INFLUENCE OF MAGNETIC FIELDS ON LUMINESCENCE INVOLVING TRIPLET EXCITONS

P. AVAKIAN

Central Research Department, E. I. du Pont de Nemours and Company,
Wilmington, Delaware 19898, USA

ABSTRACT

Several processes involving triplet excitons lead to magnetic-field sensitive luminescence in organic crystals such as anthracene and related compounds. Small magnetic fields (Zeeman energies ≪ thermal energies) at room temperature give rise to observable effects. The first class of phenomena is subject to fine structure modulation (FSM) and requires fields of 100s to 1000s of oersteds. This class includes triplet–triplet fusion leading to higher energy singlets which emit delayed fluorescence and singlet exciton fission (or inverse of triplet–triplet fusion) leading to a decrease in prompt fluorescence yield. The second class of phenomena is subject to hyperfine modulation (HFM) and fields of only 10s of oersteds are required. The key example is dye-sensitized delayed fluorescence involving an intermediate charge-transfer state. All the above phenomena involve non-equilibrium processes subject to spin restrictions. The fine structure interaction in FSM and the hyperfine interaction in HFM lead to spin 'precessional' motions which circumvent these restrictions. The external field competes with the internal magnetic interactions in affecting these spin motions.

INTRODUCTION

The purpose of my lecture is to review and discuss the effect of magnetic fields on luminescence involving triplet excitons in organic crystals. I will focus on work at our laboratory (see Acknowledgements) and will talk from an experimentalist's point of view. This means I will bring out the important physical features and qualitative theoretical ideas, but not calculational details.

I want to emphasize that all the effects which I will describe occur at modest fields and in the neighbourhood of room temperature. By modest fields I mean fields where the Zeeman energies of the relevant quasi-particles such as triplet excitons are much smaller than thermal energies or kT, such that spin polarization is negligible†. The first part of the talk will cover fine structure modulation (FSM)—involving fields of hundreds to thousands of oersteds. The second part will deal with hyperfine modulation (HFM)—involving fields of only tens of oersteds.

---

† The Zeeman energy of a triplet exciton in anthracene in a field of $10\,kOe$ is about $1\,cm^{-1}$ whereas kT is $200\,cm^{-1}$ at room temperature.

1

To begin with, let me remind you of some elementary concepts. In organic crystals absorption of light can generate excitons[1,2] or electrically neutral mobile excited states. In anthracene, for example, the allowed absorption of blue or near u.v. light can produce singlet excitons[1]. These migrate around and decay radiatively with a lifetime[3] of about 2.5×10^{-8} s, emitting blue fluorescence. Also in anthracene the weak, nearly forbidden, absorption of red light can generate lower energy metastable triplet excitons[4] (or excitons with net electronic spin of 1) (see *Figure 1*). These excitons have a lifetime[4] of about 2.5×10^{-2} s or 10^6 times longer than that for singlet excitons.
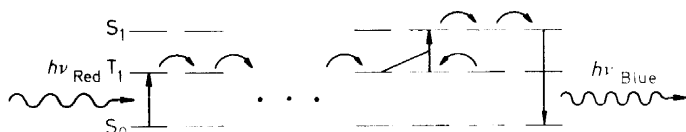
Figure 1. Schematic representation of triplet exciton processes in an anthracene crystal. The events shown are triplet exciton (T_1) generation via absorption of a photon of red light, migration of the triplet, pairwise fusion of two triplets and production of a singlet exciton (S_1), migration of the singlet and its radiative decay accompanied by emission of a blue photon of light (delayed fluorescence)

Although triplet excitons can also decay monomolecularly, they can undergo several more interesting bimolecular energy-transforming processes. The best known of these is triplet–triplet fusion[4] (or triplet–triplet annihilation), where a pair of triplets combine their energy on one molecule producing a higher excited singlet. The luminescence accompanying the radiative decay of these singlets is called *delayed* fluorescence[4] (see *Figure 1*). The spectral distribution of the delayed fluorescence is, of course, the same as that of prompt fluorescence from singlet excitons generated directly via blue or u.v. light absorption. The delayed fluorescence lifetime, however, is many orders of magnitude longer, since it is governed by the triplet lifetime of milliseconds rather than the singlet lifetime or nanoseconds.

FINE STRUCTURE MODULATION (FSM)

1. Homofusion

Homofusion or the pairwise fusion of triplet excitons of the same type is the first example of a magnetic field dependent triplet exciton phenomenon in organic crystals. The effect was first discovered[5] in anthracene and can serve as a good starting point for discussion of magnetic FSM.

Figure 2 shows a typical experimental set-up for observation of magnetic FSM of triplet–triplet fusion which results in a corresponding modulation of the delayed fluorescence intensity.

Light from a xenon arc-lamp is relayed to the crystal located between the pole pieces of an electromagnet via short wavelength cut off filters (through a hole in the base of the magnet). The anti-Stokes emitted delayed fluorescence ϕ is transmitted to a photomultiplier tube via a light guide and a short-wavelength transmitting long-wavelength cut off filter stack. Both the lamp and photomultiplier are shielded from stray fields of the magnet. The photo-

multiplier output signal is fed to the y-input of an xy-recorder. To obtain the field dependence of ϕ for a fixed orientation of the magnet the output of a Hall probe gaussmeter is fed to the x-input of the recorder. To measure the dependence of ϕ on the orientation of magnetic field of a fixed value, the magnet is rotated, and the output from an angular transducer is fed to the x-input of the recorder.
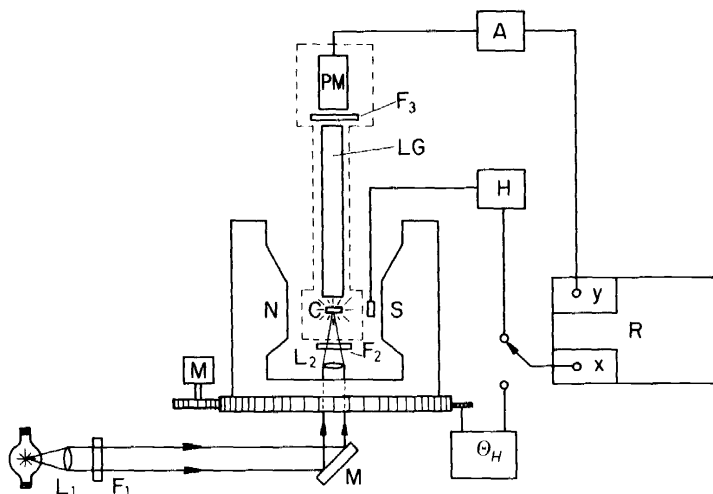

Figure 2. Schematic drawing of a typical experimental arrangement for measuring the magnetic field dependence of luminescence. Light from a xenon arc is relayed via lenses L_1 and L_2 and mirror M through filters F_1 and F_2 to the crystal C between the pole pieces of an electromagnet. The emitted luminescence travels via a light guide (LG) and filter F_3 to the photomultiplier (PM). The PM output is fed to the y-input of an xy-recorder R via the amplifier A. The x-input of the recorder is connected either to the output of the Hall probe gaussmeter H for field dependence measurements or an angular transducer Θ_H coupled to the base of the magnet for anisotropy measurements. The magnet can be rotated with a motor

The field dependence[6] of the delayed fluorescence intensity $\phi(H)$, for the magnetic field H in three different directions in the ac plane of an anthracene crystal at 25°C are shown in *Figure 3*. For the first few hundred oersteds ϕ increases. Then ϕ decreases going below the zero-field value and tends to saturate at around 5 kOe. The dark dots on *Figure 3* show the theoretically calculated[6] field dependence of the triplet–triplet fusion rate constant. Under the low-intensity excitation conditions of these experiments (where ϕ is proportional to the square of the incident intensity), $\phi(H)/\phi(0) = \gamma(H)/\gamma(0)$, where γ is the triplet–triplet fusion rate constant.

The anisotropy[6] of magnetic FSM of ϕ in anthracene is shown in *Figure 4* with the field H in the ac plane of the crystal. We see that for certain field orientations ϕ shows minima. The angular location of these minima or resonances differs at low fields ($H = 400\,\text{Oe}$) from that at high fields ($H = 4000\,\text{Oe}$). The black dots show the theoretical[6] results.

Satisfactory theoretical explanations[6, 7] exist for the above phenomena, as evidenced by the calculated[6] points shown in *Figures 3* and *4*. I do not
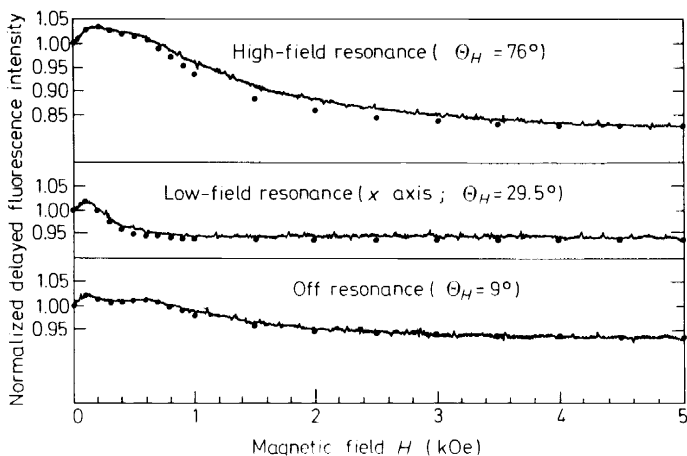
Figure 3. Magnetic field dependence of the normalized delayed fluorescence intensity from an anthracene crystal at room temperature[6]. The field is in the *ac* plane of the crystal at various angles Θ_H (see also *Figure 4*) with respect to the *a* axis. The low-field resonance direction corresponds to the *x* axis of the fine structure tensor; the given value (29.5°) was obtained with an uncertainty of ±1.5° from the low-field anisotropy measurement shown in *Figure 4* and differs slightly from the value of 27.3° deduced from e.s.r. measurements[10]. The curves were measured and the dots calculated theoretically[6]
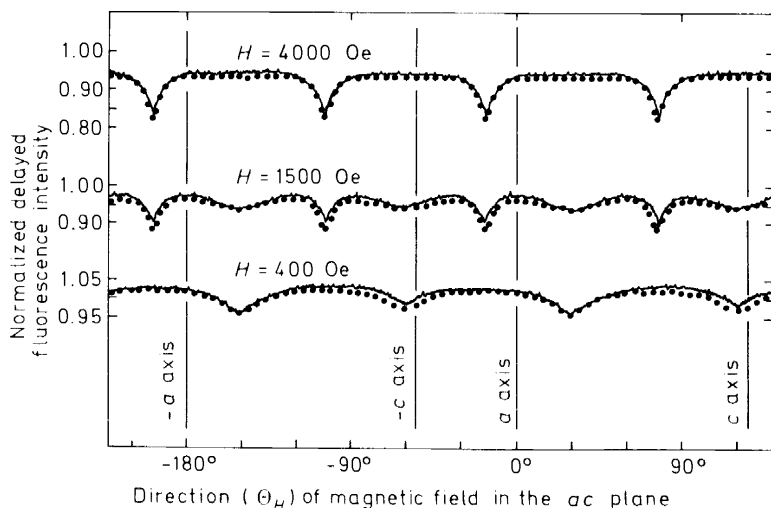

Figure 4. Dependence of the normalized delayed fluorescence intensity on orientation of a magnetic field in the *ac* plane of an anthracene crystal at room temperature. The curves were measured and the dots calculated theoretically[6]

4

intend to discuss calculational details of the theory, but I do wish to talk about the assumptions and qualitative features.

First let us consider the general conditions for existence of modulation by small magnetic fields of a process involving two or more interacting spins:
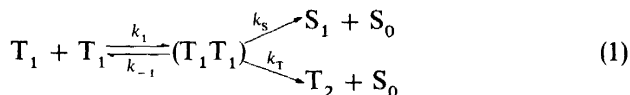
(I) There must exist a spin selection rule (or rules) allowing only certain special spin configurations to undergo the process.

(II) The Hamiltonian must be capable of transforming non-special configurations into special ones.

(III) The process must be a non-equilibrium one (i.e. it must terminate before appreciable spin relaxation occurs), in order for small fields (Zeeman energies $\ll kT$) to be effective.

(IV) Substantial spin 'precession' must take place during the process, to render the effects easily observable.

Let us now examine the triplet–triplet fusion process in reference to the above conditions. The fusion processes can be represented schematically as follows[6, 8]:

$$T_1 + T_1 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (T_1 T_1) \overset{k_S}{\underset{k_T}{\nearrow}} \begin{matrix} S_1 + S_0 \\ \\ T_2 + S_0 \end{matrix} \tag{1}$$

Free triplets, T_1 and T_1, come together with a spin-independent rate constant k_1 and enter a correlated state, $(T_1 T_1)$, which has the possibility of undergoing fusion via the singlet channel discussed already, or via the triplet channel shown in equation 1 for the first time in this discussion. It is assumed that only the singlet spin configuration of the triplet pair can undergo fusion via the singlet channel. In other words the fusion probability which leads to delayed fluorescence is proportional to the singlet character (or square of the singlet amplitude) of the spin state of the triplet pair. The fusion probability via the triplet channel is, in turn, proportional to the triplet character. (From the higher triplet state T_2, radiationless decay leads to the state T_1). Thus condition (I) is satisfied. Correlated pairs which do not fuse dissociate at a spin-independent rate constant k_{-1}.

To see how condition (II) is satisfied, let us turn to the spin Hamiltonian for a pair of triplet excitons, which in the simplest approximation is assumed to be the sum of two single particle Hamiltonians[6-8]:

$$\mathcal{H} = g\mu_B H \cdot (S_1 + S_2) + D(S_{1z}^2 + S_{2z}^2) + E(S_{1x}^2 + S_{2x}^2 - S_{1y}^2 - S_{2y}^2) \tag{2}$$

It turns out that the experimental observations on magnetic FSM of delayed fluorescence can be explained satisfactorily (see *Figures 3* and *4*) with this Hamiltonian where an inter-triplet interaction term is absent[6, 7]. The first term in equation 2 is the Zeeman term where g is the g factor for a triplet exciton in anthracene and its value has been obtained from e.s.r. measurements[9, 10] ($g = 2.003$); μ_B is the Bohr magneton; H is the external magnetic field; and S_1 and S_2 are the spin operators for triplet exciton 1 and triplet exciton 2, respectively. The remaining terms represent the fine structure or zero-field-splitting part of the Hamiltonian. The fine structure terms for each individual triplet arise from the magnetic dipolar interaction of the two unpaired electrons which comprise the triplet state[11]. Via e.s.r. measurements on triplet excitons[9, 10], it has been shown that the z axis of the fine

structure tensor is along the b axis of the crystal, while the x and y axes lie in the ac plane with x at an angle[10] of 27.3° from the a axis. The values[10] of the zero-field-splitting parameters D and E are found to be:

$$E/g\mu_B = 353 \text{ Oe} \quad \text{and} \quad D/g\mu_B = -61 \text{ Oe}.$$

It should be noted that for triplet excitons the fine structure tensor represents an average over the two inequivalent molecules of the unit cell, and that the rapid spatial motion of the excitons averages the hyperfine interactions to zero[9–11].

Let us return to the question as to why the above Hamiltonian satisfies the criterion (II) for a magnetic field effect. When a pair of triplets enter the correlated state with a given total spin, the Zeeman term, which has cylindrical symmetry, cannot alter this spin. Thus a configuration with zero singlet character cannot acquire finite singlet character and thus for this spin configuration the possibility of undergoing fusion via the singlet channel remains closed as the spin motion proceeds in the correlated state. The fine structure terms, on the other hand, have lower symmetry (orthorhombic like), and can mix states with different total spin. In the presence of the fine structure terms, a configuration starting with zero singlet character has the possibility of acquiring finite singlet character. The quantitative details for this process, furthermore, will depend on the relative importance of the Zeeman term and the fine structure terms, which opens the possibility for magnetic FSM. There is a simple classical analogue for this situation. A pair of identical particles with spin in a constant magnetic field would each have a circular precessional orbit (for the tips of the spin vectors) and the relative angle between the two spin vectors would remain constant during the motion (corresponding to a constant singlet character). In the presence of the fine structure interaction the precessional orbits would in general be irregular in shape and the angle between the spin vectors, and hence the singlet character, would change with time (cf. semiclassical calculation in Ref. 12).

That conditions (III) and (IV) for the existence of a magnetic effect are satisfied can be expressed most readily via the following inequality:

$$(2\pi)^{-1} \times \tau_{\mathcal{H}(0)} \lesssim \tau_{\text{correlated}} \lesssim \tau_{\text{spin relaxation}} \tag{3}$$

The theoretical analysis of the experimental results on the magnetic field dependence of delayed fluorescence in anthracene leads to the value[12] of about 3×10^{-10} s for the correlated state lifetime ($\tau_{\text{correlated}}$) which is less than the spin relaxation time[10] ($\tau_{\text{spin relaxation}}$) of about 10^{-8} s. Thus the triplet–triplet fusion process is a non-equilibrium phenomenon. [Triplet states for individual excitons which are spatially far from other excitons will, of course, be completely thermalized and in equilibrium, since the triplet lifetime[4] ($\tau \cong 10^{-2}$ s) is many orders of magnitude longer than the spin relaxation time[10] of about 10^{-8} s.] The left part of the inequality, furthermore, indicates that a substantial amount of spin precessional motion occurs during the correlated 'dance' of two triplet excitons. $\tau_{\mathcal{H}(0)}$ stands for the quasi-'Larmor period' for a triplet exciton in the presence of the fine structure part of the Hamiltonian in zero external field. For substantial field effects a 1-radian precession is sufficient [hence the factor 2π

in equation 3]. In the case of triplet excitons in anthracene $\tau_{\mathcal{H}(0)}$ would be comparable to the Larmor period in an external field of 350 Oe (the approximate value of the larger zero-field-splitting parameter E in oersteds) which is 1×10^{-9} s, or $(2\pi)^{-1} \tau_{\mathcal{H}(0)} = 1.6 \times 10^{-10}$ s. This means there is ample time for substantial spin 'precessional' motion and external fields indeed have a possibility of modifying the spin 'precessional' motion and giving rise to observable effects.

In order to understand the qualitative shape of the magnetic field dependence $\phi(H)$ and the anisotropy of magnetic FSM, i.e. $\phi(\Theta_H)$ at constant field values, let us discuss the triplet–triplet fusion problem in terms of basis states which are eigenstates of total spin (or total angular momentum). We will begin the discussion with high fields and then go on to low fields.

When a pair of triplet excitons enter the correlated state (capable of undergoing fusion), they can be in any one of the nine eigenstates of total spin (1 singlet, 3 triplet and 5 quintet)[8]:

$$|S\rangle = 3^{-\frac{1}{2}}(|00\rangle - |+-\rangle - |-+\rangle)$$
$$|T_{+1}\rangle = 2^{-\frac{1}{2}}(|+0\rangle - |0+\rangle)$$
$$|T_0\rangle = 2^{-\frac{1}{2}}(|+-\rangle - |-+\rangle)$$
$$|T_{-1}\rangle = 2^{-\frac{1}{2}}(|-0\rangle - |0-\rangle)$$
$$|Q_{+2}\rangle = |++\rangle \tag{4}$$
$$|Q_{+1}\rangle = 2^{-\frac{1}{2}}(|+0\rangle + |0+\rangle)$$
$$|Q_0\rangle = 6^{-\frac{1}{2}}(2|00\rangle + |+-\rangle + |-+\rangle)$$
$$|Q_{-1}\rangle = 2^{-\frac{1}{2}}(|-0\rangle + |0-\rangle)$$
$$|Q_{-2}\rangle = |--\rangle$$

In equation 4 the pure spin states have been expanded in terms of two-particle basis states $|++\rangle$, $|+-\rangle$, etc. with the individual particle spins quantized with respect to the external field.

Each individual term on the right side of equation 4 is nearly a pair eigenstate of energy in a high field situation (Zeeman interaction $\gg$ fine structure interactions). It should be noted that the singlet state and the 5 quintet states are all even under the interchange of two particles, while the triplet states are odd (see equation 4). It turns out that this is a general condition which holds for all field values[8, 13], since the spin Hamiltonian (equation 2) is even in the interchange of the two spins. This means the Hamiltonian has the possibility of mixing the quintet states with the singlet state as well as amongst each other, whereas it cannot mix the triplet states with the singlet or any of the quintets[13]. (Spin relaxation can bring about such mixing, but this process is negligible in anthracene[7, 13].) We can thus ignore the three triplet states in discussion of magnetic FSM of the triplet–triplet homofusion process via the singlet channel.

How will a high magnetic field influence the spin motion of triplet excitons which have formed correlated pairs in the pure spin states given in equation 4? It is clear that a pair of triplets which form the correlated pair in the states

$|Q_{\pm 2}\rangle$ and $|Q_{\pm 1}\rangle$, do not acquire singlet character during the life of the correlated triplet pair, since the expansions for these states do not contain any terms present in the expansion for the singlet state $|S\rangle$. These triplets, therefore, cannot undergo fusion via the singlet channel.

The states $|S\rangle$ and $|Q_0\rangle$, however, do have the possibility of mixing.

For any eigenstate $\Psi_j(t)$ of the spin Hamiltonian, we have:

$$\Psi_j(t) = e^{-i(E_j/\hbar)t}\,\Psi_j(0) \tag{5}$$

where E_j is the eigen energy of the state labelled with j; $\hbar$ is Planck's constant/2π; i is $(-1)^{\frac{1}{2}}$; and t is the time. From perturbation theory[14] the states $|00\rangle$, $|+-\rangle$, and $|-+\rangle$ are eigenstates of the *full* Hamiltonian (including both Zeeman and fine structure terms) to lowest order in the external field H, with energies given in lowest order by the expectation values of $\mathscr{H}$, e.g. $E_{00} = \langle 00 | \mathscr{H} | 00\rangle$, etc. Then in case of $\Psi(0) = |Q_0\rangle$, we get from equations 4 and 5:

$$\Psi(t) = 6^{-\frac{1}{2}}\{2e^{-i(E_{00}/\hbar)t}\,|00\rangle + e^{-i(E_{+-}/\hbar)t}\,|+-\rangle + e^{-i(E_{-+}/\hbar)t}\,|-+\rangle\} \tag{6}$$

For an arbitrary field direction, the energies E_{+-} and E_{-+} are equal, but not equal to E_{00}. The state $\Psi(t)$ (equation 6), therefore, will acquire singlet character with passage of time. The state $|S\rangle$ will, likewise, transform with time and acquire some quintet character.

When the magnetic field is in one of the resonance directions, $E_{00} = E_{+-} = E_{-+} = E$, then

$$\Psi(t) = e^{-i(E/\hbar)t}\,|Q_0\rangle \tag{7}$$

or the state starting as $|Q_0\rangle$ will be time independent (except for the single phase factor in front), and the state $|S\rangle$ likewise. This means that when triplet excitons form correlated pairs in a high magnetic field, with the field applied in a resonance direction, only those in the state $|S\rangle$ have the possibility of fusion via the singlet channel and none of those in other states (shown in equation 4). When the magnetic field is rotated to an orientation which is off resonance ($E_{00} \neq E_{+-}$), then a pair starting in the $|Q_0\rangle$ state will acquire some singlet character during the 'dance' of the triplet excitons in the correlated state (see equation 6), and this pair will also have the possibility of undergoing fusion via the singlet channel.

How this situation of a high magnetic field in an off-resonance direction can lead to a higher rate of triplet–triplet fusion via the singlet channel can be visualized easily with the help of a hydrodynamic analogue (see *Figure 5*).

In *Figure 5* the left tank in both parts (a) and (b) represents the correlated triplet pair state $|S\rangle$ and the right tank the state $|Q_0\rangle$. Corresponding to association of triplets as correlated pairs at a spin-independent rate k_1, water enters each of the tanks at the same rate. The pair dissociation at a spin-independent rate k_{-1} is indicated by the openings marked k_{-1}. The flow out of the opening marked k_S represents triplet–triplet fusion via the singlet channel. The length of the vertical arrow below each of these openings represents the relative intensity of delayed fluorescence. For simplicity the two types of channels k_{-1} and k_S are given rate constants of equal value (equal openings at the bottom of the tanks) in *Figure 5*. *Figure 5* (a) represents the

8

on-resonance field direction, and there is no interconnection between the $|S\rangle$ and $|Q_0\rangle$ tanks. We can increase the radiative fusion rate by turning the field to an off-resonance direction and placing a connection between the two tanks as shown in *Figure 5(b)*. The extreme case of complete mixing of the states $|Q_0\rangle$ and $|S\rangle$ is illustrated. We see that the back and forth flow of water from the quintet into the singlet tank raises the level of water in the singlet tank, and the higher head (or height) of water in this tank increases the flow rate out of the fusion channel marked k_s.
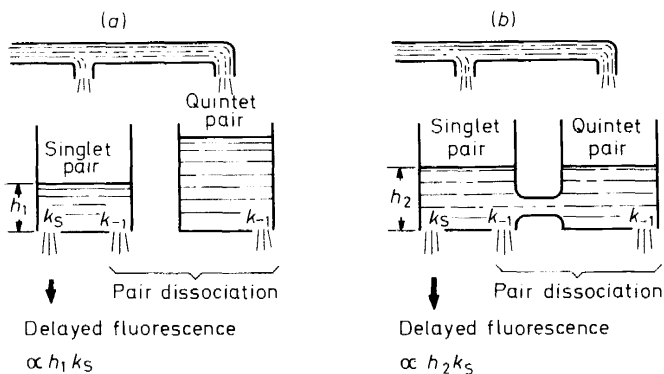
Figure 5. Hydrodynamic analogue comparing the relative delayed fluorescence intensity ϕ for (*a*) a high magnetic field in a resonance direction with ϕ for (*b*) the field in an off-resonance direction; ϕ is proportional to the length of the vertical arrows below the openings marked k_s. The left tank in each case represents the singlet state $|S\rangle$ for correlated triplet exciton pairs and the right tank the quintet state $|Q_0\rangle$. The horizontal pipe connecting the two tanks in part (*b*) represents the mixing of the $|S\rangle$ and $|Q_0\rangle$ states by the spin Hamiltonian

What happens at lower fields? Let us turn to *Figure 6* where a hydrodynamic model representing all nine states of total spin is given.

The lower half of *Figure 6* represents the high-field on-resonance and off-resonance situations which we have just discussed, and the upper half the low-field (off-resonance) and zero-field conditions. (Since in homofusion the Hamiltonian does not mix the triplet pair states with the quintets and the singlet, as mentioned above, we don't need to talk about the triplet tanks.)

As we go to lower field values where the Zeeman and fine structure interactions are comparable, then the spin Hamiltonian has the possibility of mixing all of the quintet states amongst each other and with the singlet state[8]. In the hydrodynamic model, we consider such an extreme case by interconnecting all the quintet tanks to each other and to the singlet tank. Since all the quintet tanks can contribute to the water in the singlet tank, this raises the water level in the singlet tank and consequently the flow rate out of the radiative fusion channel.

In order to discuss what happens at zero field, let us present the eigenstates of total spin for a triplet exciton pair in terms of the basis of the eigenstates of the pair Hamiltonian at zero field[8]:
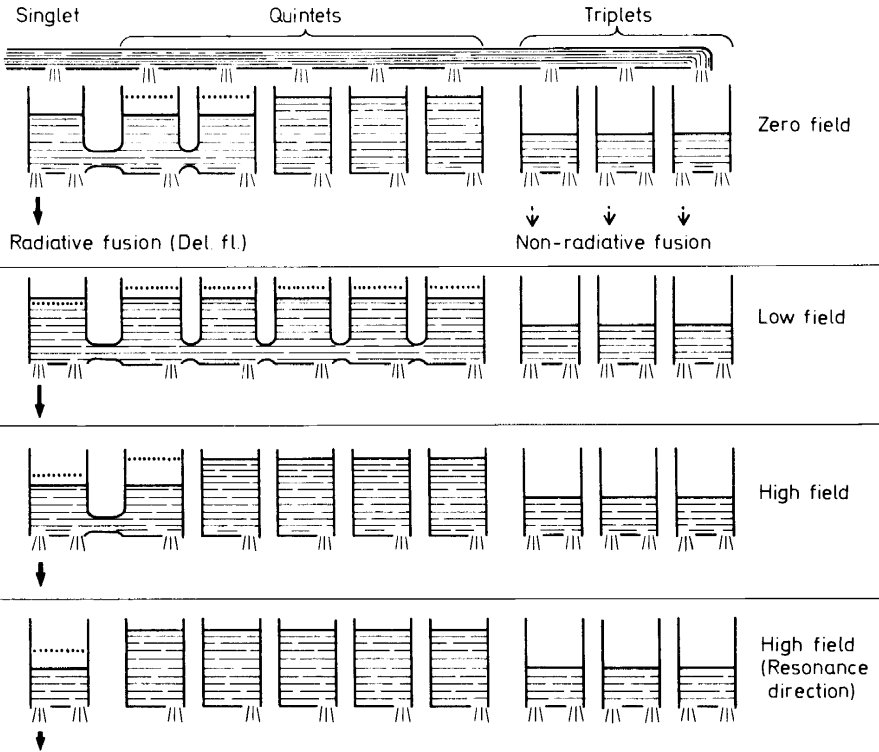
9

Figure 6. Hydrodynamic analogue for magnetic FSM of triplet–triplet homofusion and delayed fluorescence for an organic crystal such as anthracene. The intensity of delayed fluorescence is proportional to the length of the vertical arrows on the left. Mixing of the quintet states among each other and with the singlet by the spin Hamiltonian is indicated by the horizontal pipes interconnecting the various tanks. As more and more quintet tanks interconnect with the singlet, the level of the water is raised in the singlet tank and the intensity of the delayed fluorescence is correspondingly higher

$$|S\rangle = 3^{-\frac{1}{2}}(|xx\rangle + |yy\rangle + |zz\rangle)$$
$$|T_x\rangle = 2^{-\frac{1}{2}}(|yz\rangle - |zy\rangle)$$
$$|T_y\rangle = 2^{-\frac{1}{2}}(|zx\rangle - |xz\rangle)$$
$$|T_z\rangle = 2^{-\frac{1}{2}}(|xy\rangle - |yx\rangle)$$
$$|Q_a\rangle = 2^{-\frac{1}{2}}(|xx\rangle - |yy\rangle)$$
$$|Q_b\rangle = 6^{-\frac{1}{2}}(|xx\rangle + |yy\rangle - 2|zz\rangle)$$
$$|Q_x\rangle = 2^{-\frac{1}{2}}(|yz\rangle + |zy\rangle)$$
$$|Q_y\rangle = 2^{-\frac{1}{2}}(|zx\rangle + |xz\rangle)$$
$$|Q_z\rangle = 2^{-\frac{1}{2}}(|xy\rangle + |yx\rangle)$$

(8)

10

For each of the terms appearing on the right side of equation 8, the individual particle spins are in a plane at right angles to the direction indicated[8] (e.g. $S_x|x\rangle = 0$).

At zero field an interesting symmetry condition comes into the problem. In the absence of an external magnetic field the Hamiltonian acquires orthorhombic-like symmetry. Only two of the quintet states $|Q_a\rangle$ and $|Q_b\rangle$ (shown in equation 8) mix with the singlet, and thus the level of water in the singlet tank diminishes. Hence intensity of delayed fluorescence at zero field is smaller than that at a low finite field.

The low-field resonances arise when the external field is directed along the x, y or z axes of the fine structure tensor[6]. These field directions restore partially the orthorhombic-like symmetry present at zero field, (except with the difference that reversal of the field direction from say $+x$ to $-x$ brings about a sign change in the Zeeman term). The symmetry restoration decreases the coupling between the quintet manifold and the singlet pair state, and hence the delayed fluorescence intensity (as compared to the field in an off-resonance direction) also decreases.

It should be noted that the length of the solid arrow in *Figure 6* which represents the relative intensity of delayed fluorescence follows the qualitative behaviour of the experimentally observed field dependence of ϕ (see *Figure 3*). Upon increase of the field from zero the arrow gets longer. Then it decreases in length below the zero-field value at higher fields.

We thus see that the qualitative features of magnetic FSM on triplet–triplet homofusion and delayed fluorescence can be understood on the basis of the influence of the spin Hamiltonian on the time development of triplet pairs in the correlated state. For quantitative work the reader is referred to Refs. 6 and 7.

Studies of magnetic FSM of delayed fluorescence have given a great deal of information on the microscopics of the triplet–triplet fusion process. Quantitative evaluation of the measurements described above and those at higher excitation intensities[13] in anthracene have shown that 4 per cent of triplets entering the correlated state fuse via the singlet channel, 14 per cent via the triplet channel, and the rest dissociate[8]. Upon entering the correlated state, a pair of triplets recollide (finding themselves on nearest neighbour molecules) on the average five times before fusing or leaving the correlated state[12]. It is these recollisions, arising from the 'two dimensionality' of triplet exciton diffusion in anthracene[7], which extend the lifetime of the correlated state sufficiently to satisfy condition (IV) for the observability of FSM[7, 12].

2. Fission

So far, we have discussed magnetic FSM on delayed fluorescence. Under certain circumstances, magnetic FSM on prompt fluorescence can be observed. This occurs under circumstances where singlet fission (or inverse of triplet–triplet fusion) is an important avenue for destruction of singlet excitons. This effect can be readily observed in tetracene crystals[15, 16], where the energy of two triplet excitons is sufficiently close to that for a singlet[17], such that thermally induced fission becomes possible.

That prompt fluorescence should be subject to magnetic FSM in the presence of fission follows from a simple thermodynamic consideration[16]. If we consider the fusion and fission reactions under equilibrium:

$$T_1 + T_1 \underset{\gamma'}{\overset{\gamma}{\rightleftarrows}} S_1 + S_0 \tag{9}$$

then the rate of the reaction going from the left to the right must be equal to the rate of the reverse reaction (going from the right to the left), and the fission rate constant γ' will be proportional to the fusion rate constant γ, with the proportionality constant $c(T)$ depending on the temperature T, but *not* magnetic field:

$$\gamma' = c(T)\gamma \tag{10}$$

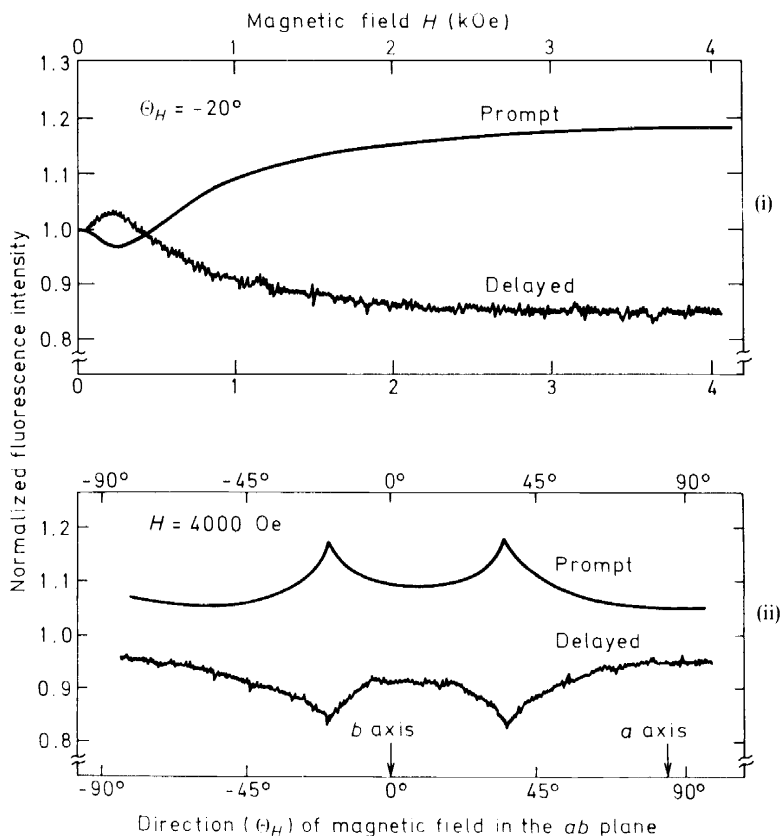Consequently, the field dependence of γ will imply the same field dependence for γ'.

Figure 7. Experimentally observed[19] dependence of both prompt and delayed fluorescence intensity on (*i*) magnetic field strength and (*ii*) orientation of a magnetic field in the *ab* plane of the crystal. The measurements were carried out on a tetracene crystal at 238 K where the magnitudes of FSM on prompt and delayed fluorescence are nearly equal[19]

The magnetic FSM of both delayed (ϕ) and prompt (F) fluorescence for a tetracene crystal[19] are shown in *Figure 7*. These results are for a temperature of 238 K, where the two FSMs are comparable in magnitude[19]. We see that the F(H) and $\phi(H)$ are inverse of each other [*Figure 7(i)*] and that the resonance directions coincide [*Figure 7(ii)*]. The reason why the two effects are inverse of each other is that an increase in γ increases the delayed fluorescence intensity by increasing the population of singlet excitons formed by triplet--triplet fusion. In the prompt fluorescence measurement where the singlet excitons are generated directly via light absorption, an *increase* in γ' *decreases* the population of singlet excitons and hence the fluorescence emission intensity.

Recently, optically induced fission for singlet excitons in anthracene was demonstrated[20]. A small magnetic FSM of prompt fluorescence was observed upon excitation of the crystal with photons having sufficient energy for generation of triplet exciton pairs.

3. Heterofusion and other phenomena

Magnetic FSM has also been observed in a number of physical processes other than those described above. For example the rate of triplet--triplet fusion between free triplets in an anthracene crystal and triplets trapped at guest tetracene molecules can be influenced with a magnetic field[21]. In this system the interchange symmetry in the spin Hamiltonian is broken in that heterofusion involves a free triplet exciton and triplets trapped at tetracene molecules at either of two possible substitutional sites in the crystal[22]. Thus the magnetic FSM of the green delayed fluorescence arising from heterofusion shows qualitative differences from the FSM of the blue delayed fluorescence arising from homofusion[21]. Magnetic FSM of heterofission of singlet excitons (or inverse of heterofusion) has been demonstrated in pentacene-doped tetracene crystals[23].

In closing this section I would like to point out that magnetic FSM has been demonstrated for a triplet--doublet interaction involving the quenching of triplet excitons by free radicals[24], and there have also been reports of magnetic FSM on photoconductivity[25-27].

HYPERFINE MODULATION (HFM)

Next, I would like to turn to the second and shorter part of my talk. I would like to discuss dye-sensitized delayed fluorescence and its magnetic hyperfine modulation (HFM). I say hyperfine modulation because we are talking about effects at only 10s of oersteds and again at room temperature.

Since the direct generation of triplet excitons is inefficient due to the very small singlet--triplet absorption coefficient[4] (about 10^{-3} cm^{-1} in anthracene), triplet production has been sensitized[28] by using an adsorbed dye layer on the crystal surface. As is shown in *Figure 8*, one can use the allowed singlet--singlet absorption in the dye for excitation into the singlet state ($^1D_1$). Via intersystem crossing a substantial number of dye molecules convert into the triplet state ($^3D_1$) and can inject this triplet excitation into the crystal. (Frequently the adsorbed dye species is an ion rather than a neutral molecule.)

One can thus obtain several orders of magnitude enhancement in the sensitized delayed fluorescence intensity as compared to the direct generation of triplet excitons via light absorption in the crystal.

The type of triplet injection just discussed is found to be insensitive to magnetic fields. The delayed fluorescence from anthracene sensitized with eosin Y shows the same type of magnetic field dependence as delayed fluorescence excited directly with red light. It turns out, however, that for certain dyes there is a second mechanism for triplet exciton injection involving an intermediate charge-transfer (CT) state which is very sensitive to small fields[29].
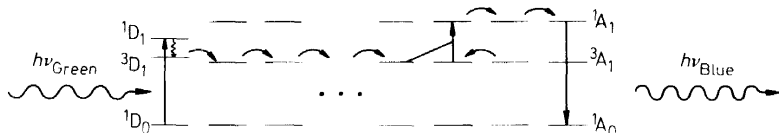

Figure 8. Schematic representation of photoexcitation of a dye molecule on the surface of an anthracene crystal into its first excited singlet state, intersystem crossing of the dye into its triplet state, and triplet exciton injection into the crystal followed by triplet–triplet fusion and delayed fluorescence emission. The processes shown do not give rise to magnetic HFM of sensitized delayed fluorescence. (The HFM phenomenon involves an intermediate charge-transfer state)

The experimental set-up is essentially the same as that shown in *Figure 2*, except that the crystal is immersed in an aqueous solution of the dye (e.g. rhodamine B plus sodium bisulphate, which makes the system more stable). *Figure 9* (solid curve) presents the magnetic field dependence of rhodamine B sensitized delayed fluorescence in an anthracene crystal (with the sample excited with green light at 570 nm)[29]. The dye concentration was 2×10^{-6} M (and the sodium bisulphate concentration 0.1 M). There is a small initial rise in the delayed fluorescence reaching a peak of about 1 per cent at 5 Oe in the emission intensity followed by a rapid decrease. At 50 Oe the intensity is down to 60 per cent of the zero-field value, continues to decrease, and saturates at a field strength of between 200 and 300 Oe. For comparison the field dependence of the delayed fluorescence excited directly with red light (680 nm) is presented as the dashed curve in *Figure 9*. The amplitude of HFM and the broadness of the field-dependence curve depend on sample history and dye concentration. Decreasing the dye concentration from that used in the experiment of *Figure 9* by a factor of 10 tends to sharpen the field-dependence curve[30] (half the total modulation occurs at about half the field value as that for the higher concentration).
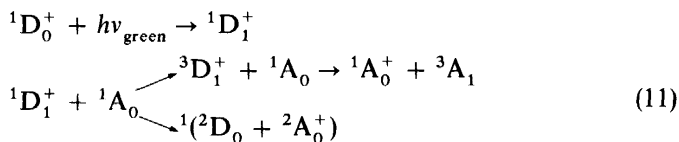
For the magnetic field in the *ab* plane of the crystal, HFM is independent of field orientation[29]. Recently[30], it was discovered that with the field in the *ac* plane, the sensitized delayed fluorescence intensity does depend on the field direction.

A number of dyes sensitize photoconductivity in anthracene[31]. Rhodamine B sensitized photoconductivity is also sensitive to a magnetic field, but the HFM of sensitized photoconductivity is inverse of that of sensitized delayed fluorescence and is about six times smaller in amplitude[29].

In contrast to FSM, a quantitative theory for HFM does not exist as yet. The key physical features, however, have been identified.

Let us consider possible energy pathways in dye sensitization (e.g. rhodamine B adsorbed on the surface of an anthracene crystal):

$$^1D_0^+ + h\nu_{green} \rightarrow {}^1D_1^+$$

$$^1D_1^+ + {}^1A_0 \underset{\nwarrow^1(^2D_0 + {}^2A_0^+)}{\overset{\nearrow^3D_1^+ + {}^1A_0 \rightarrow {}^1A_0^+ + {}^3A_1}{}} \tag{11}$$

In equation 11 D stands for dye (or donor) and A for anthracene (or acceptor). The subscript 0 indicates a ground state and subscript 1 an excited state. The superscript on the left indicates the multiplicity of the species.
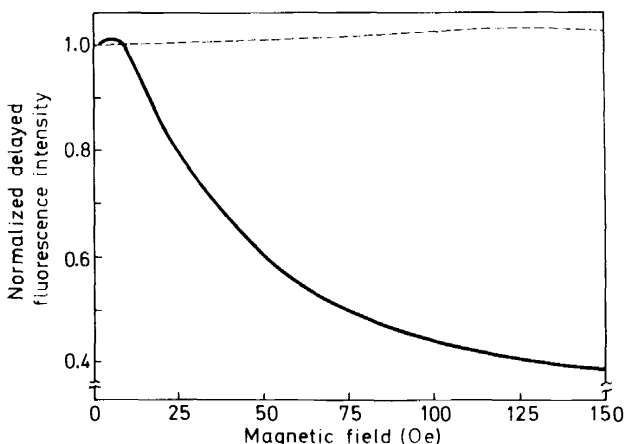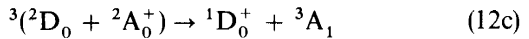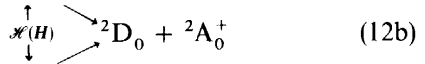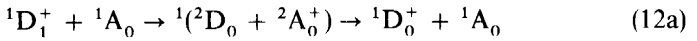

Figure 9. Observed magnetic field modulation of normalized delayed fluorescence intensity for an anthracene crystal in an aqueous solution of rhodamine B at 2×10^{-6} M (and 0.1 M $NaHSO_3$) at room temperature[29]. The solid curve is for excitation with 570 nm light via the dye and the dashed curve is for direct excitation of the crystal with 680 nm light

Absorption of a photon of light can excite a dye molecule (a cation in the case of rhodamine B) into its first excited singlet state ($^1D_1^+$). Via intersystem crossing the dye can change into its triplet state ($^3D_1^+$) and then transfer this triplet excitation to the crystal. The triplet excitons ($^3A_1$), in turn, can undergo pairwise fusion leading to emission of delayed fluorescence. The direct triplet injection process just described is found to be insensitive to magnetic fields.

The magnetic field sensitive route begins with the abstraction of an electron from a neighbouring anthracene molecule by the excited dye molecule or, equivalently, the transfer of a positive hole to the anthracene molecule and the formation of a charge-transfer (CT) state at the surface of the crystal (see equation 11). This CT state will be formed in the singlet state since it is produced from a singlet parent state. It is assumed that upon recombination, the singlet CT state cannot inject a triplet exciton into the

15

crystal. For triplet injection a triplet CT state is required. This spin selection rule fulfils condition (I) (of the previous section, p 5) for the existence of a magnetic field effect. The spin Hamiltonian, furthermore, in the presence of hyperfine interactions, can induce transitions between singlet and triplet CT states as discussed below, and condition (II) for the existence of a magnetic field effect is fulfilled. The experimental observation of magnetic HFM of dye sensitized delayed fluorescence implies that conditions (III) and (IV) for a magnetic field effect are also satisfied. The lack of a quantitative theory for the HFM phenomenon and the lack of experimental data on the hole spin relaxation time in an anthracene crystal, however, prevent us from giving the experimentally deduced numerical values for the relevant times in inequality 3, p 6, as applied to the correlated CT state.

Let us now consider in detail the possible fates of the initially formed singlet CT state:

$$^1D_1^+ + {}^1A_0 \rightarrow {}^1(^2D_0 + {}^2A_0^+) \rightarrow {}^1D_0^+ + {}^1A_0 \qquad (12a)$$

$$\mathscr{H}(H) \searrow {}^2D_0 + {}^2A_0^+ \qquad (12b)$$

$$^3(^2D_0 + {}^2A_0^+) \rightarrow {}^1D_0^+ + {}^3A_1 \qquad (12c)$$

Equation 12a represents singlet-channel recombination with the unexcited dye ion and a ground state anthracene molecule ($^1A_0$) as the product. Equation 12b represents hole injection into the crystal. It is assumed that this process has no spin restriction. The vertical double ended arrow represents transitions between the singlet and triplet correlated CT states induced by the Hamiltonian $\mathscr{H}$ which is a function of the magnetic field H. Equation 12c represents triplet-channel recombination followed by triplet exciton injection into the crystal. Since only the triplet CT state can inject triplet excitons into the crystal, the modulation of the singlet–triplet transformation rate in the CT state modulates the triplet exciton injection rate and the consequent delayed fluorescence intensity.

In considering the effect of the Hamiltonian on the 'precessional' spin motion of the electron and hole comprising the CT state, let us write down the eigenstates of total spin for the electron-hole (e-h) pair (1 singlet, 3 triplet)[32].

$$\begin{aligned}
|S\rangle &= 2^{-\frac{1}{2}}(|\alpha_e\beta_h\rangle - |\beta_e\alpha_h\rangle) \\
|T_+\rangle &= |\alpha_e\alpha_h\rangle \\
|T_0\rangle &= 2^{-\frac{1}{2}}(|\alpha_e\beta_h\rangle + |\beta_e\alpha_h\rangle) \\
|T_-\rangle &= |\beta_e\beta_h\rangle
\end{aligned} \qquad (13)$$

where $|\alpha\rangle$ and $|\beta\rangle$ are the two possible spin functions for the individual electron or the hole, e.g. with quantization with respect to the external field. The spin Hamiltonian, furthermore, has three types of terms in it:

$$\mathscr{H} = \mathscr{H}_{Zeeman} + \mathscr{H}_{hyperfine} + \mathscr{H}_{e-h} \qquad (14)$$

where

$$\mathscr{H}_{Zeeman} = g\mu_B H \cdot (S_e + S_h)$$

with g the g factor for the electron and for the hole (which are assumed to be equal), μ_B the Bohr magneton, H the external field, and S_e and S_h the spin operators for the electron and the hole, respectively. $\mathcal{H}_{hyperfine}$ represents the hyperfine interaction between the hole on the anthracene with the protons in the anthracene and the hyperfine interaction of the unpaired electron with the protons in the dye radical. The last term represents the interactions between the electron spin and the hole spin. The Zeeman interaction of the protons is negligible.

The singlet state $|S\rangle$ is odd under the interchange of the two particles while all the triplets are even (see equation 13). Therefore, $\mathcal{H}_{Zeeman}$, which is also even under interchange of the two particles, cannot mix triplets with the singlet. In the presence of $\mathcal{H}_{Zeeman}$ alone, an electron–hole pair forming a correlated singlet CT state with zero triplet character would continue to have zero triplet character and could not give rise to triplet exciton injection. $\mathcal{H}_{hyperfine}$ provides the necessary unsymmetrical term in the Hamiltonian which gives rise to singlet–triplet mixing. The point is that the protons which interact with the hole on the anthracene ion are not the same as those which interact with the unpaired electron on the dye radical. Hence the Hamiltonian is not symmetric under the interchange of the electron and the hole. In the presence of the $\mathcal{H}_{hyperfine}$, therefore, electron–hole pairs forming singlet CT states can acquire triplet character during their 'dance' in the correlated CT state and give rise to triplet exciton injection. An external field partially restores the symmetry of the Hamiltonian, reducing the singlet–triplet transition rate as the Zeeman interaction becomes large compared to the hyperfine interaction ($H \gtrsim 10$ Oe).

Magnetic HFM of photoconductivity arises because of a difference in the rate constants for processes 12a and 12c giving rise to HFM of the *total* CT state population. The hole injection rate, since it is assumed to obey no spin selection rule, is proportional to the total CT state population. The observed sense of the magnetic HFM of photoconductivity implies that the rate constant for process 12c is greater than that for process 12a.

The simplest possible theoretical model which shows the qualitative features of the HFM phenomenon is one in which the hyperfine interaction of the hole only (or electron only) is considered and it is assumed to be that of a single proton, e.g. with the hole on the anthracene:

$$\mathcal{H}_{hyperfine} = aS_h \cdot I \tag{15}$$

where I is the spin operator for a single proton interacting with the hole via a contact[32] hyperfine interaction of strength a. With this hyperfine term and with $\mathcal{H}_{e-h} = 0$, the triplet CT state population as a function of magnetic field has been calculated[29] and the result is presented in *Figure 10*. The triplet exciton injection rate, in turn, will be proportional to the triplet CT state population. Thus the model displays qualitatively the experimentally observed features.

The observed anisotropy in the HFM with the field in the *ac* plane of the crystal can be explained by including an anisotropic spin–spin interaction term ($\mathcal{H}_{e-h}$) in the Hamiltonian (equation 14)[30].

In closing this section I would like to point out that some of the magnetic field effects reported by Frankevich *et al.*[33] may be due to a mechanism similar
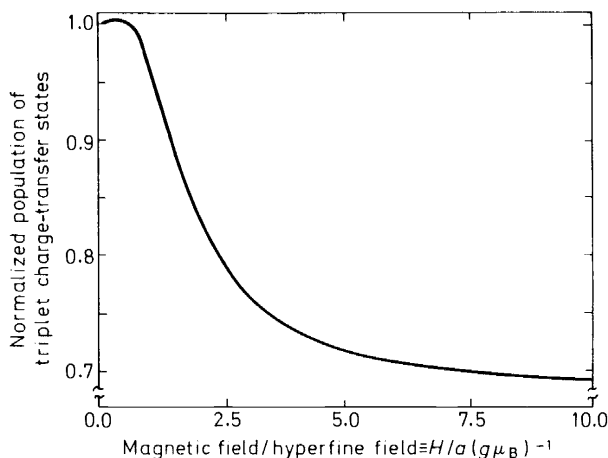
Figure 10. Calculated magnetic HFM of the normalized population of electron–hole pairs in triplet charge-transfer states. The calculation was carried out for the one-proton model presented in the text. The value of the dissociation rate constant for the CT state (see equation 12) was chosen so as to obtain a curve similar to the observed field dependence

to that discussed above. Finally, it should be noted that there is a close similarity between the correlated CT state discussed above and the radical pair in chemically induced dynamic nuclear polarization (CIDNP) phenomena[34-36].

CONCLUSION

In this talk, I have discussed two classes of phenomena in which luminescence involving triplet excitons can be modulated by small magnetic fields at high temperatures. The main examples of FSM phenomena are triplet–triplet fusion leading to delayed fluorescence and its inverse or singlet fission. The key example of HFM is that of dye-sensitized delayed fluorescence involving an intermediate charge-transfer state. All the phenomena involve non-equilibrium processes subject to spin restrictions. The fine structure interaction in FSM and the hyperfine interaction in HFM lead to spin 'precessional' motions which circumvent these restrictions. The external field competes with the internal magnetic interactions in affecting these spin motions.

The main materials studied so far have been anthracene and tetracene. Investigation of other systems, both pure and doped, as well as a look at effects of temperature change would be worthwhile. Furthermore, it would be interesting to look for other novel phenomena which might also satisfy the above conditions for sensitivity to small magnetic fields.

ACKNOWLEDGEMENTS

The research described in this paper has been carried out mainly by the following people: R. E. Merrifield and A. Suna have done the theory; R. C.

Johnson, R. P. Groff and I the experiments; and G. J. Sloan has prepared the crystals. I am very grateful to Drs Merrifield, Groff, and especially Dr Suna for helpful discussions during the preparation of the manuscript. *Figures 3* (Ref. 6), *4* (Ref. 6), *7* (Ref. 19), *9* (Ref. 29) and *10* (Ref. 29) have been taken from the references given in the parentheses (with some modifications). I am grateful to the authors and the editors of the respective journals for permission to present these figures here.

REFERENCES

[1] H. C. Wolf, *Advances in Atomic and Molecular Physics*, Vol. 3, p. 119, (ed. D. R. Bates and I. Estermann) Academic Press, New York (1967); and references cited therein.

[2] A. S. Davydov, *Theory of Molecular Excitons*, Nauka, Moscow (1968), in Russian. [English translation by S. B. Dresner, Plenum Press, New York (1971)].

[3] J. B. Birks, T. A. King and I. H. Munro, *Proc. Phys. Soc. (London)*, **80**, 355 (1962).

[4] P. Avakian and R. E. Merrifield, *Mol. Cryst.*, **5**, 37 (1968); and references cited therein.

[5] R. C. Johnson, R. E. Merrifield, P. Avakian and R. B. Flippen, *Phys. Rev. Letters*, **19**, 285 (1967).

[6] R. C. Johnson and R. E. Merrifield, *Phys. Rev.*, **B1**, 896 (1970).

[7] A. Suna, *Phys. Rev.*, **B1**, 1716 (1970).

[8] R. E. Merrifield, *Pure and Appl. Chem.*, **27**, 481 (1971).

[9] D. Haarer, D. Schmid and H. C. Wolf, *Phys. Status Solidi*, **23**, 633 (1967).

[10] D. Haarer and H. C. Wolf, *Mol. Cryst., Liquid Cryst.*, **10**, 359 (1970).

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

[12] P. Avakian and A. Suna, *Mat. Res. Bull.*, **6**, 891 (1971).

[13] R. P. Groff, R. E. Merrifield and P. Avakian, *Chem. Phys. Letters*, **5**, 168 (1970).

[14] L. I. Schiff, *Quantum Mechanics*, 2nd ed., Ch. 7, McGraw-Hill, New York (1955).

[15] N. Geacintov, M. Pope and F. Vogel, *Phys. Rev. Letters*, **22**, 593 (1969).

[16] R. E. Merrifield, P. Avakian and R. P. Groff, *Chem. Phys. Letters*, **3**, 155 (1969).

[17] Y. Tomkiewicz, R. P. Groff and P. Avakian, *J. Chem. Phys.*, **54**, 4504 (1971).

[18] C. E. Swenberg and W. T. Stacy, *Chem. Phys. Letters*, **2**, 327 (1968).

[19] R. P. Groff, P. Avakian and R. E. Merrifield, *Phys. Rev.*, **B1**, 815 (1970).

[20] G. Klein, R. Voltz and M. Schott, *Chem. Phys. Letters*, **16**, 340 (1972).

[21] R. P. Groff, R. E. Merrifield, P. Avakian and Y. Tomkiewicz, *Phys. Rev. Letters*, **25**, 105 (1970).

[22] V. C. Sinclair, J. M. Robertson and A. M. Mathieson, *Acta Cryst.*, **3**, 251 (1950).

[23] N. E. Geacintov, J. Burgos, M. Pope and C. Strom, *Chem. Phys. Letters*, **11**, 504 (1971).

[24] V. Ern and R. E. Merrifield, *Phys. Rev. Letters*, **21**, 609 (1968).

[25] P. Delannoy and M. Schott, *Phys. Letters*, **30A**, 357 (1969).

[26] N. E. Geacintov, M. Pope and S. Fox, *J. Phys. Chem. Solids*, **31**, 1375 (1970).

[27] E. L. Frankevich and I. A. Sokolnik, *Solid State Commun.*, **8**, 251 (1970).

[28] B. Nickel, H. Staerk and A. Weller, *Chem. Phys. Letters*, **4**, 27 (1969).

[29] R. P. Groff, R. E. Merrifield, A. Suna and P. Avakian, *Phys. Rev. Letters*, **29**, 427 (1972).

[30] R. P. Groff, A. Suna, P. Avakian and R. E. Merrifield, *Phys. Rev.*, **B9**, No. 6 (1974).

[31] B. J. Mulder, *Philips Res. Rep.*, Suppl. No. 4 (1968).

[32] A. Carrington and A. D. McLachlan, *Introduction to Magnetic Resonance with Applications to Chemistry and Chemical Physics*, Harper and Row, New York (1967).

[33] E. L. Frankevich and B. M. Rumyantsev, *Zh. Eksperim. i Teor. Fiz.*, **63**, 2015 (1972). English translation: *Soviet Phys.–JETP*, **36**, 1064 (1973).

[34] G. L. Closs, *XXIIIrd Int. Congr. Pure and Appl. Chem.*, Vol. 4, p. 19, Butterworths, London (1971).

[35] R. G. Lawler, *Accounts of Chem. Res.*, **5**, 25 (1972).

[36] H. R. Ward, *Free Radicals*, Vol. 1, Ch. 6, (ed. J. K. Kochi), Wiley, New York (1973).