PHYSICAL REVIEW B VOLUME 24, NUMBER 8 15 OCTOBER 1981

Influence of spin relaxation on triplet-triplet exciton annihilation in organic crystals. Application to naphthalene

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(Received 17 February 1981)

The influence of exciton spin relaxation on the magnetic-field modulation of delayed fluorescence in organic crystals is discussed. It is shown that proper inclusion of the anisotropy of spin relaxation due to exciton hopping between nontranslationally equivalent molecules explains several observations, such as maxima of fluorescence for certain directions of the field, or asymmetric resonances of varying shapes. The model is here more specifically applied to naphthalene.

I. INTRODUCTION

The theory of the interaction between two triplet excitons has been treated in different ways by Johnson and Merrifield,[1] hereafter referred to as I, and by Suna,[2] referred to as II. Both theories account satisfactorily for the modulation by magnetic fields of the resulting delayed fluorescence in anthracene at room temperature. However, except in tetracene,[3] direct application of these theories to other materials is hampered by several problems.

(a) At "high"[4] magnetic fields, I and II predict delayed fluorescence minima for specific field directions, the so-called "resonances." However, unexplained maxima are observed in other field directions in most materials: naphthalene,[5,6] pyrene,[6] 1, 4-dibromonaphthalene,[7] and *trans*-stilbene.[8]

(b) In several nonprincipal planes[9] of naphthalene and pyrene, the line shapes of the two resonances are different,[6,10] sometimes very different, whereas theories I and II predict that both resonances should have the same shape and width.

(c) The variation of delayed fluorescence intensity with magnetic field strength at high field, for a given field direction, should be weak and monotonic, whereas maxima are observed for different field strengths in *trans*-stilbene[8] or 9,10-diphenylanthracene.[11]

An explanation for observation (a) in naphthalene has been proposed by Altwegg[5] by considering anisotropic spin relaxation, taken as a transition between different exciton magnetic sublevels. Results of Reineker's[12] high-field spin relaxation calculations are used in a perturbation calculation.

The unit cell of almost all molecular crystals contains nontranslationally equivalent molecules. In such crystals, the main physical origin of spin relaxation is the hopping of the excitation between such molecules[13] in the temperature range in which exciton transport is a diffusive incoherent hopping process. When the hopping time is shorter than the precession time on a site, an excitonic fine-structure tensor can be defined[13] and measured, and the well-known limit of motional narrowing is obtained.[14] So the same process, exciton diffusion, brings in both exciton interaction and exciton spin relaxation.[2,13] In the present paper, it is shown that all experimental data on the magnetic field modulation of delayed fluorescence in naphthalene [observations (a) and (b) above] are accounted for if spin relaxation is properly taken into account, that is, including both secular and nonsecular parts of $1/T_2$ and not only the latter.[5] Our purpose is to understand the physical processes, not to reproduce quantitatively experimental data, whose quality is at present, for practical reasons, not sufficient. We shall, therefore, introduce simple changes in existing theories and the corresponding equations. The approach is general and its validity is not restricted to the material used here for illustration, naphthalene.

II. THEORY

In the class of molecular crystals considered here—essentially aromatic hydrocarbons and similar molecules—triplet excitons are localized. Their motion is accurately described at "high" temperature—i.e., $T > 100$ K, at least—as random hopping of an excitation from a molecule to one of its nearest neighbors.[15] The triplet-triplet interaction is very short ranged, so that only interaction between nearest neighbors is usually considered. The interaction is then the result of two different processes, diffusion and subsequent reaction, and the kinematics of the interaction is governed by the diffusion process.[2]

A common feature of theories I and II is that since annihilation proceeds through a spin-allowed channel (delayed fluorescence is indeed an efficient radiative process), the probability of annihilation is equal to the fractional singlet amplitude S_n of the interacting exciton pair $|n\rangle$,[1,2] multiplied by a spin-independent constant treated as an adjustable parameter (there is no theory accounting satisfactorily for its value). The variations of S_n with magnetic field intensity and direction due to the interplay of fine-structure and Zeeman terms are observed as an anisotropic magnetic field modulation of the delayed fluorescence.

In theory I, the interaction is written as a chemical reaction by introducing a triplet pair (TT),

$$T + T \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (TT) \xrightarrow{k_2} S^* \ . \tag{1}$$

The elements of the density matrix describing the pair-state evolution are given by [I, Eq. (10)]:

$$\left[1 + \frac{i(E_m - E_n)}{k_{-1}}\right]\rho_{mn} + \tfrac{1}{2}k \sum_l (S_m^* S_l \rho_{nl} + S_l^* S_n \rho_{ml}) = \alpha\delta_{mn} \tag{2}$$

from which the magnetic-field-dependent rate constant for triplet-pair fusion is [I, Eq. (8)]

$$\gamma_S(H)n^2 = k_2 \sum_{m,n} S_m S_n^* \rho_{mn} \ , \tag{3}$$

where $k = k_2/k_{-1}$ and $\alpha = k_1 n^2/9k_{-1}$ in which n is the triplet exciton density, assumed to be constant in space. In the high magnetic field limit $S_n \neq 0$ for only two of the nine spin states of the pair, labeled 1 and 2, and Eq. (3) becomes

$$\gamma_S(H)n^2 = k_2 \left[\tfrac{1}{3}\rho_{11} + \frac{\sqrt{2}}{3}(\rho_{12} + \rho_{21}) + \tfrac{2}{3}\rho_{22}\right] \ . \tag{4}$$

In II, the spatial distribution of the excitons and the effect of exciton transport properties are explicitly treated, and it is shown that the dimensionality of this transport may cause a spatial correlation of the excitons during their random walk. This correlation exists only in one- and two-dimensional systems. It could be present in three dimensions as well, provided there exists a strong enough attractive exciton-exciton interaction, of which there is as yet no experimental evidence. In one or two dimensions, the correlation can only be destroyed, either by destruction of one exciton (by intersystem crossing) or of both (by fusion), or by a change in the total spin state due to spin relaxation of one exciton. Usually the last process is the fastest.

In the material explicitly considered here, napthalene, triplet diffusion is almost but not strictly two dimensional,[16] as in anthracene.[17] Motion within one *ab* plane is relatively fast and isotropic and occasional out-of-plane hopping into a neighboring *ab* plane occurs with frequency ψ_{out}. Such a hopping is yet another decorrelating event and indeed the dominant one in anthracene.[2] The effective-pair decay rate β is then written

$$\beta = \psi_{\text{out}} + \zeta \ , \tag{5}$$

where ζ expresses the influence of the only other significant decay process, spin relaxation.

As pointed out above, a rapid enough hopping between nonequivalent molecules (frequency ψ_T) results in the averaging of the molecular fine-structure Hamiltonians $\mathcal{H}_{ssj}$ into an exciton Hamiltonian $\mathcal{H}_{ss} = \frac{1}{2}(\mathcal{H}_{ss1} + \mathcal{H}_{ss2})$, for instance in naphthalene, and in the averaging out to zero of the hyperfine structure.[18] The exciton magnetic Hamiltonian is $\mathcal{H}_m = g\mu_B H + \mathcal{H}_{ss}$. The same process is at the same time a spin relaxation process: During its residence time τ on a molecule, the excitation feels a local field $\vec{h}$ (superimposed on the external field $\vec{H}$), whose magnitude is given by molecular fine-structure terms D and E, which are a few hundred gauss, and whose orientation depends on the molecular position in the unit cell. Its z component h_z ($0z \parallel \vec{H}$) affects the precession around $\vec{H}$, hence a dephasing $\Delta\phi = g\mu_B h_z$ during the residence time τ and a secular component to spin relaxation[14]

$$\frac{1}{T_2'} = (g\mu_B h_z)^2 \tau \ . \tag{6}$$

It is reasonable to take $\Delta\phi \sim 1$ rad as a limit for such a description. If $\tau^{-1} > g\mu_B h_z$, exciton motion will be said to be rapid. In the other limit, equivalent to the rigid lattice limit in motional narrowing studies, the notion of an excitonic Hamiltonian is no longer adequate. In particular, triplet-triplet exciton fusion must be treated as an "heterofusion."[19] This is true, for instance, for some interactions in 1, 4-dibromonaphthalene.[7,20] The components h_x and h_y of $\vec{h}$ can modify the exciton spin states and contribute in the relaxation to nonsecular terms.[14]

In the naphthalene structure, each molecule has four nontranslationally equivalent nearest neighbors in the *ab* plane, so

$$\tau = \frac{1}{8\psi_T} \ , \tag{7}$$

and the local field variation "seen" by the exciton is[2,12,21]

$$h = \tfrac{1}{2}(\mathscr{H}_{ss1} - \mathscr{H}_{ss2}) \ . \tag{8}$$

A convenient way for expressing the relaxation from one triplet sublevel $|n\rangle$ to state $|j\rangle$, both being eigenfunctions of $\mathscr{H}_m$ with energies E_n and E_j, is a matrix with elements

$$\zeta_{nj}(H) = \frac{16\psi_T}{64\psi_T^2 + (E_n - E_j)^2} \, |\langle n \, | h | \, j \rangle|^2 \ , \tag{9}$$

provided, as previously, $\psi_T > D, E$. Equation (9) is valid at all field strengths. Diagonal terms $\Delta m_s = 0$ are secular, and nondiagonal ones $\Delta m_s = \pm 1, \pm 2$, are nonsecular terms. A straightforward calculation shows that $\sum_{n,j} |\langle n \, | h | \, j \rangle|^2$ is independent of $\vec{H}$. Therefore in all cases where $\psi_T >> |E_n - E_j|$, an average relaxation rate, valid for all triplet sublevels, can be defined as

$$\zeta_{\text{av}} = \frac{1}{12\psi_T} \sum_{n,j} |\langle n \, | h | \, j \rangle|^2 \ . \tag{10}$$

This is always valid at zero or low fields once the condition for "homofusion" is met, and is valid at high fields too in some cases (see below). Calculated values of ζ_{av} for naphthalene and anthracene are shown in Table I, together with the parameters used in the calculation.

The important parameter is the correlation time[2] of the triplet pair β^{-1}; we must then compare ψ_{out} and ζ_{av}. Table I shows that ζ_{av} is 10 times larger in naphthalene than in anthracene, while ψ_{out} has no reason to be larger if one considers the relative values of ψ_T, the similarity of crystal structures, and excited-state wave functions—in fact, one may rather expect ψ_{out} to be smaller in napthalene. The effect of spin relaxation on the magnetic field modulation of delayed fluorescence is therefore expected to be much larger in naphthalene. Conversely, in the larger molecule tetracene, spin relaxation has a negligible effect, as shown by the very good agreement between theory and experiment.[3]

At higher magnetic field, where $|E_n - E_j| \sim g\mu_B H \Delta m_s$, some nondiagonal terms are very much reduced, hence a large anisotropy of the relaxation and of β. For illustration, Fig. 1 displays the high-field behavior of the average $\zeta(H) = \frac{1}{3}\sum_{n,j}\zeta_{nj}$. Nonsecular terms found here behave as those in Ref. 5 and become negligible at high enough field. However, inclusion of secular terms drastically changes the results. The values of $\zeta_{nj}(H)$, calculated according to Eq. (9), are used to obtain

$$k_{-1}^{(n)}(H) = k_{-1} + \sum_j \zeta_{nj}(H) \ , \tag{11}$$

which is then introduced into the density matrix, Eq. (2).

In other words, we are using the simpler formalism of I, but k_{-1} is no longer a scalar, and its elements given by (11) are introduced in the equations for the corresponding ρ_{mn}. In fact, almost identical results at high field are obtained using the average scalar $\zeta(H)$, which is easier, since it can be introduced into analytical expression (5).

It is known that theories I and II predict identical results exactly on resonance, and also far enough from resonance, precisely where the extra maxima [observation (a)] are found, and theory I is therefore accurate enough here. The off-resonance annihilation rate is written [I, Eq. (19)]

TABLE I. Average exciton spin-relaxation rates ζ_{av}. [$\mathscr{D}_{\text{in}}$ is the almost isotropic two-dimensional diffusion coefficient in the *ab* plane. ψ_T is calculated as in Refs. 2 and 3. ζ_{av} is obtained from Eq. (10).]

	Anthracene	Ref.	Naphthalene	Ref.
$\mathscr{D}_{\text{in}}$ (cm^2/sec)	1.5×10^{-4}	17	3×10^{-5}	16
ψ_T (sec^{-1})	4.1×10^{10}		8.8×10^{9}	
D^* (cm^{-1})	$+0.0689$	21	$+0.0967$	21
E^* (cm^{-1})	-0.0081		-0.0159	
ζ_{av} (sec^{-1})	8.2×10^{7}		7.5×10^{8}	

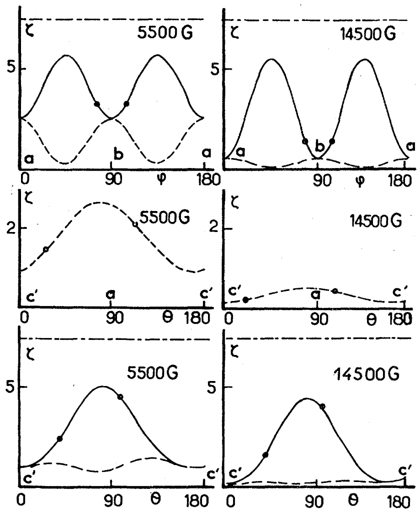

FIG. 1. Calculated anisotropy of the nonsecular part and of the total spin relaxation, expressed as $\zeta(H)=\frac{1}{3}\sum_{n,j}\zeta_{nj}(H)$, in naphthalene. - - - nonsecular; —total; -·-·- $H=0$. ζ in units of 10^8 sec^{-1}. Open circles: calculated resonances positions (see Fig. 2). Upper part: field rotation in *ab* plane; middle: *ac* plane, in which the secular part only is present; lower part: a nonprincipal plane $\phi=60°$. For orientations, see inset in Fig. 2.

$$\gamma_{\text{off}}(H)=\frac{4kk_1}{9\alpha}\frac{1+\frac{4}{9}k}{(1+\frac{1}{3}k)(1+\frac{2}{3}k)} \tag{12}$$

in which k_{-1} is now replaced by $k_{-1}+\zeta(H)$. This expression can be used for a preliminary calculation to estimate the influence of secular relaxation terms. In naphthalene, to a first approximation $k\approx 0.5$ and γ_{off} varies as $[k_{-1}+\zeta(H)]^{-1}$. A minimum of $\zeta(H)$ corresponds to a maximum of γ_{off}. The same result is obtained[20] in theory II using the equivalence [II, Eq. (40)] $k_s \propto H_0^1(iR\sqrt{\beta/\mathscr{D}_{\text{in}}})$. R in the Hankel function is the average intermolecular distance. Since our approach to $\zeta(H)$ differs from that of Altwegg,[5] so will our calculated values of $\gamma_{\text{off}}(H)$.

In crystallographic planes where the secular terms vanish by symmetry, as in the *ac* plane of naphthalene, the two calculations are equivalent, but in all these cases $\zeta(H)<\psi_{\text{out}}$ and its anisotropy is not very important. In other planes, the two approaches predict very different data. For instance, $\zeta(H)$ is found here to be minimum along the *b* axis, where a maximum of delayed fluorescence is indeed observed, whereas inverse behavior is predicted in Ref. 5 (see Figs. 4 and 6 of Ref. 5). The introduction of secular terms is therefore necessary to the understanding of the anisotropy of the magnetic field effect in most planes. In what follows, Eqs. (2), (4), and (9) are used for a more exact calculation in the high-field limit of $\gamma(H)$, not only of $\gamma_{\text{off}}(H)$, and for comparison with experiment.

III. RESULTS AND DISCUSSION

Experimental setups have been described previously.[3] The naphthalene crystals were excited by the 4759-Å line of an Ar$^+$ laser (Spectra Physics 165), with a BG18 glass filter between laser and crystal and a GG435 filter between the crystal and an EMI 9558 QB phototube. The light flux was kept low enough for the triplet exciton decay to be monomolecular, so $F(H)/F(0)=\gamma(H)/\gamma(0)$. Delayed fluorescence F was recorded while the magnetic field was rotated in various crystal planes identified by angles θ and ϕ (see inset in Fig. 2), the crystal itself being kept fixed. The field strengths used were 5.5 and 14.5 kG. Most experiments were performed at room temperature.

In the high-field limit, the field directions for resonance are given by the solutions of

$$(d-1)(\vec{\mathrm{H}}\cdot\vec{\mathrm{X}})^2+(d+1)(\vec{\mathrm{H}}\cdot\vec{\mathrm{Y}})^2=0 \tag{13}$$

with $d=D^*/E^*$ and X,Y,Z are the axes of the excitonic fine-structure tensor. When referring to crystal axes, the calculations are straightforward but tedious.[6]

Figure 2 shows the experimental resonance directions compared to the values calculated using the experimental free-exciton zero field-splitting (ZFS) parameters measured by EPR.[21] The overall agreement shows that we are dealing here with a free-triplet—free-triplet interaction.

Figures 3 and 4 show anisotropy curves of the delayed fluorescence in several crystal planes. Also shown are computed results, using parameters $k_{-1}^{(n)}(H)=3\times 10^9+\zeta_n(H)$ and $k_2=1.8\times 10^9$ sec^{-1}. Note in particular that in the *ab* plane, a fluorescence maximum is found as expected, and that in general, linewidths are correctly reproduced by the calculation.

These data confirm in several ways the validity of the present approach. For instance, the anisotropy of magnetic field effect in the *ab* plane should increase with field strength, and data taken at 5.5 and 1.45 kG indeed show that trend (Fig. 3). The experiment is in good agreement with the calculated variation of $\zeta(H)$ in both cases.

In the *ac* plane [Fig. 4(a)], the secular terms vanish and spin relaxation is already unimportant at 5.5

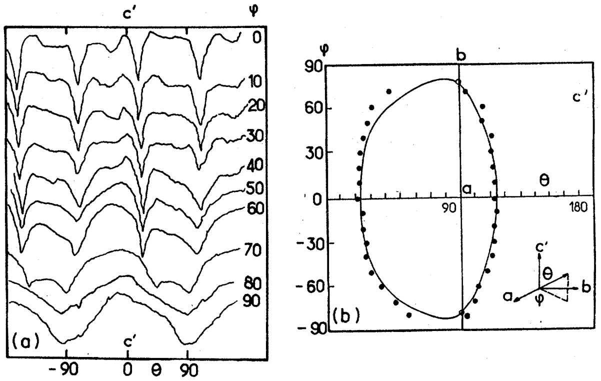

Fig. 2. (a) Modulation of the naphthalene delayed fluorescence by a 5.5-kG magnetic field, rotated in several planes displaced by successive 10° rotation around the crystal c' axis. $\phi = 0$ for the ac plane. (b) Resonance positions. Dots: as read from (a). Open dots are for H rotated in the ab plane. Solid line: as calculated using the experimental exciton ZFS (Ref. 21). The discrepancy for $\phi = 60°$, already observed by others (Ref. 10), may be due to the difficulty of accurately positioning the crystal in such positions, or to a slight error in ZFS parameters. Inset: definition of angles θ and ϕ.

kG. The residual extrema in the directions of the fine-structure tensor axes are due to the fact that the high-field limit is not yet completely reached at 5.5 kG since D^* and E^* are large; a high-field calculation does not account for them.

In nonprincipal planes, the resonances have asymmetric and different widths [Figs. 4(b) and 4(c)]. This effect is not predicted in I or II, but is accounted for qualitatively by the anisotropy of spin

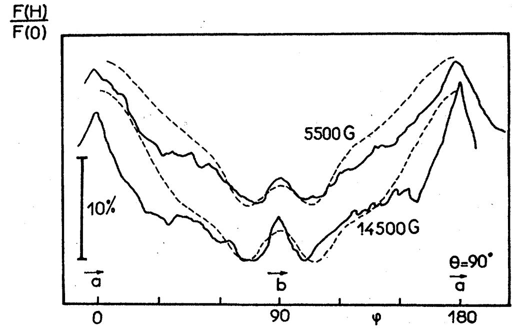

FIG. 3. Effect of magnetic field strength on the anisotropy of modulation in the ab plane. Solid lines: experiment, taken at very low exciton concentration to ensure that $F(H)/F(0) = \gamma(H)/\gamma(0)$ (hence the residual noise). Dotted lines: calculation taking into account anisotropic spin relaxation with parameters k_{-1} (constant part) $= 3 \times 10^9$ sec^{-1}, $k_2 = 1.8 \times 10^9$ sec^{-1}. The vertical scales are shifted for clarity.

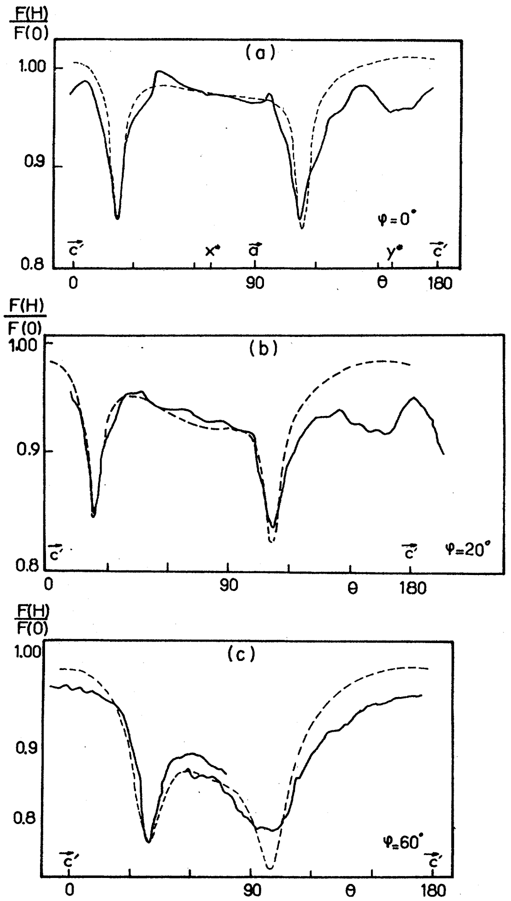

FIG. 4. Modulation of delayed fluorescence in naphthalene by a 5.5-kG magnetic field rotated in several crystal planes. Solid lines: experiment; dotted lines: calculated with k_{-1} (const) $= 3 \times 10^9$ sec^{-1} and $k_2 = 1.8 \times 10^9$ sec^{-1}. (a): ac plane; (b): plane for $\phi = 20°$; (c): plane for $\phi = 60°$. Since, in case (c), calculated and experimental resonance positions do not coincide [Fig. 2(b)], the latter have been displaced to make comparison of linewidths easier.

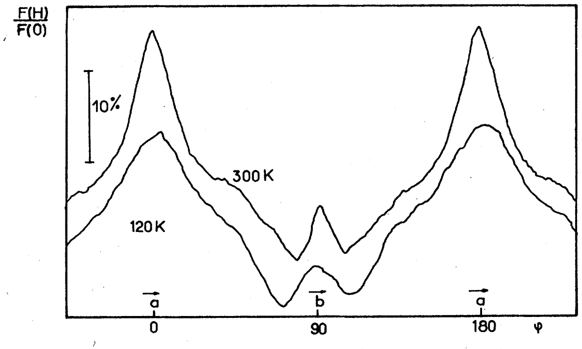

FIG. 5. Delayed fluorescence anisotropy of a 6.7-kG field rotated in the ab plane of naphthalene at 300 K (upper curve) and 120 K (lower curve), displaced vertically for clarity.

TABLE II. Ratio of the widths Γ of the two resonances calculated from Eq. (14) for several planes. ($H = 5000$ G, $\psi_{\text{out}} = 10^8\ \text{sec}^{-1}$.)

Plane	Resonance position (deg)	$\zeta(H)$ ($10^8\ \text{sec}^{-1}$)	Ratio of widths
ab	±77	3	1
ac	22	1.3	1.2
$\phi = 0°$	113	2.1	
$\phi = 20°$	23	1.4	1.3
	112	2.9	
$\phi = 50°$	32	2	1.4
	105	4.6	
$\phi = 60°$	40	2.5	1.2
	100	4.4	

relaxation. Another way of displaying this is to calculate the resonance linewidths Γ in theory II as [II, Eq. (48b)]

$$\Gamma = 2.24(\beta \mathscr{D}_{\text{in}}/R^2)^{1/2} \ , \tag{14}$$

where β is taken as $\psi_{\text{out}} + \zeta(H)$. Note that proper inclusion of spin-relaxation anisotropy in II will change the exact expression for Γ, so such a calculation is only indicative. Results are displayed in Table II, using the physically reasonable $\psi_{\text{out}} = 10^8\ \text{sec}^{-1}$ (Suna uses $2 \times 10^8\ \text{sec}^{-1}$ for his fit to anthracene results). Differences in width are clearly marked. A much smaller ψ_{out} does not affect the results qualitatively, since then $\beta \approx \zeta(H)$. For much larger ψ_{out}, for example, $10^9\ \text{sec}^{-1}$, the difference in widths, of course, tends to vanish.

If the temperature is lowered, in-plane diffusion should increase as has been found in anthracene,[22] and spin relaxation and its influence too should decrease.[13] The maxima associated with the anisotropy of $\zeta(H)$ should then decrease and eventually vanish. Figure 5 shows that this is indeed the case between 295 and 120 K.

IV. CONCLUSION

This work shows that to understand the magnetic field modulation of delayed fluorescence, all processes leading to pair decorrelation and not only exciton motion itself must be taken into account. Consider, for instance, a case in which exciton transport is essentially two dimensional. Two kinds of hopping events are possible for each triplet: an out-of-plane jump, or a jump between two molecules which are not translationally equivalent, the latter inducing spin relaxation. When triplet diffusion is rapid, $\psi_{\text{out}} >> \zeta(H)$, ζ, or at least its anisotropy, can be neglected. This is true in tetracene,[3] and almost true in anthracene.[2] In most crystals in which delayed fluorescence has been studied, however, this is no longer true, and the observed anisotropy is also dependent on the anisotropy of $\zeta(H)$, hence the effects already mentioned: narrow maxima and unequal resonance line shapes (depending on the relative positions of resonance directions and direction of the extrema of ζ). This simple model is applicable not only to naphthalene as done here, but also to pyrene[20] or 1,4-dibromonaphthalene.[7,20] In the latter case, exciton transport is essentially one dimensional, and since all molecules of a stack are translationally equivalent, intrastack motion does not induce spin relaxation in the present model. Much slower interstack jumps also occur and are sufficient to explain the maxima observed; introduction of a contribution of molecular librations to spin-lattice relaxation[12,23] is not necessary.

Finally, magnetic field modulation of delayed fluorescence is very similar to an EPR experiment in that it gives information on exciton ZF tensor and on spin relaxation. But whereas EPR characterizes only one type of exciton jump through ψ_T, the experiments discussed here are sensitive and can give information, in the case of anisotropic exciton transport, both on (assumed isotropic) in-plane hopping frequency and an out-of-plane hopping.

ACKNOWLEDGMENT

We are very much indebted to G. J. Sloan for the gift of the naphthalene crystals used here, and to A. Dugourd for assistance in some of the experiments.

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