MAGNETIC FIELD EFFECT ON TRIPLET EXCITON QUENCHING IN ORGANIC CRYSTALS

V. Ern and R. E. Merrifield
Central Research Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

(Received 17 July 1968)

The rate of quenching of triplet excitons by paramagnetic impurities in anthracene crystals at room temperature is found to be magnetic-field dependent. A theory of the effect is presented.

We wish to report discovery of a magnetic field dependence of the rate of quenching of triplet excitons by free-radical impurities in organic crystals at room temperature. The existence of a field dependence of the triplet-doublet interaction was suggested by the theory developed by one of us[1] to account for the field dependence of triplet-triplet annihilation.[2] The experimental confirmation of this prediction was sought through measurements of triplet exciton lifetimes in x-irradiated anthracene crystals. It is known[3] that room-temperature triplet exciton lifetime in anthracene is drastically shortened by low dosages of high-energy radiation. Although the exact nature of the radiation damage is not known, it was expected that mostly paramagnetic quenchers (i.e., free radicals) are introduced by irradiation and that a magnetic field dependence of triplet quenching could be observed in this system. We have indeed observed such an effect in x-irradiated anthracene crystals.

Anthracene crystals, about 3 mm thick, were either cleaved along the *ab* plane, or *ac*-plane cut and polished from melt-grown ingots of highly purified anthracene.[4] The samples were irradiated with x rays from a lead target placed in the beam of a General Electric 2-MeV Electron Beam unit. The irradiation rate was 6×10^3 R min^{-1}. Dosages ranged from 1 to 4×10^3 R. The decrease of triplet exciton lifetime upon irradiation was consistent with the results of Weisz et al.[3] for similar doses of gamma radiation. In a typical case, a triplet exciton lifetime before irradiation (τ) of 22.0 msec decreased to a value (τ') of 1.5 msec after a dose of 4×10^3 R.

Magnetic field dependence of the triplet exciton lifetime was measured from the time dependence of delayed fluorescence resulting from the triplet-triplet annihilation for several field strengths and orientations relative to the crystal axes. All measurements were done at room temperature. The beam of a He-Ne laser (6328 Å, Spectra Physics Model 125), focused on a chopper blade and recollimated, fell onto either the *ab* or *ac* plane of the sample. Magnetic fields of $(0.3, 0.6, 0.9, 1.2, \text{ and } 2.0)\times10^3$ G were applied in the plane of the sample by adjusting its position with respect to the two pole pieces of a permanent magnet. The field was measured to be uniform within ±20 G over the excited volume of the crystal (ca. 0.08 cm^3). For each field strength crystals were rotated around the beam axis so as to apply the field along preselected crystallographic directions. Laser beam intensity was controlled with a pair of Glan prisms to a sufficiently low level of excitation to assure a negligible contribution of triplet-triplet annihilation to the measured triplet lifetime. The blue delayed fluorescence from the crystal was led by a 1-m fiber-optics light guide to a photomultiplier (RCA 6199 with Corning filters C.S. 5-57, 5-56, and 4-72), and simultaneously the exciting-light wave form was observed by another photomultiplier (RCA 6199 with C.S. 2-59 and 1-69 filters). The outputs of the photomultipliers were fed via identical operational amplifiers to the two channels of a fixed-bandwidth (5 cps) tracking filter (Ad-Yu Electronics, Type 1034) driven by a synchronous converter (Ad-Yu Electronics, Type 1036) tuned to the frequency of the first harmonic of the exciting-light wave form. The outputs of the tracking filter, phase coherent with the first harmonics of the input wave forms, were fed to a digital phase computer (Ad-Yu Electronics, Type 524A3), and the phase lag of delayed fluorescence with respect to the exciting light was measured. For square-wave excitation the phase shift in the first harmonic is $\varphi = \arctan(\omega\tau)$, where ω is the angular chopping frequency and τ the triplet exciton lifetime. Maximum sensitivity for changes in τ is obtained when $\omega\tau\approx1$. For the range of lifetimes studied here, this required chopping frequencies between 25 and 90 cps. The standard deviation in the phase-angle measurements was estimated to be less than 0.2°, and therefore a change of ±1% in triplet lifetime could be detected by this method. In some runs the delayed fluorescence decay curve was also accumulated in a computer of average transients (CAT 400, Technical Measurement Corporation).

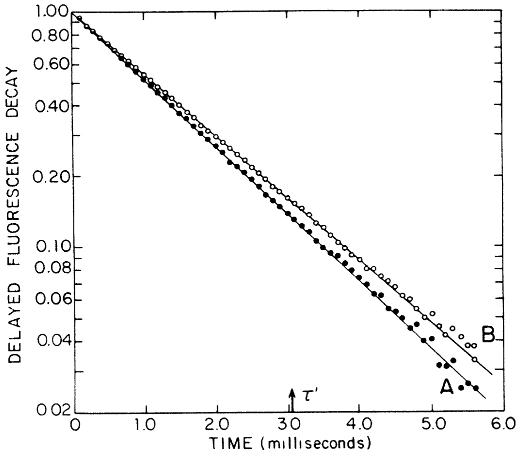

FIG. 1. Comparison of decays of delayed fluorescence of x-irradiated (2×10^3 R) anthracene crystal: *A*, no magnetic field; *B*, $H=2\times10^3$ G applied parallel to the crystal *b* axis. CAT 400 resolution: 1×10^{-4} sec per channel. Both decays normalized to same CAT channel.

The magnetic field dependence of steady-state delayed fluorescence intensity, before and after irradiation, was recorded using an experimental setup similar to that described by Johnson et al.[2]

The increase of triplet lifetime in irradiated anthracene upon application of a field of 2×10^3 G is illustrated in Fig. 1.[5] Figure 2 shows typical magnetic field dependence of lifetime for several field orientations with respect to the crystal axes. The directly measured points are shown together with the dependence as deduced from the ratio at each field strength of steady-state intensities before and after irradiation.[6] Thus, within experimental error, the only effect of irradiation on the magnetic field dependence of delayed fluorescence intensity is the introduction of a field dependence of the triplet lifetime.

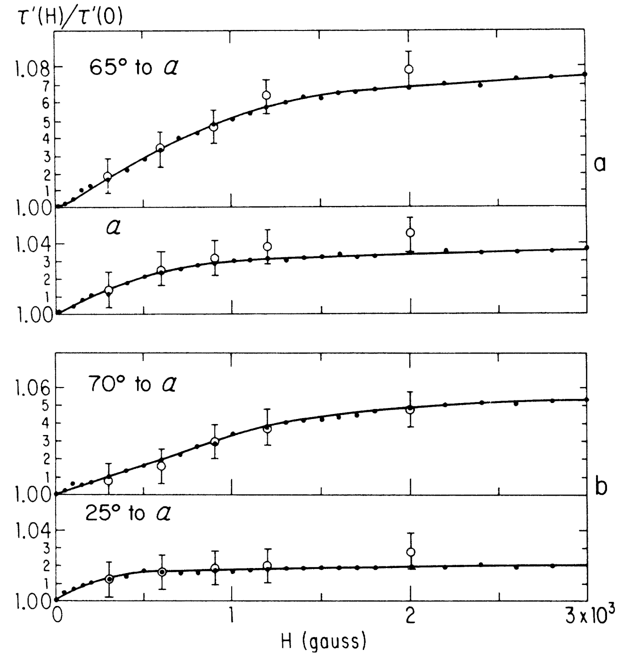

FIG. 2. Typical magnetic field dependence of the normalized (to zero field) triplet exciton lifetime, $\tau'(H)/\tau'(0)$, in x-irradiated anthracene. (a) *ab*-plane cleaved crystal, dose 4×10^3 R, $\tau'(0)=1.55\times10^{-3}$ sec. *H* in *ab* plane in directions at 65° (resonance) and 0° with respect to the *a* axis. (b) *ac*-plane cut crystal, dose 1×10^3 R, $\tau'(0)=4.95\times10^{-3}$ sec. *H* in *ac* plane along 70° (resonance) and 25° to *a* directions. Open circles: direct measurements. Curves drawn from steady-state fluorescence intensity ratios.

The foregoing experimental results can be qualitatively understood on the basis of the theory[1] of the magnetic field dependence of triplet-triplet annihilation, modified to take account of the different set of spin states involved in the present case. For an interacting triplet exciton ($S=1$) and free radical ($S=\frac{1}{2}$) there are six spin states which will in general be doublet-quartet mixtures. There are two possible outcomes of an exciton-radical collision: scattering, for which there are no spin selection rules; and quenching, whose final state consists of a singlet (presumably an excited vibrational level of the ground state) and a doublet. There are spin selection rules for the quenching process since the final state is a pure doublet while the initial state is a doublet-quartet mixture. The transition rate for quenching from the lth initial state can be written $k_l=k(|D_l^+|^2+|D_l^-|^2)$, where $D_l^{\pm}=\langle\psi_l \times|{}^2\psi_{\pm\frac{1}{2}}\rangle$ is the amplitude of the $M_S=\pm\frac{1}{2}$ doublet component of the initial state. If k' denotes the transition rate for the scattering process, the probability of quenching from the lth initial state is $k_l/(k'+k_l)$ and the total exciton quenching rate due to the presence of paramagnetic impurities becomes

$$Q=\tfrac{1}{6}A\sum_{l=1}^{6}k_l/(k'+k_l), \tag{1}$$

where A is the total rate of exciton-radical collisions.

The doublet amplitudes are constrained by the sum rule $\sum_l|D_l^{\pm}|^2=1$; when these two units of doublet character are shared equally by all six states, i.e., when $|D_l^+|^2+|D_l^-|^2=\frac{1}{3}$ for all l, Eq. (1) attains its maximum value. Concentration of the doublet character in fewer states reduces Q, the minimum value occurring when the initial states comprise an exact doublet and quartet.

The spin Hamiltonian for the triplet exciton has the form[7]

$$\mathcal{H} = g\beta\vec{H}\cdot\vec{S}+DS_z^{\,2}+E(S_x^{\,2}-S_y^{\,2}), \tag{2}$$

where the first term is the Zeeman interaction and the remaining terms describe the zero-field splitting. At zero field the eigenfunctions of (2) are[8] $|x\rangle$, $|y\rangle$, and $|z\rangle$ with the property that, e.g., $S_x|x\rangle=0$, $S_y|x\rangle=i|z\rangle$, and $S_z|x\rangle=-i|y\rangle$. Combining these with the $|\pm\frac{1}{2}\rangle$ states of the radical, assumed to be adequately described by an isotropic g factor, yields the zero-field states $|\alpha,\pm\frac{1}{2}\rangle$ $(\alpha=x,y,z)$. In terms of these states the doublet components are $|^2\psi_{\pm1/2}\rangle=3^{-1/2}(\pm|x,\pm\frac{1}{2}\rangle+i|y,\pm\frac{1}{2}\rangle+|z,\pm\frac{1}{2}\rangle)$, so that the condition $|D_l^{\,+}|^2+|D_l^{\,-}|^2=\frac{1}{3}$ is satisfied for all six zero-field states and hence the quenching rate is expected to be a maximum at zero field, as found experimentally.

In the high-field limit, i.e., when the Zeeman energy is large compared with the zero-field splitting, all spin states are quantized along the external field and in terms of these states the doublet components are

$$|^2\psi_{-1/2}\rangle=3^{-1/2}(|0,\pm\tfrac{1}{2}\rangle-2^{1/2}|\pm1,\mp\tfrac{1}{2}\rangle). \tag{3}$$

Thus there are at most four states with doublet character and hence a smaller Q than at zero field. From (2) one finds for the difference in energy of the $|0,\pm\frac{1}{2}\rangle$ and $|\pm1,\mp\frac{1}{2}\rangle$ states in the high-field limit

$$E(0,\pm\tfrac{1}{2})-E(\pm1,\mp\tfrac{1}{2})=\tfrac{1}{2}D(1-3\cos^2\gamma)$$
$$+\tfrac{3}{2}E(\cos^2\beta-\cos^2\alpha), \tag{4}$$

where α, β, and γ are the angles made by $\vec{H}$ with the x, y, and z axes, respectively, of the zero-field splitting tensor. In general (4) will be nonzero and the states $|0,\pm\frac{1}{2}\rangle$ and $|\pm1,\mp\frac{1}{2}\rangle$ individually will be eigenstates. At the special field orientations at which (4) vanishes[9] the pure doublet combination (3) will become one of the eigenstates, and hence the quenching rate will be a minimum. Thus one expects to observe high-field level-crossing resonances for quenching similar to those found for triplet-triplet annihilation.[2]

The experimental results confirm the principal qualitative predictions of the theory, namely, that the maximum quenching occurs at zero field, that the field dependence saturates when the Zeeman splitting is large compared with the zero-field splitting, and that the high-field quenching rate is anisotropic with minima for field orientations at which the $|0,\pm\frac{1}{2}\rangle$ and $|\pm1,\mp\frac{1}{2}\rangle$ levels cross. Quantitative comparison of theory and experiment will require diagonalization of (2) and evaluation of Eq. (1) under the appropriate conditions as well as knowledge of the actual number of paramagnetic impurities present in the irradiated crystals.

We wish to thank R. C. Johnson for assisting with the measurements of field dependence of delayed fluorescence, G. J. Sloan for supplying the crystals, and A. MacLachlan for providing irradiation facilities.

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[1] R. E. Merrifield, to be published.

[2] R. C. Johnson, R. E. Merrifield, P. Avakian, and R. B. Flippen, Phys. Rev. Letters 19, 285 (1967). A quite different behavior was recently observed [G. C. Smith and R. C. Hughes, Phys. Rev. Letters 20, 1358 (1968)] at low temperatures when most of the excitons become trapped.

[3] S. Z. Weisz, P. Richardson, A. Cobas, and R. C. Jarnagin, Mol. Crystals 3, 168 (1967).

[4] G. J. Sloan, Mol. Crystals 1, 161 (1966).

[5] A similar effect was found by observing directly the decay of the weak phosphorescence (decay time equal to triplet exciton lifetime) emitted by the crystal under 6328-Å excitation.

[6] At low intensities of excitation, $F\propto\gamma f\alpha^2\tau^2$, where F is the steady-state delayed fluorescence intensity, γ the triplet-triplet annihilation rate constant leading to fluorescence, f the singlet fluorescence quantum efficiency, α the singlet-triplet absorption coefficient, and τ the triplet lifetime. It has been shown (Ref. 2) that $F(H)/F(0)=\gamma(H)/\gamma(0)$ for the nonirradiated crystal. Evidence is given in Ref. 3 that neither γ, f, nor α is affected by a 10^2- to 10^4-R dose of irradiation. Thus one expects for the irradiated crystal a magnetic field dependence $F'(H)/F'(0)=\gamma(H)\tau'^2(H)/\gamma(0)\tau'^2(0)$. $\tau'(H)/\tau'(0)$ will be given then by $[F'(H)F(0)/F(H)F'(0)]^{1/2}$, where the primed quantities refer to the irradiated crystal.

[7] H. Sternlicht and H. M. McConnell, J. Chem. Phys. 35, 1793 (1961).

[8] J. H. Van der Waals and M. S. de Groot, Mol. Phys. 2, 333 (1959).

[9] For the anthracene crystal these orientations are calculated to be at −19° ± 2° and +74° ± 2° with respect to the a axis when H lies in the ac plane (Ref. 2) and at ±69 ± 2° with respect to the same axis when H is in the ab plane. The zero-field splitting parameters given by D. Haarer, D. Schmid, and H. C. Wolf [Phys. Status Solidi 23, 633 (1967)] were used to calculate these level-crossing angles.