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Magnetic Hyperfine Modulation of Dye-Sensitized Delayed Fluorescence in an Organic Crystal

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(Received 1 June 1972)

Magnetic fields were found to decrease rhodamine-B-sensitized delayed fluorescence in anthracene by up to 60% at 10 mTorr. An inverse but smaller effect was found on sensitized photoconductivity. The observations are explained in terms of a magnetic-field-dependent recombination of surface electrons and injected holes, with the field scale being fixed by hyperfine interactions.

We report a new effect of magnetic fields on delayed fluorescence in organic crystals at room temperature. Magnetic modulation of the intensity of delayed fluorescence from an anthracene crystal by as much as 75% results when triplet excitons are injected into the crystal from an adsorbed layer of the sensitizing dye, rhodamine B. In its response to a magnetic field, dye-sensitized delayed fluorescence differs from that produced by direct optical excitation of the crystal in that appreciable modulation is produced by much smaller fields, e.g., a field of 10 mTorr (100 Oe) changes the output intensity by 60% compared with a 2% change for an unsensitized crystal. In view of the field strength over which this modulation occurs, we call it hyperfine modulation (HFM). A similar field dependence (but smaller in amplitude and of opposite sense) has also been observed on rhodamine-B-sensitized photoconductivity. We believe these phenomena result from field-dependent surface recombination of electrons and holes.

Anthracene crystals were sensitized with rhodamine B following the procedure of Nickel, Staerk, and Weller,[1] and the sample was placed between the pole pieces of an electromagnet.

The solid line of Fig. 1 shows the magnetic field dependence of rhodamine-B-sensitized delayed fluorescence (excited at 570 nm) in anthracene. The magnetic field was applied parallel to the a axis with the exciting light incident normal to the ab plane. As the field is increased, the sensitized emission increases at first, reaching a maximum ca. 1% above its zero-field value at 0.3–0.7 mTorr. Further field increases result in a monotonic decay toward saturation at 20–30 mTorr. The overall amplitude of the effect depends on sample history and preparation. The dashed line of Fig. 1 shows the field dependence of delayed fluorescence from direct excitation of triplet excitons (680 nm light) in the same crystal.[2, 3] This field dependence has been adequately

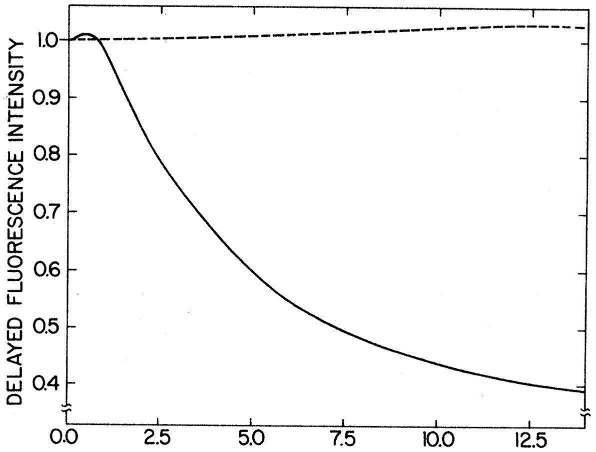

FIG. 1. Observed magnetic field modulation of normalized delayed fluorescence intensity; solid line, 570-nm excitation; dashed line, 680-nm excitation.

TABLE I. Steps in dye sensitization. In the notation ${}^{m}X_{s}$, where X = A (anthracene) or D (dye), m is the multiplicity and $s = 0$ or 1 for a ground or excited state, respectively.

(1) Direct triplet injection	
${}^{1}\mathrm{D}_{1}{}^{+} \rightarrow {}^{3}\mathrm{D}_{1}{}^{+}$	(1a)
${}^{3}\mathrm{D}_{1}{}^{+} + {}^{1}\mathrm{A}_{0} \rightarrow {}^{1}\mathrm{D}_{0}{}^{+} + {}^{3}\mathrm{A}_{1}$	(1b)
(2) Charge injection and recombination	
${}^{1}\mathrm{D}_{1}{}^{+} + {}^{1}\mathrm{A}_{0} \rightarrow {}^{2}\mathrm{D}_{0} + {}^{2}\mathrm{A}_{0}{}^{+}$	(2a)
${}^{2}\mathrm{D}_{0} + {}^{2}\mathrm{A}_{0}{}^{+} \rightarrow {}^{1}\mathrm{D}_{0}{}^{+} + {}^{3}\mathrm{A}_{1}$	(2b)
$\rightarrow {}^{1}\mathrm{D}_{0}{}^{+} + {}^{1}\mathrm{A}_{0}$	(2c)
$\rightarrow {}^{1}\mathrm{D}_{0}{}^{+} + {}^{1}\mathrm{A}_{1}$	(2d)
(3) Triplet quenching via injected holes	
${}^{3}\mathrm{A}_{1} \xrightarrow{{}^{2}\mathrm{A}_{0}{}^{+}} {}^{1}\mathrm{A}_{0}$	(3)
(4) Delayed fluorescence	
${}^{3}\mathrm{A}_{1} + {}^{3}\mathrm{A}_{1} \rightarrow {}^{1}\mathrm{A}_{1} + {}^{1}\mathrm{A}_{0}$	(4a)
${}^{1}\mathrm{A}_{1} \rightarrow {}^{1}\mathrm{A}_{0} + h\nu$	(4b)

explained in terms of field-induced changes in the triplet-triplet fusion rate constant.[3,4]

Rhodamine-B-photosensitized hole currents in anthracene[5] also have a magnetic field dependence inverse to that of sensitized delayed fluorescence but ca. 6× smaller. In most cases the photocurrent i^{+} was proportional to both applied photon flux I and electric field E. Typical values for rhodamine-B-sensitized photocurrents were $i^{+} \sim 6\times10^{-3}$ A m^{-2} at $E = 3\times10^{5}$ V m^{-1}, and $I \sim 50$ W m^{-2}.

Processes involved in dye-sensitized delayed fluorescence following the excitation of the dye to its lowest excited singlet state are summarized in Table I.

Processes (1) are expected to be magnetic field independent.[6] Processes (3) and (4) are known to be field dependent,[3,4,7,8] but the magnitude of the modulation and the field scale are not characteristic of HFM. HFM appears to arise from changes in the triplet population resulting from processes (2) which can influence both generation (2b) and destruction [(2a) with (3)] rates of triplet excitons. A direct influence on the singlet population (2d), i.e., on prompt rather than delayed fluorescence, has been ruled out experimentally.[9]

The underlying cause of the magnetic field dependence of processes (2) is that their relative rates depend on the total spin state of the interacting electron-hole pair. Since singlet and triplet states have opposite parity with respect to interchange of the electron and hole, only an unsymmetrical spin Hamiltonian can lead to transitions between them. We believe that the essential spin Hamiltonian for the present case consists of the unsymmetrical hyperfine interaction of the electron and of the hole together with the symmetrical (assuming nearly identical g factors) Zeeman term. Thus at low fields, such that hyperfine interactions are dominant, singlet-triplet transitions can occur, while at large fields the symmetry of the Zeeman term prohibits such transitions except for the $m = 0$ state.

We have been unable to account for the observed magnitude of HFM except on the basis of triplet production via geminate surface recombination as the dominant field-dependent process. Thus, we believe that an electron-hole pair is created in a singlet state and that it stays together (by virtue of the Coulomb interaction) long enough for significant spin motion to occur, leading to a triplet state.

The following model incorporates what we think are the key physical features of HFM in the mathematically simplest form. Suppose that the spin Hamiltonian of the electron and hole has the form

$$\mathcal{H} = g\mu_{B}\vec{\mathrm{H}}\cdot(\vec{\mathrm{S}}_{1} + \vec{\mathrm{S}}_{2}) + a\vec{\mathrm{S}}_{1}\cdot\vec{\mathrm{I}},$$

where $\vec{\mathrm{S}}_{1}$, and $\vec{\mathrm{S}}_{2}$ are the respective spin operators for the electron and hole, $\vec{\mathrm{I}}$ is the spin operator for a single proton interacting with particle l via a contact hyperfine interaction of strength a. Suppose furthermore that electron-hole pairs are created in the singlet state at a rate k_{1} and dissociate at a rate k_{-1} independent of spin. The steady-state equation of motion of the spin density matrix ρ has the form

$$k_{1}P = k_{-1}\rho + i\hbar[\mathcal{H}, \rho],$$

where $P \equiv \frac{1}{4} - \vec{\mathrm{S}}_{1}\cdot\vec{\mathrm{S}}_{2}$ is the singlet projection operator. This equation is easily solved for ρ by diagonalizing $\mathcal{H}$. The quantity $\mathrm{Tr}[(1-P)\rho]$ represents the triplet pair population and will be proportional to the rate of generation of triplet excitons, provided the rate of depletion of electron-hole pairs due to such generation is small compared to k_{-1}. It will also be proportional to the diminution of the photocurrent, caused by recombination. The triplet pair population has been plotted in Fig. 2, for a value of $\hbar k_{-1}/a$ chosen to bring out similarities with the experimental observations.

A realistic theory of HFM is rather complex, as it must include hyperfine interactions of the hole and of the electron with all the important protons of the anthracene and dye molecules. Preliminary calculations show that inclusion of additional protons can enhance the amplitude of

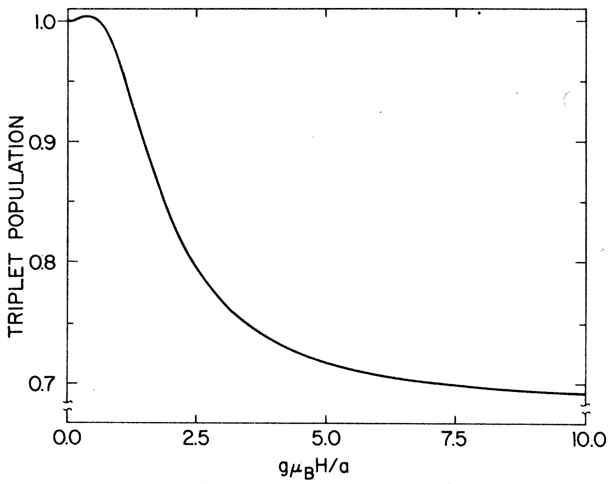

FIG. 2. Calculated magnetic field modulation of the normalized population of electron-hole pairs in the triplet state, from model in text with $\hbar k_{-1}/a=0.9$.

HFM to values comparable to those observed, even though the model, Fig. 2, gives a smaller amplitude. The field scale of the observed HFM can be roughly accounted for in terms of the known contact hyperfine interactions of the anthracene cation[11] together with an estimate for the hyperfine interactions of the dye radical. It appears that a quantitative fit to experiment will further require the inclusion of the electron-hole dipolar interaction as well as the finite rate of triplet depletion due to exciton production.[12] Finally, comparison with experiment necessitates separating out the contribution to delayed fluorescence of directly injected triplet excitons [process (1b) of Table I].

Although we have not at this point presented a quantitative theory of HFM, the success of the simple model in accounting for the essential features of HFM indicates that the underlying physical phenomena have been identified.

We are grateful to G. J. Sloan for the crystals and to B. M. Monroe and D. W. Wiley for helpful discussions.

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[10] We do not believe significant HFM can occur for bulk recombination, even geminate. The motion of the charge transfer state will average the hyperfine interactions towards zero. In addition, since electron and hole hyperfine interactions in anthracene are nearly the same [A. Carrington and A. D. McLachlan, *Introduction to Magnetic Resonance with Applications to Chemistry and Chemical Physics* (Harper and Row, New York, 1967), p. 90], the rapid exchange of electrons and holes between nearest neighbors will tend to remove the asymmetry necessary for transitions between singlet and triplet states. Thus, for example, no evidence for HFM is found in prompt or delayed electroluminescence in anthracene [Cf. H. P. Schwob and D. F. Williams, Chem. Phys. Lett. 13, 581 (1972)].

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[12] A finite triplet depletion rate will also lead to HFM for nongeminate recombination, although much smaller than for geminate. In the model presented here nongeminate production, i.e., a source term proportional to a unit matrix in the equation for ρ, gives no HFM.