivalent triplets.[1,2] Our results provide a new tool for investigating triplet-exciton traps and free-trapped triplet-fusion phenomena.[3]

For fusion of a pair of free triplet excitons in a pure anthracene crystal the nine eigenstates of the pair spin Hamiltonian can be divided into a group of six states which are even under the interchange of the two excitons, and a group of three which are odd under this operation. This division into odd and even states is solely a consequence of symmetry and is independent of magnetic field.[4] The even pair states are (field-dependent) singlet-quintet mixtures, while the odd states are pure triplets (field independent).[4] The introduction of a small concentration of exciton-trapping guest molecules (tetracene) leads to a new process (heterofusion, i.e., fusion between a free triplet exciton and one trapped at the impurity), which lacks the above symmetry. As a consequence all nine pair spin states are (field dependent) singlet-triplet-quintet mixtures, and hence a given pair state can fuse via the singlet or triplet channel. Thus we can represent the fusion process as follows:

$$\begin{aligned} &T+T \to (TT)_l \quad (\text{rate } k_1), \\ &(TT)_l \to T+T \quad (\text{rate } k_{-1}), \\ &\qquad \to S^* \quad (\text{rate } k_2|S_l|^2, \\ &\qquad \to T \quad (\text{rate } k_3|\vec{T}_l|^2), \end{aligned} \tag{1}$$

where T and S^* represent triplet and singlet excitons, respectively, and $(TT)_l$ represents an interacting triplet pair in the lth spin state. The rate constants k_1, k_{-1}, k_2, and k_3 correspond to collision, scattering, and fusion via singlet and triplet channels, respectively, and $|S_l|$ and $|\vec{T}_l|$ are the singlet and triplet amplitudes of the lth pair state. By following a procedure similar to that employed in Ref. 2, we find that the rate of production of excited singlets via heterofusion is proportional to

$$\sum_l \frac{S_l^2}{k_{-1}+k_2|S_l|^2+k_3|\vec{T}_l|^2}. \tag{2}$$

By explicit calculation from the zero-field wave functions, the following relation can be found:

$$|\vec{T}_l|^2 = \tfrac{1}{2} - \tfrac{3}{2}|S_l|^2. \tag{3}$$

Thus, near zero field the rate of heterofusion is proportional to the quantity

$$\sum_l \frac{S_l^2}{1+kS_l^2}, \tag{4}$$

with

$$k = \frac{k_2 - \frac{3}{2}k_3}{k_{-1}+\frac{1}{2}k_3}. \tag{5}$$

Expression (4) has the same form as that found for homofusion,[1] except that k can now be negative. For negative k the theory[1] predicts an initial decrease at low fields as contrasted to the increase found for positive k. Another consequence of the broken symmetry is the appearance of multiple sets of level-crossing resonances[1,2] because of the possibility of exciton trapping at impurities located at different sites of the unit cell.[5] We have demonstrated the existence of both phenomena experimentally.

In melt-grown crystals of anthracene with a small concentration of tetracene (down to 0.01 ppm),[6] the existence of fusion between free and trapped triplet excitons at room temperature was demonstrated by spectroscopic observations and time-dependent luminescence measurements. In addition to the usual (blue) anthracene emission centered at 4450 Å, the delayed fluorescence emission (red-light excitation) contained a (green) tetracene component with peaks at 4960 and 5310 Å. Upon excitation of the crystal with pulsed red light (10-μsec duration), the maximum in the intensity of the green delayed emission from tetracene occurred at a later time than that for

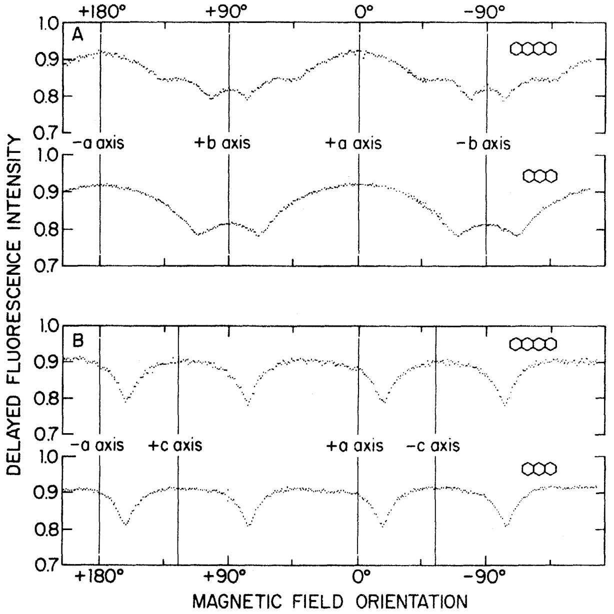

FIG. 1. Dependence of anthracene and tetracene components of delayed fluorescence emission on the orientation of a 4-kOe magnetic field in the *ab* (top) and *ac* (bottom) crystallographic planes. Time averaging was used for signal-to-noise enhancement (resolution 1 deg/channel). (The tetracene concentration is ~0.01 ppm.)

the blue delayed emission from the host crystal due to the time required for diffusion and trapping of triplet excitons. From these measurements the lifetimes of the free and trapped triplets in the 0.01-ppm doped crystal were found to be 0.9 and 0.4 msec, respectively. Furthermore, the ratio of green to blue components in the delayed fluorescence emission spectrum (with low triplet concentrations) was two orders of magnitude greater than that in the prompt fluorescence emission (uv excitation).[7] This reflects the fact that the diffusion length for triplet excitons[8] is much greater than that for singlet excitons so that very few singlets become trapped.

We investigated the dependence of the blue and green delayed emission intensities on magnetic field (4 kOe) orientation, as well as on the magnitude of the field for several different fixed field orientations at room temperature. The blue (host crystal) emission exhibited four level-crossing resonances identical to those observed for homofusion in pure anthracene[1,2] in both the *ab* and *ac* planes (see Fig. 1). However, the green (tetracene impurity) emission showed eight resonances in the *ab* plane and four in the *ac* plane. The additional resonances in the *ab* plane arise because annihilations of a free exciton with an exciton trapped at the two different sites of the unit cell can now be distinguished. The field dependence of the blue anthracene emission (Fig. 2) was identical to that for a pure crystal.[1,2] The field dependence of the green emission intensity for certain field orientations showed an initial dip (of about 2.5 % at 250 Oe) followed by a dependence similar to that of the blue emission at higher fields (see Fig. 2).

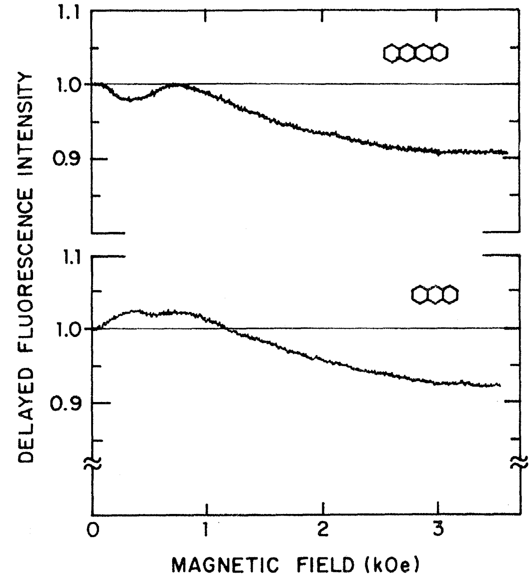

FIG. 2. Field dependence of the green, tetracene (top) and blue, anthracene (bottom) emission in an anthracene crystal doped with ~0.01 ppm tetracene. The field was oriented along the *a* axis.

The magnetic field experiments described above provide a new tool for investigating the fusion between inequivalent triplet excitons (e.g, free and trapped triplets). For example, from comparison of the observed positions of the level-crossing resonances with those calculated using the experimental value for the ratio of the zero-field splitting parameters,[9] we conclude that tetracene molecules in an anthracene host enter the lattice approximately substitutionally. This conclusion is consistent with polarized optical absorption measurements of tetracene-doped anthracene crystals.[10,11]

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[7] From the above measured values of the lifetimes and ratio of green to blue emission (0.6) in delayed fluorescence we conclude that the value of the radiative heterofusion rate constant is approximately $\frac{2}{3}$ that for homofusion. G. C. Smith [Phys. Rev. 166, 839 (1968)] has suggested that the value of the heterofusion rate constant could be as much as 15 times that for homofusion.

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COUPLED ORDER-DISORDER PHONON SYSTEM WITH DAMPING: KH_2PO_4

B. D. Silverman
IBM Research Laboratory, San Jose, California 95114

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The frequency-dependent susceptibility has been obtained for the pseudospin-phonon system previously considered by Kobayashi. Various limiting cases are discussed and connection is made with the dielectric properties of KH_2PO_4.

Neutron-diffraction measurements[1] indicate that in the ferroelectric phase of KH_2PO_4 the protons account for only a small fraction of the spontaneous polarization. The major contribution to the polarization results from phosphate-group and potassium-atom displacements. Consequently, there have been several investigations[2] concerning the implications of proton-lattice coupling with respect to the dielectric properties of this crystal. Kobayashi proposed coupling the pseudospin motion of the protons, as described by de Gennes,[3] to a transverse-optic phonon of the lattice. The purpose of the present work is to extend this treatment of the coupled system to consideration of the frequency-dependent susceptibility of KH_2PO_4 with the inclusion of damping.

The Hamiltonian is written

$$H=\tfrac{1}{2}(P^2+\omega_0{}^2Q^2)-J\langle S_x\rangle S_x-fS_z -aQS_x-\mu E(e^{-i\omega t}+e^{-i\omega t})Q. \tag{1}$$

The first term is the contribution from a transverse-optic phonon of frequency ω_0. The next two terms describe the uncoupled proton system. The Ising term represents the energy associated with proton ordering. The spin one-half operators are used to designate the proton distribution between the two troughs. The second term, the "tunneling term," allows the proton to tunnel between the two troughs and therefore splits the level degeneracy. The coupling energy involving the coupling constant a, is bilinear in the spin and phonon coordinates. As the lattice displaces, the protons experience an effective field which preferentially orders them in one of the two troughs. Conversely, any preferential proton ordering or nonvanishing expectation value of S_x drives the phonon from equilibrium and a resultant c-axis polarization develops. The last term describes the coupling of a sinusoidal electric field polarized along the c axis of the crystal. It is assumed that the electric field couples only to the phonon since as stated previously the major contribution to the polarization results from the phonon displacements.

The linearized equations of motion are

$$\begin{aligned}
&\dot{S}_x=\omega_f S_y-(S_x-\langle S_x\rangle_t)/T_1,\\
&\dot{S}_y=(2a/\hbar)S_z{}^0Q+(\Omega S_z{}^0-\omega_f)S_x-S_y/T_1;\quad \mathring{S}_z=0,\\
&\ddot{Q}+\gamma\dot{Q}+\omega_0{}^2Q=aS_x+\mu E(e^{i\omega t}+e^{-i\omega t}),\\
&\Omega=2J/\hbar;\quad \omega_f=2f/\hbar.
\end{aligned}\tag{2}$$

$S_z{}^0$ is the tunneling-field-induced equilibrium value of the z component of spin. This spin component is stationary. Ω and ω_f are the exchange and tunneling frequencies, respectively. The spin components are damped by the addition of Bloch-type damping terms to the spin equations of motion. It is assumed that the spins relax to an equilibrium value determined by the instantaneous field.[4] T_1 is the spin relaxation time. The phonon is damped by the usual viscous-type