Fission of singlet excitons into triplet-exciton pairs in molecular crystals

M. Chabr and D. F. Williams

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

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A kinetic model of singlet-exciton fission into pairs of triplet excitons in aromatic hydrocarbon crystals is presented. The model is based on Suna's hopping model for triplet-exciton fusion. The assumptions made in this description of fission and the relationship between fusion and fission are analyzed in detail. According to this theoretical model, the magnetic field modulation of anthracene hot singlet fission is the reverse of the modulation of triplet fusion. Accurate observations of fission, however, have shown there are some consistent differences, and these differences are discussed in terms of the fission process.

I. INTRODUCTION

Fission of a singlet exciton into a pair of triplet excitons was first proposed by Swenberg and Stacy[1] as the explanation for the anomalously low fluorescence quantum yield in tetracene crystals, which was later confirmed experimentally.[2,3] Fission has since been studied in tetracene and anthracene crystals[4-6] but attempts to observe fission in naphthalene and pyrene crystals have so far failed.[7] The fission of a singlet exciton in a molecular crystal is generally thought as the reverse of triplet-exciton fusion.[8-11] However, fission and fusion are not strictly the reverse of each other, because both singlet and triplet excitons may exist in many different excited states so each process may actually proceed via different intermediate channels. In this paper we shall examine the consequences of these differences.

There is, however, a close relationship between the fission and fusion processes and one would expect that their theoretical descriptions are similar. An important common characteristic is their magnetic field dependence, caused by the interaction of the field with triplet pairs in both fusion and fission. These magnetic field effects have proven to be a powerful tool for studying fusion[10] and may be even more important for fission studies. Fusion is the better known process and we shall use the accepted descriptions to develop a model for fission.

The first description of triplet-exciton fusion which successfully explained the magnetic field dependence of delayed fluorescence in anthracene crystals was given by Johnson and Merrifield.[10] The central part of their model is a density-matrix equation for the creation and dissociation of triplet pairs. Triplet excitons are considered either "free," or in a "correlated pair state." An interplay between the Zeeman interaction and the triplet-exciton fine structure determines the distribution of the overall spin character of the correlated triplet pair states and the dynamics of their spin motion. Only a pair with some singlet character can annihilate, and yield a singlet exciton. Since the Zeeman interaction is a function of a magnetic field, the annihilation rate and consequently the delayed fluorescence intensity are influenced by the magnetic field.

This pair state model has been extended to describe singlet-exciton fission,[6,12,13] but it has been concluded that for tetracene at least, this model was not completely satisfactory.[14] This is in agreement with earlier conclusions which led Suna[11] to develop a detailed description of fusion (referred to as S I hereafter) in which a density-matrix equation describing triplet-pair motion in terms of a hopping model was derived and solved. In this paper we extend this hopping model to the fission process, and compare its predictions to experimental data.

II. CONSIDERATIONS ON A GENERALIZED HOPPING MODEL DESCRIBING EXCITON FISSION

In view of the close relationship between fission and fusion, it is to be expected that an equation describing fission would be very similar. The equation describing triplet fusion given in S I, Eq. (30), for steady state and with $\hbar = 1$ is given by

$$0 = -i[H, \rho(\vec{R})] + 2\beta(\tfrac{1}{3}nv)^2 I - 2\beta\rho(\vec{R})$$
$$+ 2\sum_{\vec{R}'} \psi(\vec{R} - \vec{R}')\rho(\vec{R}')$$
$$- 2\rho(\vec{R})\left(\sum_{\vec{R}} \psi(\vec{R}') - \psi(\vec{R})\right)$$
$$- \tfrac{1}{2}[\Lambda(\vec{R})\rho(\vec{R}) + \rho(\vec{R})\Lambda(\vec{R})] \tag{1}$$

together with the boundary condition

$$\rho(0) = 0, \tag{2}$$

which expresses that no two excitons can occupy the same site. In these equations $\rho(\vec{R})$ is the exciton-pair density matrix as defined in Appendix

B of SI. The trace over the spin variables of $\rho(\vec{R})$ is equal to the probability of finding an exciton pair on two molecules for which the vector difference of their positions is equal to $\vec{R}$. The Hamiltonian operator H of the exciton pair is assumed to be independent of $\vec{R}$, n is the triplet-exciton density, β is the reciprocal triplet lifetime, v is the volume per molecule, and I is a 9×9 unit matrix. $\psi(\vec{R})$ is the exciton jump rate between molecules separated by $\vec{R}$. $\Lambda(\vec{R})$ is the annihilation operator given by

$$\Lambda(\vec{R}) = \lambda_S(\vec{R})P_S + \lambda_T(\vec{R})P_T + \lambda_Q(\vec{R})P_Q , \qquad (3)$$

where P_S, P_T, and P_Q are projection operators into the singlet, triplet, and quintet spin manifolds of pair states, and $\lambda_S, \lambda_T, \lambda_Q$, the corresponding annihilation rates for triplet pairs separated by $\vec{R}$.

The macroscopic triplet annihilation rate γ_s for annihilation events which lead to a singlet exciton is calculated from $\rho(\vec{R})$ by the relation

$$\gamma_s n^2 = \frac{1}{v} \sum_{\vec{R}} \lambda_s(\vec{R}) \mathrm{Tr}[P_s \rho(\vec{R})] . \qquad (4)$$

In the case of fusion, as described by Eqs. (1)–(4), the triplet pairs are produced from uncorrelated individual triplet excitons which are distributed homogeneously throughout the crystal bulk. This is why the source term $2\beta(\frac{1}{3}nv)^2 I$ in Eq. (1) is proportional to the square of the equilibrium density and to the unit matrix.

In the case of fission the triplet pairs are generated by decaying singlet excitons. Therefore, we expect the triplet-pair source term to be proportional to the singlet exciton density m, multiplied by the projection operator P_S. At the moment of the singlet-exciton fission, the triplet pairs formed in this manner will be highly spacially correlated. These pairs will then either annihilate or dissociate. Dissociation followed by spin relaxation and then reforming of a triplet pair would appear as an uncorrelated triplet-pair source term, described by the term $2\beta(\frac{1}{3}nv)^2 I$ of Eq. (1). However, if the singlet-exciton density m is kept small, $n \propto m$, then $2\beta(\frac{1}{3}nv)^2$ is small, and can be neglected. Any correlation due to interactions between singlet and triplet excitons can also be neglected in this low-density limit, because the corresponding terms are proportional to the product mn.

In the source term important for fission studies, we must consider intersystem crossing and the subsequent fission of the highly excited triplet exciton into two low-energy triplet excitons, i.e.,

$$S^* \to T^* \to T + T , \qquad (5)$$

which is the reverse of the observed process[15]

$$T + T \to T^* . \qquad (6)$$

It is of course implicit that the processes shown in Eqs. (5) and (6) are energetically possible.

Thus with similar methods to those given in Appendixes A and B of SI, we find that the equation describing singlet-exciton fission is given by

$$
\begin{aligned}
0 = 2mv\left(\kappa_s(\vec{R})P_s + \sum_{i=1}^{3} \frac{C_i}{\beta_T^*} \kappa_{iT}(\vec{R})P_{iT}\right) \\
- i\,[H, \rho(\vec{R})] - 2\beta\rho(\vec{R}) + 2\sum_{\vec{R}'} \psi(\vec{R} - \vec{R}')\rho(\vec{R}') \\
- 2\rho(\vec{R})\left(\sum_{\vec{R}'} \psi(\vec{R}') - \psi(\vec{R})\right) \\
- \tfrac{1}{2}[\Lambda(\vec{R})\rho(\vec{R}) + \rho(\vec{R})\Lambda(\vec{R})] .
\end{aligned}
\qquad (7)
$$

Here, $\kappa_s(\vec{R})$ and $\kappa_{iT}(\vec{R})$ denote the probability per unit time that two triplet excitons with a separation $\vec{R}$ are created from a singlet exciton, or from a triplet exciton in its spin state $|i\rangle$, respectively. C_i is the intersystem crossing rate from the singlet state into the triplet spin state i, P_{iT} is the corresponding projection operator, and β_T^* is the decay rate of the hot triplet state. The only difference between this equation describing exciton fission and Eq. (1) describing fusion is the source term.

In order to experimentally investigate singlet-exciton fission, the crystal is excited with a low density of light of greater energy than twice the lowest triplet energy. The primary fission process, described by the functions $\kappa_s(\vec{R})$ and $\kappa_{iT}(\vec{R})$, is not influenced by a magnetic field, however, the immediate annihilation of this triplet pair to reform a singlet exciton is magnetically active. In exactly the same way as the exciton fusion rate is a function of the magnetic field strength and orientation, so the net fission rate is a function of these two experimental parameters. Thus the important point in our theoretical analysis is an examination of the reannihilation events which lead back to singlet excitons. We can write Γ_s the rate of reproducing singlet excitons per unit time and volume as

$$\Gamma_s = \frac{1}{2}\frac{1}{v} \sum_{\vec{R}'} T_r[P_s\rho(\vec{R})]\lambda_s(\vec{R}) . \qquad (8)$$

Equation (8) can be directly compared to Eq. (4), which describes the annihilation rate for triplet fusion events leading to singlet excitons, the difference being the factor $\frac{1}{2}$, which is necessary since two triplet excitons produce only one singlet exciton. Naturally the same boundary condition, Eq. (2), must be invoked, together with Eq. (7). We need to calculate Γ_s. Now, since the pair Hamiltonian is invariant under exciton exchange, the eigenstates are either even or odd under this

exciton interchange, the odd states being pure triplet states. We express Eq. (7) in a basis of these eigenstates. From Eq. (8), it then follows that in calculating Γ_s we need only to consider the even-even elements of the density matrix $\rho(\vec{R})$. Equation (7) then reduces to

$$0 = mv\kappa_s(\vec{R})(P_s)_{kl} - [\beta + \tfrac{1}{2}i(E_k - E_l)]\rho_{kl}(\vec{R})$$
$$+ \sum_{\vec{R}'} \psi(\vec{R} - \vec{R}')\rho_{kl}(\vec{R}') - \rho_{kl}(\vec{R})\left(\sum_{\vec{R}'} \psi(\vec{R}') - \psi(\vec{R})\right)$$
$$- \tfrac{1}{4}\lambda_s(\vec{R})[\rho(\vec{R})P_s + P_s\rho(\vec{R})]_{kl} , \tag{9}$$

where E_k are the triplet-state eigenvalues and here quintet states have been assumed energetically inaccessible, i.e., $\lambda_Q = 0$. Thus the problem is reduced to solving Eq. (9) with the boundary condition $\rho(0) = 0$, Eq. (2).

Equation (9) is formally solved by the following expression, which is analogous to Eq. (30) in S I:

$$\rho_{kl}(R) = \sum_{\vec{R}'} g(\vec{R} - \vec{R}')\{\tfrac{1}{4}\lambda_s(\vec{R}')[\rho(\vec{R}')P_s + P_s\rho(\vec{R}')]_{kl}$$
$$- \psi(\vec{R}')\rho_{kl}(\vec{R}') - mv\kappa_s(\vec{R}')(P_s)_{kl}\}$$
$$+ g(\vec{R})\sum_{\vec{R}'} \psi(\vec{R}')\rho_{kl}(\vec{R}') . \tag{10}$$

Equation (10) contains a Green's function $g(\beta, \vec{R})$, with β as a complex parameter. This function is defined by

$$\delta_{RO} = \sum_{\vec{R}'} \psi(\vec{R} - \vec{R}')g(\beta, \vec{R}')$$
$$- g(\beta, \vec{R})\sum_{\vec{R}'} \psi(\vec{R}') - \beta g(\beta, \vec{R}) . \tag{11}$$

Then we perform so-called smooth approximation,[11] where $\rho(\vec{R})$ and $g(\beta, \vec{R})$ are replaced by their averages $\bar{\rho}$ and $\bar{g}(\beta)$, respectively, the average being taken over all values of $\vec{R}$ for which either $\lambda_s(\vec{R}) \neq 0$, or $\kappa_s(\vec{R}) \neq 0$, or $\psi(\vec{R}) \neq 0$. This smooth approximation can be made if $g(\beta, \vec{R})$ and $\rho(\vec{R})$ vary only slightly over all such values of $\vec{R}$. Finally we find

$$\bar{\rho}_{kl} = G[\beta + \tfrac{1}{2}i(E_k - E_l)]$$
$$\times [-mv\kappa(P_s)_{kl} + \tfrac{1}{4}\lambda(\bar{\rho}P_s + P_s\bar{\rho})_{kl}] , \tag{12}$$

where G is a function defined by

$$G(\beta) = (\beta + \psi)\bar{g}(\beta)/\psi[1 + \beta\bar{g}(\beta)] , \tag{13}$$

and λ, κ, and ψ are sums of all nonzero terms:

$$\lambda = \sum_{\vec{R}} \lambda_s(\vec{R}), \quad \kappa = \sum_{\vec{R}} \kappa_s(\vec{R}), \quad \text{and } \psi = \sum_{\vec{R}} \psi(\vec{R}) . \tag{14}$$

The reannihilation rate of triplet-exciton pairs is given by the smooth approximation of Eq. (8),

$$\Gamma_s = \tfrac{1}{2}(1/v)\lambda\text{Tr}(P_s\bar{\rho}) . \tag{15}$$

This rate equation can be evaluated easily if all energy levels are sufficiently far apart so that

$$G[\beta + \tfrac{1}{2}i(E_k - E_l)] \ll G(\beta), \quad k \neq l . \tag{16}$$

The solution of Eq. (12) is then straightforward and Eq. (15) yields

$$\Gamma_s = m\kappa \sum_l \frac{K|S_l|^4}{1 + K|S_l|^2} , \tag{17}$$

where K is

$$K = -\tfrac{1}{2}\lambda G(\beta) \tag{18}$$

and S_l is the singlet component of the lth eigenfunction. If the inequality (16) does not hold the solution of Eq. (12) is obtained similarly as in S I.

So far we have described a fission process in which both the triplet pair and the singlet have the same energy. A more general case which is closer to a real situation will be considered next.

III. ENERGY DEPENDENCE OF SINGLET EXCITON FISSION

The starting point of the calculations in Sec. II is Eq. (9), which can be represented by the following kinetic scheme:

$$\tag{19}$$
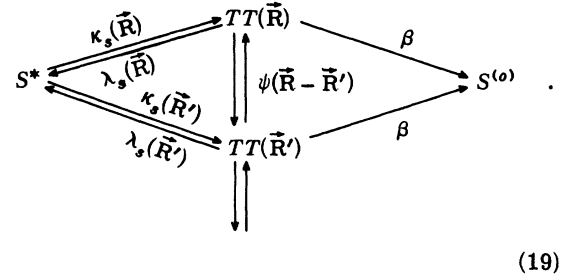
Here $TT(\vec{R})$ represents a triplet pair with mutual separation $\vec{R}$ and $S^{(o)}$ is the electronic ground state. All other symbols were defined earlier. In accordance with the calculations which follow Eq. (9), Eq. (19) can be abbreviated to

$$S^* \underset{\Gamma_s}{\overset{\kappa}{\rightleftharpoons}} [TT] \overset{\beta}{\longrightarrow} S^{(o)} , \tag{20}$$

where $[TT]$ represents all possible spatial configurations of the triplet pair.

In the model for fission, so far we have assumed S^* to be made up of identical excited singlets, and likewise all triplet pairs which annihilate are identical. In reality, however, these assumptions may not be satisfactory; i.e., there can be different electronically excited singlet states, even charge-transfer states. We shall label all singlet states in our model by their energy alone, without considering of which electronic and vibrational states they are composed. This is shown schematically

in Fig. 1(a). Each excited singlet state can emit phonons of a wide range of energies in relaxing to lower states. If we divide the energy scale into equal intervals ΔE, where ΔE is larger than the average energy of the emitted phonons, then the probability that any excited state will decay by an energy greater than ΔE in a single event is small. Naturally, this probability can be adjusted by a judicious choice of ΔE. We shall represent all states in each of these intervals as a single entity $S^{(p)}$, where the superscript p denumerates the given energy interval. These energy intervals, which we shall call levels, may contain different electronic states as well as vibrational states. Such differences in character have to be taken into account by a proper definition of the parameters which describe the whole level. The population of each level is equal to the sum of the populations of all substates in this level, and the decay rate $\beta_s^{(p)}$ of each level is equal to the total transfer rate to the next lower level. This is shown in Fig. 1(b). Other parameters are defined in a similar way.

The same approximation can be performed for the triplet pair states. By $TT^{(p)}(\vec{R})$ we shall represent all triplet pairs with mutual separation $\vec{R}$ and total energy within the pth energy interval. The effective decay rate for such a group of triplet pairs is $2\beta_T^{(p)}$. The state $TT^{(p)}(\vec{R})$ can annihilate with the effective probability $\lambda_s^{(p)}(\vec{R})$ of creating the singlet state $S^{(p)}$. Any singlet state above the fission threshold energy can transform into a triplet-pair state $TT^{(p)}(\vec{R})$ with the effective probability $\kappa_s^{(p)}(\vec{R})$. With the abbreviated notation of the scheme Eq. (20), Fig. 2 represents an overall description of fission. It is actually a composition of generalized versions of the elementary scheme Eq. (20), stacked on top of each other and connected by the vibrational relaxation processes. The generalization consists of considering all triplet pairs with total energy within the pth energy interval rather than triplet pairs of one kind only.

We can now follow the process of fission as it is described by Fig. 2. First, highly excited singlet excitons $S^{(n)}$ are generated at a rate $\alpha^{(n)}$, for example, by direct absorption of light. Each exciton $S^{(n)}$ can undergo fission, yielding all possible configurations of the triplet pair $[TT^{(n)}]$ with a total rate $\kappa^{(n)}$, provided that $n \geq k_0$, where k_0 denotes the lowest energy for which fission is possible. Second, $S^{(n)}$ can relax to a lower-energy singlet state $S^{(n-1)}$ at a rate $\beta_s^{(n)}$, or decay to a different electronic state or states at a rate $C^{(n)}$. We will not specify these different electronic states, but simply assume that the transfer rates $C^{(n)}$ are independent of magnetic field and that there is no feedback into either the triplet-pair manifolds or singlet manifolds of Fig. 2. Similar
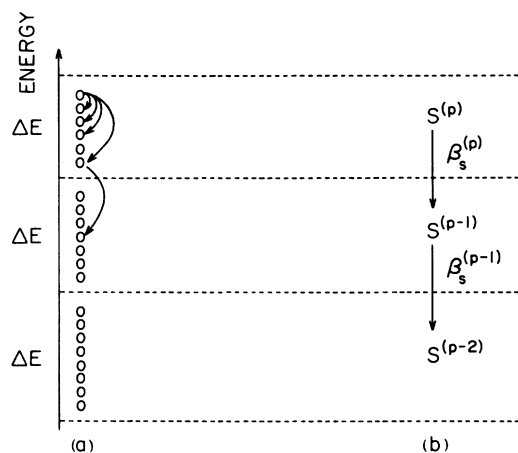

FIG. 1. (a) Schematic representation of the singlet vibrational decay. Each circle represents an excited singlet state, and the arrows denote some possible decay channels. ΔE is approximately the maximum energy of emitted phonons. (b) Mathematical representation of the decay processes of 1(a). $S^{(p)}$ is the singlet state which corresponds to all states within the pth energy interval; $\beta_s^{(p)}$ is the vibrational decay rate.
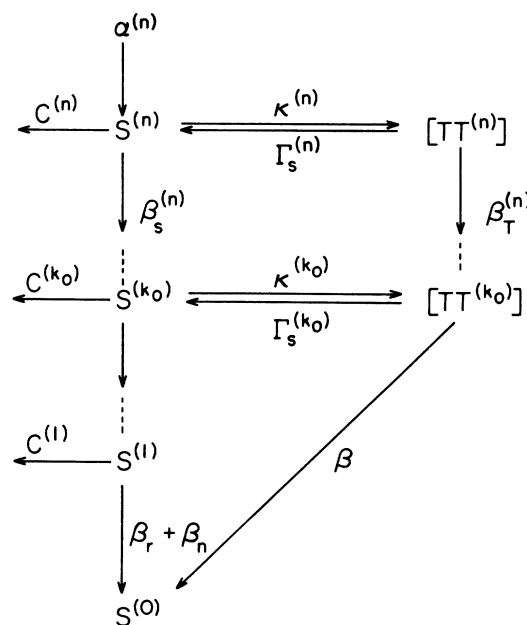

FIG. 2. Kinetic scheme of singlet-exciton fission into triplet pairs. $\alpha^{(n)}$ is singlet generation rate, $S^{(p)}$ are excited singlet states, and $[TT^{(p)}]$ are all triplet pairs with total energy within the pth energy interval (see Fig. 1). $\beta_s^{(p)}$, $\beta_T^{(p)}$, β_n, and β are vibrational, internal conversion, and intersystem crossing rates. β_r is the radiative decay rate. $\kappa^{(p)}$ and $\Gamma_s^{(p)}$ are singlet fission and triplet fusion rates, respectively. $C^{(p)}$ can be any decay rates which are independent of magnetic field and do not feed back into the $S^{(1)}$-$S^{(n)}$ or $[TT^{(k_0)}]$-$[TT^{(n)}]$ manifolds.

consideration applies to lower singlet states with the exception of $S^{(1)}$, the decay of which is only governed by β_r, β_n, and $C^{(1)}$, which are the radiative, nonradiative internal conversion, and intersystem crossing rates, respectively.

The highly excited triplet pairs which have been produced by singlet fission can either decay to a triplet pair of lower energy or annihilate back to the singlet manifold. Thus at each level of the vibrational decay a fusion feedback is possible, which enhances the singlet concentration and consequently the fluorescence intensity. However, a detailed description of the fusion feedback at each level is not simple. The individual excitons of each triplet pair produced by fission may not be of the same kind. They may be of different energy and they may have different fine structure and transport properties. Thus the exchange symmetry of the pair is broken and we have to deal with heterofusion, which is more complicated than homofusion, and for which no suitable model is available so far.

We shall only consider cases where the description of the fusion feedback is simple. Since highly excited states in molecular crystals in general decay very rapidly, it will be useful to consider an approximation in which the relaxation rates $\beta_T^{(p)}$ of the triplet pairs are sufficiently large, that the fusion feedback is negligible at all stages of the vibrational decay except at the level k_0. Then we may set

$$\Gamma_s^{(p)} = 0 , \quad p = k_0 + 1, \ldots, n$$

$$\Gamma_s^{(k_0)} = \Gamma_s .$$

(21)

The fusion feedback at the level k_0 can be described by Eq. (9). Only a different source term is needed because the triplet-pair population at this level is composed of pairs which were generated by the fission at higher levels. The source term required is a sum of density matrices which describe the triplet pairs at the moment their decay to the level k_0 has been completed. During this decay both the spatial configuration and the spin-wave function of the triplet pairs change. It will therefore be useful to assume that the decay rates $\beta_T^{(p)}$ are much larger than the triplet-exciton hopping rates and the frequency of spin precession at all levels p for $p > k_0$. In view of the rapid vibrational relaxation rates, this assumption is quite realistic. The source term is then given by the expression

$$\sum_{p=k_0}^{n} v m^{(p)} \kappa_s^{(p)}(\vec{R}) P_s ,$$

(22)

where $m^{(p)}$ is the singlet population at the level p.

The fission process in a steady-state condition can now be described by the following system of coupled equations:

$$0 = \alpha^{(n)} - (\beta_s^{(n)} + \kappa^{(n)} + C^{(n)}) m^{(n)} ,$$

(23)

$$0 = \beta_s^{(p+1)} m^{(p+1)} - (\beta_s^{(p)} + \kappa^{(p)} + C^{(p)}) m^{(p)} ,$$

$$p = k_0 + 1, \ldots, n - 1$$

(24)

$$0 = \beta_s^{(k_0+1)} m^{(k_0+1)} - (\beta_s^{(k_0)} + \kappa^{(k_0)} + C^{(k_0)}) m^{(k_0)} + \Gamma_s ,$$

(25)

where Γ_s is obtained by inserting the source term (22) into Eq. (9) in place of the old source term $m v \kappa_s(\vec{R}) P_s$, solving this new Eq. (9) for ρ and using ρ in Eq. (8).

Since Eqs. (8) and (9) are linear in ρ, then in the smooth approximation we can write Γ_s as

$$\Gamma_s = \epsilon \sum_{p=k_0}^{n} m^{(p)} \kappa^{(p)} ,$$

(26)

where ϵ is a factor independent of the source term, that is, only a function of the magnetic field. It is equal to the proportion of triplet pairs which reannihilate to form a singlet state. In the special case where there is no level crossing, ϵ is given by

$$\epsilon = \sum_{l=1}^{6} \frac{K |S_l|^4}{1 + K |S_l|^2}$$

(27)

which is obtained from Eqs. (17) and (26).

Since the feedback ratio ϵ is magnetic field dependent, also the singlet-state populations at and below the level k_0 and the fluorescence intensity F are a function of magnetic field. A convenient experimental quantity which represents this magnetic field dependence is the relative change of the fluorescence intensity in a magnetic field B, which can be written

$$\Delta_{rel} F = [F(B) - F(0)] / F(0) .$$

(28)

From the decay scheme in Fig. 2 it is clear that F is proportional to the singlet population $m^{(k_0)}$, so that we may write Eq. (28) as

$$\Delta_{rel} F = \frac{m^{(k_0)}(B) - m^{(k_0)}(0)}{m^{(k_0)}(0)} .$$

(29)

Let us assume that

$$\frac{\kappa^{(k_0)}}{\beta_s^{(k_0)}} \ll \sum_{p=k_0+1}^{n} \frac{\kappa^{(p)}}{\beta_s^{(p)}}$$

(30)

which means that a significant proportion of fission does not occur on the lowest possible level, but is distributed along the whole singlet decay path. Further we assume large decay rates $\beta_s^{(p)}$, i.e.,

$$\sum_{p=k_0}^{n} \frac{\kappa^{(p)} + C^{(p)}}{\beta_s^{(p)}} \ll 1.$$

(31)

Then by solving the system of equations (23) through (26) for $m^{(k_0)}$ and substituting $m^{(k_0)}$ into Eq. (29) we obtain

$$\Delta_{rel}F = [\epsilon(B) - \epsilon(0)] \sum_{p=k_0}^{n} \frac{\kappa^{(p)}}{\beta_s^{(p)}} \, . \tag{32}$$

From Eq. (32), $\Delta_{rel}F$ can be split into a product of two factors. The first factor $\epsilon(B) - \epsilon(0)$ is a function of magnetic field. In the smooth approximation this factor is related to the triplet annihilation rate γ_s from Eq. (4) by

$$\epsilon(B) - \epsilon(0) = -\frac{9\gamma_s(0)}{v\lambda} \frac{\gamma_s(B) - \gamma_s(0)}{\gamma_s(0)} \, . \tag{33}$$

The second factor is

$$\sum_{p=k_0}^{n} \frac{\kappa^{(p)}}{\beta_s^{(p)}} \, ,$$

which is a nondecreasing function of the excitation energy.

Similar equations to Eqs. (32) and (33) have been derived for the pair-state model,[16] but in contrast the equations given here are directly related to the microscopic parameters of singlet fission which can thus be calculated from experimental results. A further important difference is the assumption of the smooth approximation, which has no analog in the pair-state model. The relevance of the smooth approximation together with the other assumptions made here will be discussed next.

IV. VALIDITY OF THE EXCITON FISSION MODEL

One of the assumptions made in Sec. III was that the annihilation feedback into the singlet manifold at all energy levels except k_0 is negligible because of the very fast relaxation rates $\beta_T^{(p)}$. To show that this is a good assumption we must calculate the annihilation rate for each level. As we have already mentioned, Eq. (7) need not be valid with very large excess energies, i.e., very high levels. However, since we only need to estimate the rates $\Gamma_s^{(k_0+1)}$ to $\Gamma_s^{(n)}$, even an approximate calculation will be useful. We let the triplet-pair population at each level p for $p = k_0 + 1, \ldots, n$ consist mainly of pairs which are symmetric with respect to particle interchange, decay with an average rate $\beta_T^{(p)}$, and whose motion can be described in terms of the hopping model. The highest feedback rate will occur on pair-level crossing resonance at high magnetic fields. In this case there is only one pair eigenstate with a singlet component equal to 1. Since there are no other pair eigenstates with a nonzero singlet component, this case can be treated as if no level crossing existed. Then from Eq. (27), the feedback factor $\epsilon^{(p)}$ at level p can be written

$$\epsilon^{(p)} = K^{(p)}/(1 + K^{(p)}), \tag{34}$$

where

$$K^{(p)} = -\tfrac{1}{2}\lambda^{(p)}G^{(p)}(\beta_T^{(p)}). \tag{35}$$

The decay rates $\beta_T^{(p)}$ and the feedback ratios $\epsilon^{(p)}$ are a function of ΔE. Therefore, in the estimate of $\epsilon^{(p)}$ we have to specify ΔE, and as an example let us set $\Delta E = 1$ eV.

For convenience we can rewrite Eq. (35) as

$$K^{(p)} = \frac{\lambda^{(p)}}{\psi^{(p)}} [-\tfrac{1}{2}\psi^{(p)}G^{(p)}(\beta_T^{(p)})] \tag{36}$$

because it can be seen from Eq. (13) and from the continuum approximation for the Green's function in S I that $-\tfrac{1}{2}\psi^{(p)}G^{(p)}(\beta_T^{(p)})$ is an increasing function of $\psi^{(p)}/\beta_T^{(p)}$ only. The meanings of $G^{(p)}$, $\lambda^{(p)}$, and $\psi^{(p)}$ in Eqs. (35) and (36) are analogous to those in Eqs. (13) and (14).

Thus we can write $K^{(p)}$ as a product of two factors, one of which is equal to $\lambda^{(p)}/\psi^{(p)}$ and the other is an increasing function of $\psi^{(p)}/\beta_T^{(p)}$. The estimate of the magnitude of $K^{(p)}$ is then based on the estimate of ratios $\lambda^{(p)}/\psi^{(p)}$ and $\beta_T^{(p)}/\psi^{(p)}$.

Both $\lambda^{(p)}$ and $\psi^{(p)}$ are determined by the overlap of the molecular wave functions. For anthracene at the lowest level ($p = k_0$) the ratio $\lambda^{(p)}/\psi^{(p)}$ is equal to 1.2.[11] At higher levels we expect that this ratio is even larger, since with increasing energy the excited molecular states are more delocalized. The decay rates $\beta_T^{(p)}$ may be expected to be between 10^{12} and 10^{13} sec^{-1}.[17] With the value of 2.5×10^{11} sec^{-1} for $\psi^{(k_0)}$ in the case of anthracene[11] we can estimate $\psi^{(p)} > 10^{11}$ sec^{-1}. This gives $\psi^{(p)}/\beta_T^{(p)} > 10^{-2}$ in the most favorable case.

Combining all these results and using the continuum approximation for the Green's function[11] we obtain $\epsilon^{(p)} \approx K^{(p)} > 10^{-5}$ for three-dimensional motion and $\epsilon^{(p)} \approx K^{(p)} > 10^{-4}$ for quasi-two-dimensional motion. We see that this approximation yields only the lower limit for the feedback ratio $\epsilon^{(p)}$. For $\beta_T^{(p)}/\psi^{(p)} \gg 1$ the Green's functions are nearly exponential functions and $K^{(p)}$ is very sensitive to $\beta_T^{(p)}/\psi^{(p)}$.

From this estimate it appears that the fusion feedback at high energy levels may not be negligible with respect to $\Gamma_s^{(k_0)}$. However, with $\beta_T^{(p)} = 10^{12}$–10^{13} sec^{-1} for $p > k_0$ the natural width of the pair energy levels with a singlet character is 10^2 to 10^3 times larger than their mutual separation given by the fine-structure interaction. Due to such large linewidths the resonance line shapes can be considered nearly Lorentzian, which means that the magnetic field modulation of $\epsilon^{(p)}$ is only 10^{-6} to 10^{-4} and the feedback rates can be considered practically independent of magnetic field. In the first approximation this is the same as re-

placing the fission rates $\kappa^{(p)}$ by suitable effective fission rates $\kappa_{eff}^{(p)}$, which are smaller than $\kappa^{(p)}$, and setting $\Gamma_s^{(p)} = 0$ for $p > k_0$. With this result we shall further substitute

$$\lambda_s(\vec{R}) = \lambda_s^{(k_0)}(\vec{R}); \tag{37}$$

$\lambda_s^{(p)}(\vec{R})$ for $p > k_0$ is not important in the system under discussion.

Another important question is how far apart the exciton pair can dissociate during its decay from some level $p > k_0$ to the lower level k_0. The dissociation is essentially determined by the branching ratios $\beta_T^{(r)}/\psi^{(r)}$ at all stages r between p and k_0. If $\beta_T^{(r)}$ is so fast that no change of spin state occurs during the decay, we can account for this dissociation by replacing the functions $\kappa_s^{(p)}(\vec{R})$ in the source term (22) by the appropriate pair distribution functions obtained from the equation of hopping motion. We shall therefore use the source term (22), where the dissociation during the decay of the pair from level p to level k_0 is already included in the function $\kappa_s^{(p)}(\vec{R})$. All calculations and results of Sec. III remain of course the same provided that the smooth approximation is valid. However, if the hopping rates $\psi^{(r)}$ are relatively large, the source term (22) is nonzero even for larger $\vec{R}$ than just for that which corresponds to nearest neighbor separation, and the conditions of the smooth approximation may not be fulfilled: the function $g(\vec{R})$ and the density matrix $\rho(\vec{R})$ may have different values for those $\vec{R}$ for which the source term (22) is nonzero. For this case the smooth approximation procedure has to be modified. We shall split each source function $\kappa_s^{(p)}(\vec{R})$ into a sum of two functions:

$$\kappa_s^{(p)}(\vec{R}) = \kappa_s'^{(p)}(\vec{R}) + \kappa_s''^{(p)}(\vec{R}), \tag{38}$$

where $\kappa_s'^{(p)} = \kappa_s^{(p)}(\vec{R})$ for all $\vec{R}$ for which $\lambda_s(\vec{R}) \neq 0$, and $\kappa_s'^{(p)}(\vec{R}) = 0$ for the remaining values of $\vec{R}$. Since Eq. (9) is a linear equation in ρ, the resulting density matrix is also a sum of two terms

$$\rho(\vec{R}) = \rho'(\vec{R}) + \rho''(\vec{R}), \tag{39}$$

where $\rho'(\vec{R})$ is calculated by substituting $\sum_p m^{(p)}\kappa_s'^{(p)}(\vec{R})P_s$ as a source term in Eq. (9) and $\rho''(\vec{R})$ is calculated in the same way from $\sum_p m^{(p)}\kappa_s''^{(p)}(\vec{R})P_s$. We shall assume for all $\vec{R}$ for which $\lambda_s(\vec{R})$ or $\psi^{(k_0)}(\vec{R})$ are nonzero that

$$g(\beta, \vec{R}) = \bar{g}(\beta), \quad \rho'(\vec{R}) = \bar{\rho}', \quad \rho''(\vec{R}) = \bar{\rho}''. \tag{40}$$

Using this assumption and the linearity of Eq. (9) then

$$\Gamma_s = \epsilon \sum_{p=k_0}^{n} m^{(p)}\kappa'^{(p)} + \sum_{\vec{R}} \epsilon(\vec{R}) \sum_{p=k_0}^{n} m^{(p)}\kappa_s''^{(p)}(\vec{R}), \tag{41}$$

where ϵ is given by Eq. (27) and $\epsilon(\vec{R})$ is the feedback ratio for triplets generated with a mutual distance $\vec{R}$. In the special case of no level crossing

$$\epsilon(\vec{R}) = \epsilon g(\beta, \vec{R})/\bar{g}(\beta) \leq \epsilon, \tag{42}$$

which means that the larger the mutual distance $\vec{R}$, the smaller the reannihilation probability, because $|g(\beta, \vec{R})|$ is a nondecreasing function of the length of the vector $\vec{R}$. In general the linewidth of the level crossing resonances decreases with increasing p, although for larger $\vec{R}$ the pair dissociation is faster. Line narrowing will also occur where the higher singlet states are more delocalized, since the triplet pairs are generated further apart.

If the spin state of the triplet pair changes significantly during the decay to the k_0 level, we have to replace not only $\kappa_s^{(p)}(\vec{R})$ by new source functions, but also replace the projection operator P_s in the source term by more general operators determined by the evolution of the pair spin state from the initial singlet state during the decay. Since some of the pair states on the decay ladder may be nonsymmetrical with respect to the particle interchange, these pairs can acquire a nonzero triplet component during their decay. After such pair states have decayed to the lowest level and have become symmetric with respect to particle interchange, they cannot annihilate back to the singlet manifold. This can again be described by a feedback factor which is decreasing with increasing excitation energy. Putting this feedback factor equal to ϵ from Eq. (27) introduces an error per level which is given by the ratio of the asymmetry of the pair spin Hamiltonian to the triplet decay rate $\beta_T^{(p)}$. Since this asymmetry is smaller than the fine-structure interaction, the error is less than 10^{-2} to 10^{-3}.

Triplet spin relaxation at the k_0 level may also be important. With the term describing the spin relaxation [S I, Eq. (49)] included in Eqs. (1) and (7) and the branching ratio C_i/β_T^* equal to only 10^{-3}–10^{-4},[17] then

$$9\gamma_s/\lambda v + \epsilon = 1 - \delta(1 - \epsilon), \tag{43}$$

where

$$0 \leq \delta \leq \frac{1}{6}\sum_{\vec{R}} \lambda_T(R)[G(\beta + \xi) - G(\beta)] \tag{44}$$

and ξ is the average spin relaxation rate as defined in S I. Equation (43) is an approximation valid only for $\delta \ll 1$; for $\delta = 0$ it is equivalent to Eq. (33). From Eq. (43) if ξ is a function of magnetic field, then the magnetic field modulations of fusion and of fission are different. For anthracene $\lambda_T \approx \lambda$,[15] $\delta \approx 1.5 \times 10^{-2}$ and to $B = 4$ kG, ξ is nearly independent of magnetic field,[11] so the influence of the spin relaxation is negligible.

The smooth approximation will also fail when interplane annihilation in the nearly-two-dimension-

al system is not negligible. We can consider this special case in the following manner. Similar to Eqs. (38) and (39), we split the source function and the density matrix into two components. For the source function we write

$$\kappa_s^{(p)} = \kappa_s'^{\,(p)}(\vec{R}) + \kappa_s''^{\,(p)}(\vec{R}),\tag{45}$$

where in this case $\kappa_s''^{\,(p)}(\vec{R}) = \kappa_s^{(p)}(\vec{R})$ for all $\vec{R}$ which connect different planes of fast diffusion (in anthracene these are the ab planes) and $\kappa_s''^{\,(p)}(\vec{R}) = 0$ for all remaining values of $\vec{R}$. This implies a decomposition of the density matrix ρ into two components ρ' and ρ'' as described by Eq. (39). The reason for this failure of smooth approximation is the large anisotropy of exciton motion. Therefore we have to separate the microscopic annihilation rate $\lambda_s(\vec{R})$ into the intraplane component $\lambda_s'(\vec{R})$ and the interplane component $\lambda_s''(\vec{R})$

$$\lambda_s(\vec{R}) = \lambda_s'(\vec{R}) + \lambda_s''(\vec{R})\tag{46}$$

which is similar to Eq. (45). If the interplane motion is much slower than intraplane motion, each component can be treated separately because from Eqs. (8), (39), and (46) it follows that

$$\Gamma_s = \frac{1}{2}\frac{1}{v}\sum_{\vec{R}}\,[\lambda_s'(\vec{R}) + \lambda_s''(\vec{R})]$$
$$\times\{\mathrm{Tr}[P_s\rho'(\vec{R})] + \mathrm{Tr}[P_s\rho''(\vec{R})]\},$$
$$\tag{47}$$

where the cross products can be neglected. This means

$$\Gamma_s = \frac{1}{2v}\sum_{\vec{R}}\,\{\lambda_s'(\vec{R})\,\mathrm{Tr}[P_s\rho'(\vec{R})]$$
$$+\lambda_s''(\vec{R})\,\mathrm{Tr}[P_s\rho''(\vec{R})]\}.\tag{48}$$

If we solve Eq. (9) with the source terms

$$\sum_{p=k_0}^{n} vm^{(p)}\kappa_s'^{\,(p)}(\vec{R})P_s$$

and

$$\sum_{p=k_0}^{n} vm^{(p)}\kappa_s''^{\,(p)}(\vec{R})P_s$$

we obtain ρ' and ρ'', respectively. From Eq. (48) we find

$$\Gamma_s = \sum_{p=k_0}^{n} m^{(p)}(\kappa'^{\,(p)}\epsilon' + \kappa''^{\,(p)}\epsilon''),\tag{49}$$

where ϵ' and ϵ'' are the magnetic-field-dependent feedback ratios for the intraplane and interplane fission, respectively. If the smooth approximation can be made for each of the two equations describing intraplane and interplane annihilation, then ϵ' and ϵ'' are independent of the source term.

From Eqs. (23), (24), (25), and (49) under the

assumptions Eqs. (30) and (31),

$$\Delta_{\mathrm{rel}}F = [\epsilon'(B) - \epsilon'(0)]\sum_{p=k_0}^{n}\frac{\kappa'^{\,(p)}}{\beta_s^{(p)}}$$
$$+[\epsilon''(B) - \epsilon''(0)]\sum_{p=k_0}^{n}\frac{\kappa''^{\,(p)}}{\beta_s^{(p)}}.\tag{50}$$

From Eq. (50) it follows that for $\epsilon'(B) - \epsilon'(0) \ge 0$ and $\epsilon''(B) - \epsilon''(0) \ge 0$, $\Delta_{\mathrm{rel}}F$ is a nondecreasing function of energy. This is a similar result as in Eq. (32). On the other hand, unlike in Eq. (32), the line shape of pair-level crossing resonances will in general depend on the excitation energy, if ϵ' and ϵ'' are different functions of the magnetic field B. For anthracene the interplane annihilation has been calculated to be approximately $\frac{1}{100}$ of the intraplane annihilation,[18] so only the intraplane fission and annihilation need to be considered.

Thus for anthracene only the influence of the dissociation of the triplet pair during the decay and the delocalization of higher singlet states have to be verified. The total influence of the other effects discussed is small, ~2%. For tetracene, however, the influence of spin relaxation and interplane annihilation have also to be verified.

V. COMPARISON WITH EXPERIMENTAL DATA FOR ANTHRACENE AND CONCLUSIONS

Equation (32) predicts that the relative change of fluorescence intensity $\Delta_{\mathrm{rel}}F$ in a magnetic field is a nondecreasing function of the excitation energy. This has been experimentally verified.[4,16] The small deviations found are of the order of the experimental error, but because the largest differences coincide with singlet absorption maxima, surface effects or high-density effects could be involved. High-density effects, which include uncorrelated $T - T$ annihilation and triplet quenching by singlet excitons would decrease magnetic field modulation, and we found they were unimportant for the modulation was independent of excitation intensity. Surface effects are more difficult to evaluate. Direct surface quenching is negligible, for the singlet absorption depth is at least 100 lattice spacings, far greater than the diffusion length of the correlated triplet pair, ~1 lattice spacing, (in two-dimension systems the decay rate of the correlated triplet pair will be approximately given by its hopping rate in the c' direction).[11] Defects and impurity centers are probably unimportant; melt-grown and sublimation flakes give similar results. Reabsorption effects have no influence for only hot singlet excitons undergo fission.

Equations (32) and (33) show that this magnetic field modulation $\Delta_{\mathrm{rel}}F$ should be proportional, but

reversed in sign to that for delayed fluorescence. Suna has shown the hopping model to be a good description for triplet fusion in anthracene, and the results of Klein et al.[4,13,16] show the magnetic field dependence of fission and fusion with respect to angular and field strength data is in accord with Eq. (33). However, a detailed comparison of the reported fission[13] and fusion line shapes showed some minor differences, which we have verified in our own room-temperature fission studies. In our experiments excitation was from a xenon arc continuum, wavelength selected by a monochromator, or from a He-Ne laser. Extraneous effect of the magnetic field on the experimental system was carefully minimized until it was less than 1 in 10^5. Mechanical effects were also minimized, and finally removed by comparing signals with and without magnetic fields. Samples were either sublimation flakes or melt-grown crystals. In all samples the magnetic field modulation of prompt fluorescence was independent of excitation energy, $\nu = 31\,500$, $34\,500$, $35\,200$, and $37\,600$ cm^{-1}, and comparable to Fig. 3, Ref. 13, $\nu = 53\,000$ cm^{-1}. In Fig. 3 results for a sublimation flake are shown, where the results for resonance intensities of delayed fluorescence are normalized to prompt fluorescence results. It is seen that fission peaks are broader than fusion peaks, and there is an additional anisotropy which causes the normalized fusion modulation to be greater than for fission in the a axis and lesser in the b axis. These differences, $\leq 15\%$, are greater than experimental error, $\leq 2\%$, and are larger than all effects discussed earlier baring the unknown influence of delocalization of the excited states formed and triplet-pair dissociation during
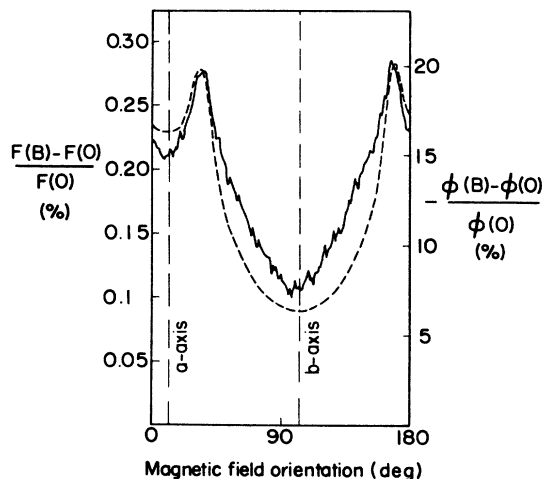

FIG. 3. Comparison of the magnetic field modulation of prompt fluorescence intensity $F(B)$ excited at $\nu = 34\,500$ cm^{-1} with the modulation of delayed fluorescence intensity $\phi(B)$ excited at $\nu = 15\,803$ cm^{-1}. Magnetic field $B = 4$ kG was rotated in the ab plane of an anthracene sublimation flake. Solid line: prompt fluorescence; broken line: delayed fluorescence.

the decay. However, these latter effects are very small, for no change in resonance linewidths with increasing excitation energy has been observed. These comparisons of experiment and theory show the hopping model of Suna, which has been shown to be the best description of triplet fusion, can be extended to provide a description of a singlet-exciton fission. However, though this description is a significant improvement over the pair state description, some experimental details of fission are still unexplained.

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