PHYSICAL REVIEW B VOLUME 20, NUMBER 10 15 NOVEMBER 1979

Triplet-exciton annihilation and triplet spin relaxation in molecular crystals

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(Received 31 May 1979)

The anisotropy of the delayed fluorescence in a magnetic field of most molecular crystals differs significantly from the well-known anisotropy of anthracene. So far it was assumed that Suna's theory, which explains the behavior in anthracene very well, is not able to describe the anisotropy in these other molecular crystals. We have measured the delayed fluorescence anisotropy of naphthalene and *p*-terphenyl in a high magnetic field at very low triplet density. For the first time a thorough comparison of the experimental results and Suna's theory has been made in a molecular crystal other than anthracene. We demonstrate that, contrary to expectations, a good fit to the data for naphthalene can be achieved, if only spin relaxation is properly taken into account. This leads to a discussion of the theory and experiments dealing with the ESR linewidths of paramagnetic triplet excitons in molecular crystals. It seems that for naphthalene the theory by Reineker for the ESR linewidths, which is based on the Haken-Strobl model, does not fully agree with the experimental findings. By respecting spin relaxation the fit of Suna's theory yields a few important kinetic parameters of triplet excitons in naphthalene such as the out-of-plane hopping rate and the nearest-neighbor annihilation rate.

I. INTRODUCTION

The kinematics of the mutual annihilation of triplet excitons in molecular crystals were treated theoretically by Suna several years ago.[1] Suna's theory has successfully been applied to the magnetic field effects on the delayed fluorescence of anthracene. However, it seems that by applying the theory to other systems discrepancies arise.

In many crystals other than anthracene, one is faced with two problems. First, in systems like naphthalene and *p*-terphenyl, a much greater dependence of the magnetic effects on the density of triplet excitons is observed than predicted by the theory.[2,3] Second, the anisotropy of the delayed fluorescence in a magnetic field of systems like naphthalene,[2] *p*-terphenyl,[4] 1,4-dibromonaphthalene,[5] pyrene,[6] etc., could so far not be explained satisfactorily. Most puzzling are certain peaks in the anisotropy curve for the crystallographic $\vec{a}$-$\vec{b}$ plane measured at high fields. As an example, Fig. 1 shows a typical curve for naphthalene. Clearly an additional peak appears between the two well-known level-crossing resonances. Because this peak points into the opposite direction than the level-crossing resonances, it has been called "antiresonance" or "reverse resonance."[5] In other crystallographic planes the agreement between theory and experiment is not satisfactory[2] either.

It is the aim of this paper to clarify this second problem, i.e., the question of the antiresonances. We will restrict ourselves to the case of the limit of low triplet-exciton density, since a detailed discussion of the other problem, the density effects, has been given previously.[3]

Another system well suited to study exciton-density effects as well as delayed-fluorescence anisotropy, i.e., the problems quoted above, is *p*-terphenyl. The anisotropy of the delayed fluorescence of naphthalene and *p*-terphenyl has been measured in a high magnetic field for several crystallographic planes. The experimental findings will be compared with Suna's theory. It will be shown that spin relaxation plays a very important role in the magnetic effects on the delayed fluorescence of molecular crystals.[7] This leads to a discussion of theories and experiments dealing with the ESR

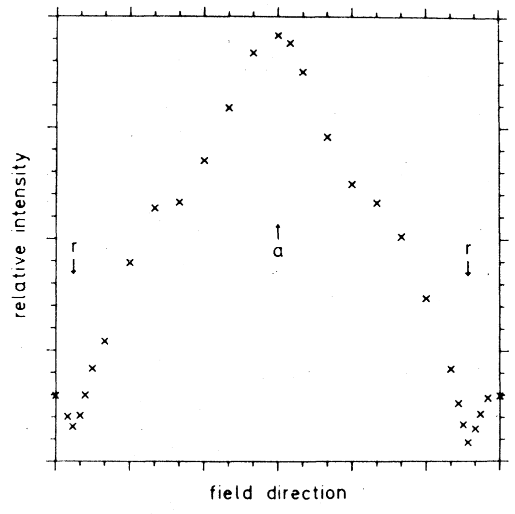

FIG. 1. Delayed-fluorescence intensity vs magnetic field direction in pure naphthalene. Measured in the crystallographic $\vec{a}$-$\vec{b}$ plane and at 8 kOe. Two-level-crossing resonances (*r*) and an "antiresonance" (*a*) along the crystallographic $\vec{a}$ axis are recognized.

linewidth of paramagnetic triplet excitons in molecular crystals. Finally, it will be shown that the so-called antiresonances are actually not due to resonance phenomena.

II. EXPERIMENTAL PROCEDURE

The method for measuring the anisotropy of the delayed fluorescence of naphthalene and of *p*-terphenyl in a magnetic field is the same we used before.[2,3] Detailed descriptions of the apparatus, the measuring procedure, and the preparation of the naphthalene samples have been given in Refs. 2 and 3.

Pure *p*-terphenyl crystals are by far more difficult to grow than naphthalene crystals.[8-10] Almost all the *p*-terphenyl crystals grown by the Bridgeman method seem not to be perfect single crystals.[8,9] With these crystals the anisotropy of the delayed fluorescence in a high magnetic field in the crystallographic $\vec{a}$-$\vec{c}$ plane produces three resonances instead of one, as is expected. These additional resonances appear irrespective of the degree of purification of the *p*-terphenyl the crystal is grown from. They are always about ±7° apart from the expected level-crossing resonances. Possible explanations for these extra resonances are microtwining of the crystal[9] or persistence of a high-temperature phase in thermal nonequilibrium.[10] In order to avoid the latter we also have tried to grow crystals from solution at room temperature. A *p*-terphenyl crystal grown from tetrahydrofuran solution was used for the experiments presented in the following. With this crystal, no additional resonances were observed. The crystal was grown to a size of $1\times2\times4$ mm^3 approximately. There was no need to cleave, cut, or polish the crystal, which is advantageous, since *p*-terphenyl crystals are known to be susceptible to mechanical damaging.[11] The triplet lifetime of *p*-terphenyl is comparable to the one of anthracene. The triplets of *p*-terphenyl were excited with the 488-nm line of an Ar laser and the triplets of naphthalene with the 472-nm line of the same laser.

Prior to each experiment presented in this paper it was verified that the triplet-exciton density was low enough to avoid exciton-density effects[3] to occur. For naphthalene, the triplet-exciton density has to be smaller than about 7×10^{10} cm^{-3}, while in the case of *p*-terphenyl the triplet-exciton density may be one order of magnitude larger.

At such a low density as 7×10^{10} cm^{-3} the resulting delayed-fluorescence intensity is very small. Long counting periods, sensitive fluorescence detecting, and stable triplet excitation are therefore essential. The experiments were all performed at room temperature.

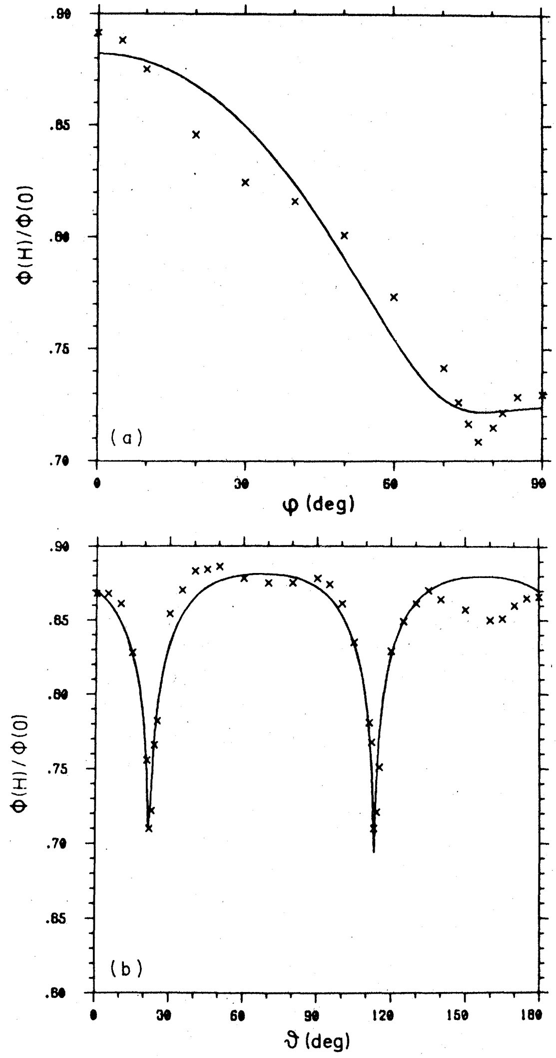

FIG. 2. Naphthalene. Ratio of the delayed-fluorescence intensities $\phi(H)/\phi(0)$ with and without magnetic field H vs the magnetic field direction. Measured in the crystallographic (a) $\vec{a}$-$\vec{b}$ plane, (b) $\vec{a}$-$\vec{c}$ plane and at $H=8$ kOe. φ and ϑ are the angles of the magnetic field with the crystallographic $\vec{a}$ and $\vec{c}^*$ axes, respectively. The experimental points (crosses) are fitted with Suna's theory assuming *isotropic triplet spin relaxation* (solid curve). This fit yields the following values for the kinetic parameters of the triplet excitons: $\lambda_S = 4.0\times10^{11}$ sec^{-1}, $\psi_{oop}+\zeta = 1.7\times10^{9}$ sec^{-1} for the $\vec{a}$-$\vec{b}$ plane; and $\lambda_S = 8.8\times10^{10}$ sec^{-1}, $\psi_{oop}+\zeta = 9.9\times10^{7}$ sec^{-1} for the $\vec{a}$-$\vec{c}$ plane.

III. EXPERIMENTAL RESULTS

In this section the measurements of the anisotropy of the delayed fluorescence in a magnetic field are presented. We begin with the results for pure naphthalene crystals. In Fig. 2(a) the ratio of the intensities of the delayed fluorescence with and without magnetic field $\phi(H)/\phi(0)$ is plotted versus the angle φ between the field direction and the crystallographic $\vec{a}$ axis. The magnetic field of 8 kOe was rotated in the crystallographic $\vec{a}$-$\vec{b}$ plane. Due to the symmetry of the monoclinic crystal the anisotropy curve is mirror symmetric with respect to the $\vec{a}$ axis ($\varphi = 0°$). Therefore only an angle of 90° is displayed in Fig. 2(a). The experimental points are identical with those in the right-hand half in Fig. 1. Figure 2(b) displays the corresponding experiment for the crystallographic $\vec{a}$-$\vec{c}$ plane. ϑ is the angle between the crystallographic $\vec{c}^*$ axis and the magnetic field direction.

The anisotropy curves in Figs. 1, 2(a), and 2(b) are of quite different shape than is known from anthracene. In addition to the sharp resonances in Fig. 2(b), which are well known from anthracence, a dip at $\vartheta = 65°$ and another, deeper one at $\vartheta = 155°$ are seen. Such dips have never been observed in anthracene at high fields. We would also like to draw attention to the considerable effect a magnetic field has on the delayed-fluorescence intensity in naphthalene; on resonance and at 8 kOe the delayed-fluorescence intensity is only 70% of its zero-field value.

As to *p*-terphenyl, Fig. 3 displays the anisotropy of the delayed fluorescence measured in a magnetic field of 8 kOe. Figure 3(a) shows the anisotropy in the crystallographic $\vec{a}$-$\vec{b}$ plane and Fig. 3(b) in the $\vec{a}$-$\vec{c}$ plane. The level-crossing resonances in Figs. 3(a) and 3(b) are very sharp. The full width at half maximum of the $\vec{a}$-$\vec{c}$ plane resonances in Fig. 3(b) is only about 3°. As for naphthalene, distinct dips appear between the $\vec{a}$-$\vec{c}$ plane resonances. Remarkable is the pronounced dip in the $\vec{a}$-$\vec{b}$ plane along the $\vec{a}$ axis ($\varphi = 0°$) in Fig. 3(a), which is not observed in anthracene or naphthalene.

From the resonance angles in the $\vec{a}$-$\vec{c}$ plane the zero-field-splitting tensor of the solution-grown *p*-terphenyl crystal can partly be determined. The angle $2\vartheta_0$ between the two resonances yields for the ratio[12]

$$D^*/E^* = 3\cos 2\vartheta_0 = 3\cos 93.5° = -0.18\,. \qquad (3.1)$$

This value is of the same order of magnitude as for anthracene,[12] where $D^*/E^* = -0.17$. Since the $\vec{x}^*$ axis of the fine-structure tensor bisects the resonances, the angle α^* between the $\vec{x}^*$ axis and the crystallographic $\vec{a}$ axis must be

$$\alpha^* = 1°\,. \qquad (3.2)$$

The high-field resonances occur at orientations, for which

$$D^*(\cos^2\gamma^* - \tfrac{1}{3}) + E^*(\cos^2\alpha^* - \cos^2\beta^*) = 0\,, \qquad (3.3)$$

where α^*, β^*, and γ^* are the angles between the magnetic field and the fine-structure tensor axes $\vec{x}^*$, $\vec{y}^*$, and $\vec{z}^*$, respectively.[12] From this equation and the values for D^*/E^* and α^* given above [Eqs. (3.1) and (3.2)], we can calculate the resonance angles φ for the $\vec{a}$-$\vec{b}$ plane of *p*-terphenyl:

$$\varphi = \arccos\left[\frac{2}{3} \Big/ \left(1 - \frac{E^*}{D^*}\cos^2\alpha^* + \frac{E^*}{D^*}\sin^2\alpha^*\right)\right]^{1/2} = 71°\,. \qquad (3.4)$$

Within the experimental error of about ±1° this result is consistent with the measured resonance angles for the $\vec{a}$-$\vec{b}$ plane [see Fig. 3(a)].

To sum up, the anisotropy of the delayed fluo-

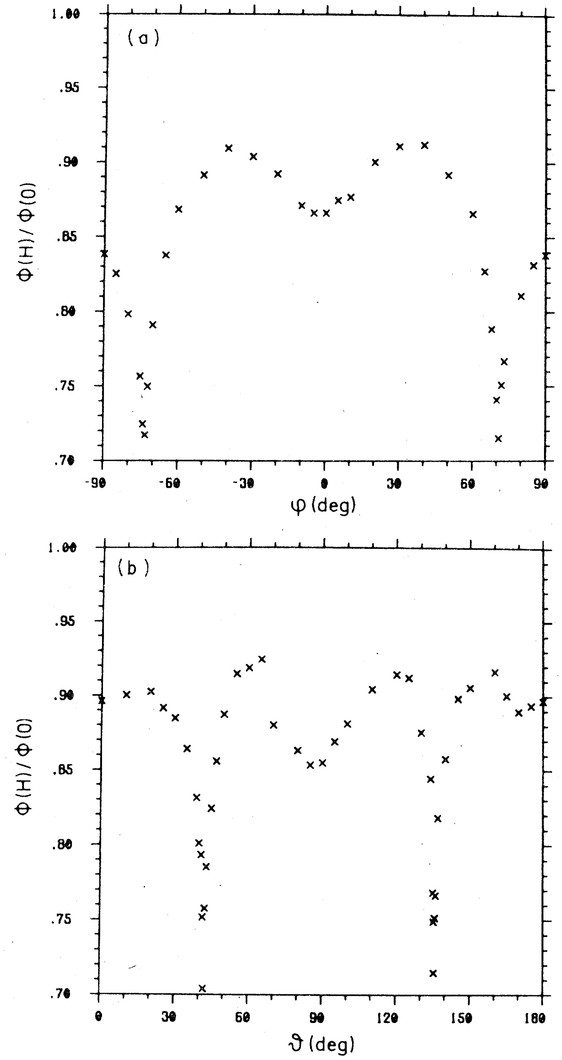

FIG. 3. *p*-terphenyl. Ratio of the delayed-fluorescence intensities $\phi(H)/\phi(0)$ with and without magnetic-field H vs the magnetic field direction. Measured in the crystallographic (a) $\vec{a}$-$\vec{b}$ plane, (b) $\vec{a}$-$\vec{c}$ plane and at $H = 8$ kOe. φ and ϑ are the angles of the magnetic field with the crystallographic $\vec{a}$ and $\vec{c}^*$ axes, respectively. A fit to theory, as for naphthalene in Fig. 2, is not feasible for *p*-terphenyl; see Sec. IV.

rescence of both naphthalene and p-terphenyl differs considerably from the well-known anthracene results. The level-crossing resonances are deeper and narrower and there are dips between the $\vec{a}$-$\vec{c}$-plane resonances. Most surprising is the shape of the $\vec{a}$-$\vec{b}$-plane anisotropy along the crystallographic $\vec{a}$ axis, where naphthalene shows an antiresonance and p-terphenyl a dip.

IV. COMPARISON BETWEEN THEORY AND EXPERIMENT ASSUMING ISOTROPIC SPIN RELAXATION OF THE TRIPLET EXCITONS

We now compare the experimental results for naphthalene with Suna's theory.[1] We shall calculate the ratio $\phi(H)/\phi(0)$, which in the limit of low triplet-exciton density equals the ratio of the annihilation rates γ_s leading to singlets[2,3]

$$\phi(H)/\phi(0)=\gamma_s(H)/\gamma_s(0). \tag{4.1}$$

We have to point out that till now only relative variations in this ratio were calculated, when Suna's theory was applied to anthracene[1] or naphthalene.[2] Thus the zero-field value of γ_s did not need to be determined. This means that part of the experimental results was lost from comparison with theory. In the following we will always calculate the values of $\gamma_s(H)$ and of $\gamma_s(0)$ separately. For the rest, the calculations presented in this section are made under the same assumptions as in the case of anthracene, in the classical paper by Suna.[1] The lattice structure[13] and the fine-structure tensor[14] of naphthalene as well as the components D_{aa} and D_{bb} of the exciton-diffusion tensor with respect to the basis of the crystallographic axes of naphthalene[15] are taken as known quantities. Ern[15] has shown that exciton motion in naphthalene is quasi-two-dimensional. Therefore the only nonzero triplet-exciton hopping rates are taken as

$$\begin{aligned}&\psi_d=\psi[\tfrac{1}{2}(\vec{a}\pm\vec{b})]=\psi[-\tfrac{1}{2}(\vec{a}\pm\vec{b})],\\&\psi_b=\psi(\pm\vec{b}),\\&\psi_{c^*}=\psi[\pm\vec{c}\mp\tfrac{1}{2}(\vec{a}+\vec{b})]\equiv\psi_{\text{oop}},\end{aligned} \tag{4.2}$$

where $\vec{a}$, $\vec{b}$, and $\vec{c}$ are the crystallographic axes of naphthalene and ψ_{oop} is the hopping rate out of the $\vec{a}$-$\vec{b}$ plane. ψ_d and ψ_b are calculated from D_{aa} and D_{bb}. Moreover, we made use of the "smooth approximation" in Sec. III B in Suna's paper. Constant and isotropic spin relaxation is assumed, as it has always been done so far. The effect of spin relaxation is taken into account by a relaxation term, which is given by Eq. (49) in Suna's paper:

$$\begin{aligned}\left(\frac{\partial}{\partial t}\right)_{\text{rel}}&[\rho_2(\vec{R})-\tfrac{1}{9}\operatorname{Tr}\rho_2(\vec{R})1]\\&=-2\zeta[\rho_2(\vec{R})-\tfrac{1}{9}\operatorname{Tr}\rho_2(\vec{R})1],\end{aligned} \tag{4.3}$$

ρ_2 is the exciton-pair density matrix, and ζ the average spin-relaxation rate. The ansatz may be applied, whenever the out-of-plane hopping rate ψ_{oop} and the spin-relaxation rate ζ are of comparable magnitude. It will be shown later that this condition is met.

There still remain three unknown parameters: the total $\vec{a}$-$\vec{b}$-plane nearest-neighbor annihilation-rate constants in the singlet and in the triplet channels λ_S and λ_T as well as the sum $\psi_{\text{oop}}+\zeta$ of the out-of-plane hopping rate and the average spin-relaxation rate. λ_T is not needed for the calculation of $\gamma_s(H)/\gamma_s(0)$ and will therefore be discussed separately in Sec. VI. $\gamma_s(H)/\gamma_s(0)$ is now calculated from Eqs. (42) and (43) in Suna's paper treating $\psi_{\text{oop}}+\zeta$ and λ_S as freely adjustable parameters. The solid lines in Figs. 2(a) and 2(b) show the result, i.e., a fit of Suna's theory to the experimental data in naphthalene. The agreement between theory and experiment is hardly satisfactory. Surprisingly enough in Fig. 2(a) not even the level-crossing resonance can be recognized in the curve calculated for the $\vec{a}$-$\vec{b}$ plane. As ζ appears only in the fit parameter $\psi_{\text{oop}}+\zeta$, one would obtain the same curves also with zero spin relaxation.

As to p-terphenyl it is not possible to calculate corresponding curves, since the fine-structure tensor as well as the exciton-diffusion constants of p-terphenyl are not known. It might seem obvious that another magnetic-field-dependent process, which has not been considered by Suna, is responsible for the discrepancy between theory and experiment, as illustrated in Fig. 2 and possibly also for the antiresonance. In Sec. V we will demonstrate, however, that this is not the case.

V. ANISOTROPIC SPIN RELAXATION

The width of ESR lines of triplet excitons in organic crystals is equal to the inverse spin-spin relaxation time $1/T_2$. Normally the dominant mechanism causing spin-spin relaxation in crystals like naphthalene is assumed to be the motion of the excitons between the two differently oriented molecules in the crystal.[16] Reineker[16,17] has calculated the linewidth $1/T_2$ due to this motion on the basis of the Haken-Strobl model.

The part of $1/T_2$, which stems from transitions between magnetic sublevels, is the nonsecular part of $1/T_2$. We therefore may identify the spin-relaxation rate ζ defined by Eq. (4.3) with the nonsecular part of $1/T_2$:

$$(1/T_2)_{\text{ns}}=\zeta(H). \tag{5.1}$$

Highly anisotropic spin-relaxation rates $\zeta(H)$ result from this equation and Reineker's theory.

Thus it is concluded that the delayed fluorescence of naphthalene cannot correctly be predicted unless the anisotropy of spin relaxation is accounted for.

We now fit Suna's theory to the experimental curves for naphthalene using the anisotropic spin-relaxation rates $\zeta(H)$ calculated from Reineker's theory. Since it is not possible to calculate the zero-field spin-relaxation rate $\zeta(0)$ with Reineker's theory, $\zeta(0)$ is treated as a further fit parameter. The effective hopping rate Γ_1 in Reineker's theory is obtained from

$$\Gamma_1 = 2\psi_d \, , \tag{5.2}$$

where ψ_d is the nearest-neighbor hopping rate [see Eq. (4.2)]. Otherwise the same assumptions are made as in the case of constant spin relaxation, which was discussed in Sec. IV. The result of this fit is presented in Figs. 4(a) and 4(b) for the crystallographic $\vec{a}$-$\vec{b}$ and $\vec{a}$-$\vec{c}$ planes, respectively. Clearly the correspondence between theory and experiment in Fig. 4(a) is considerably better than in Fig. 2(a). Both the resonance and a peak along the $\vec{a}$ axis ($\varphi = 0°$) are obtained. For the $\vec{a}$-$\vec{c}$ plane, on the other hand, an essential improvement of the correspondence between theory and experiment is not obtained compared to Fig. 2(b).

In the following we will show how one can get good correspondence between theory and experiment for the $\vec{a}$-$\vec{c}$ plane as well. Haarer and Wolf[14] have measured the anisotropy of the ESR linewidth of triplet excitons in the crystallographic $\vec{a}$-$\vec{c}$ plane of naphthalene. In this plane the secular part of $1/T_2$ is zero due to crystal symmetry,[14,16,17] and one may therefore directly take the ESR linewidth for $\zeta(H)$. Haarer and Wolf measured the ESR linewidths at 12.5 kOe and it is assumed that at 8 kOe the ESR linewidths do not differ significantly. For angles, where no values by Haarer and Wolf exist, we evaluated $\zeta(H)$ by quadratic Lagrange interpolation. Having determined $\zeta(H)$ this way, we again fit Suna's theory to the experi-

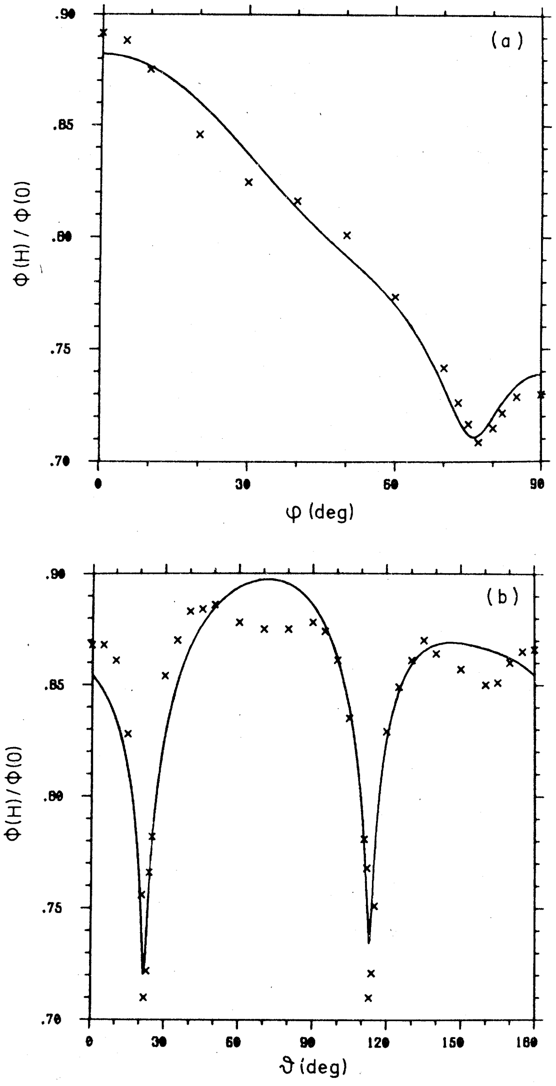

FIG. 4. Same as Fig. 2 except with an *anistropic triplet spin relaxation*, which is calculated from *Reineker's theory*. See Sec. V in the text. According to this fit the values for the kinetic parameters of the excitons are as follows: $\lambda_S = 1.1 \times 10^{11}$ sec^{-1}, $\psi_{oop} = 2.5 \times 10^8$ sec^{-1}, and $\zeta(0) = 2.4 \times 10^8$ sec^{-1} for the $\vec{a}$-$\vec{b}$ plane; and $\lambda_S = 8.9 \times 10^{10}$ sec^{-1}, $\psi_{oop} = 2.3 \times 10^8$ sec^{-1}, and $\zeta(0) = 3.0 \times 10^8$ sec^{-1} for the $\vec{a}$-$\vec{c}$ plane.

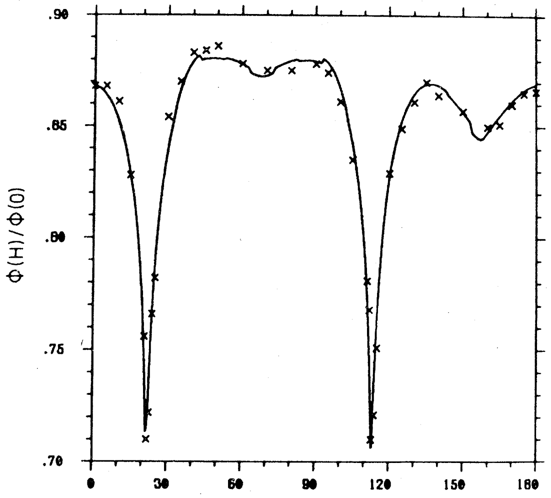

FIG. 5. Same as Fig. 4(b) (crystallographic $\vec{a}$-$\vec{c}$ plane), but with the values for the *anisotropic spin-relaxation rate* taken from *experimental* ESR *linewidths* by Haarer *et al*. See Sec. V in the text. The kinetic parameters thus obtained from this fit are resumed in Eq. (5.3)

ment. In Fig. 5 the result displays an almost perfect fit of Suna's theory. The following parameters are obtained from this fit:

$$\lambda_S = (1.14 \pm 0.07)\times 10^{11}\ \text{sec}^{-1},$$
$$\psi_{\text{oop}} = (9.1 \pm 1.5)\times 10^{7}\ \text{sec}^{-1}, \qquad (5.3)$$
$$\zeta(0) = (6.2 \pm 1.2)\times 10^{7}\ \text{sec}^{-1}.$$

VI. DISCUSSION

According to Suna the ansatz of Eq. (4.3) for the effects of spin relaxation is valid in the case of quasi-two-dimensional exciton motion as long as the out-of-plane hopping rate ψ_{oop} is comparable to the spin-relaxation rate ζ. Comparing the values for ψ_{oop} and $\zeta(0)$ in Eq. (5.3) and considering that $\zeta(H)$ and $\zeta(0)$ are of comparable magnitude, we note that this condition is met. The ansatz of Eq. (4.3) yields annihilation rates c times larger than those of zero spin relaxation, provided that the triplet-exciton decay rate is replaced by the sum $\psi_{\text{oop}}+\zeta$.[1] We have checked that within the small error of about 0.6%, c is equal to unity.

Instead of explicitly including the exciton hopping between the two differently oriented molecules into the equation of motion of the pair density matrix ρ_2, in our calculations the problem is split into two steps. First we calculated the spin-relaxation rate ζ due to hopping motion between inequivalent molecules with Reineker's theory by using two differently oriented fine-structure tensors for the two inequivalent molecules. These calculations had to be done in the $\vec{a}$-$\vec{b}$ plane, whereas in the case of the crystallographic $\vec{a}$-$\vec{c}$ plane we could take experimental ESR linewidths for ζ instead. Then we used an equation of motion for ρ_2, in which the spin Hamiltonian is the average of the Hamiltonians of the two orientations. Spin relaxation is taken into account in this second step by the ansatz of Eq. (4.3) with the values for ζ calculated in step one. By this procedure calculations are simplified and the computer time needed is kept within reasonable limits.

From the out-of-plane hopping rate ψ_{oop} in Eq. (5.3) we find that the diffusion of triplet excitons in naphthalene is highly anisotropic:

$$D_{aa}/D_{c^*c^*} = D_{aa}/[\psi_{\text{oop}}(c^*)^2] \simeq 70\,. \qquad (6.1)$$

It is important to note that the ratio $D_{aa}/D_{c^*c^*}$ found from the fit depends strongly on whether the values of $\gamma_s(H)/\gamma_s(0)$ are directly calculated or whether only relative variations in $\gamma_s(H)$ are taken into account. Unreasonably high values for $D_{aa}/D_{c^*c^*}$ would result, if one would consider relative variations in $\gamma_s(H)$ only. It is of great importance therefore that the experiments are made at low triplet-exciton density. At higher densities the measured curves are displaced to higher values due to other reasons, as we have shown previously.[3]

The parameters resulting from the fit, which are given in Eq. (5.3), yield the following value for the zero-field triplet-annihilation rate in the singlet channel:

$$\gamma_s(0) = 1.3\times 10^{-12}\ \text{cm}^3\ \text{sec}^{-1}. \qquad (6.2)$$

This rate is four times smaller than the one of anthracene. The total annihilation rate of pairs in the triplet channel γ_T, which is given by Eq. (32) in Suna's paper, still cannot be calculated, since the total nearest-neighbor annihilation rate in the triplet channel λ_T is not obtained from the fit. Nevertheless, the following upper limit is found from the parameters of Eq. (5.3) and from Eq. (32) in Suna's paper:

$$\gamma_T < \lim_{\lambda_T\to\infty} \gamma_T = 1.9\times 10^{-12}\ \text{cm}^3\,\text{sec}^{-1}. \qquad (6.3)$$

If we assume $\lambda_T = \lambda_S$, we get

$$\gamma_T = 1.2\times 10^{-12}\ \text{cm}^3\,\text{sec}^{-1}. \qquad (6.4)$$

In this paper we use the definition for γ_T given by Suna in contrast to a definition for γ_T which yields twice this value, and which is used, e.g., in Refs. 2, 3, and 18. According to the definition by Suna, the loss of triplet excitons per unit time by triplet-triplet annihilation in the triplet channel is $\gamma_T n^2$, where n is the density of triplet excitons.

The effective bimolecular annihilation rate for triplet excitons γ_{eff} according to Ref. 2 is given by

$$\gamma_{\text{eff}} = \gamma_T + (1-\tfrac{1}{2}\xi)\gamma_s\,, \qquad (6.5)$$

where ξ is the intersystem-crossing quantum yield. With the values for γ_S and γ_T from Eqs. (6.2)–(6.4) and $\xi = 0.82$ from Ref. 19 we get

$$\gamma_{\text{eff}} < 2.6\times 10^{-12}\ \text{cm}^3\,\text{sec}^{-1}, \qquad (6.6)$$

and for $\gamma_T = \gamma_S$,

$$\gamma_{\text{eff}} = 2.0\times 10^{-12}\ \text{cm}^3\ \text{sec}^{-1}. \qquad (6.7)$$

The latter values for γ_{eff} compare favorably with the value

$$\gamma_{\text{eff}} = 3.5\times 10^{-12}\ \text{cm}^3\,\text{sec}^{-1} \pm 50\% \qquad (6.8)$$

measured by Benz *et al.*[20] The ratio of the values for γ_T and γ_S from Eqs. (6.2)–(6.4) is $\gamma_T/\gamma_S < 1.5$ and $\gamma_T/\gamma_S = 0.9$, respectively. It is interesting to note that these ratios are close to the ratio 1.5 expected from the statistical weights of triplet and singlet channels.

We finally comment on different theories and different experimental values for ESR linewidths and spin-relaxation rates. In the case of the crystallographic $\vec{a}$-$\vec{b}$ plane only small differences

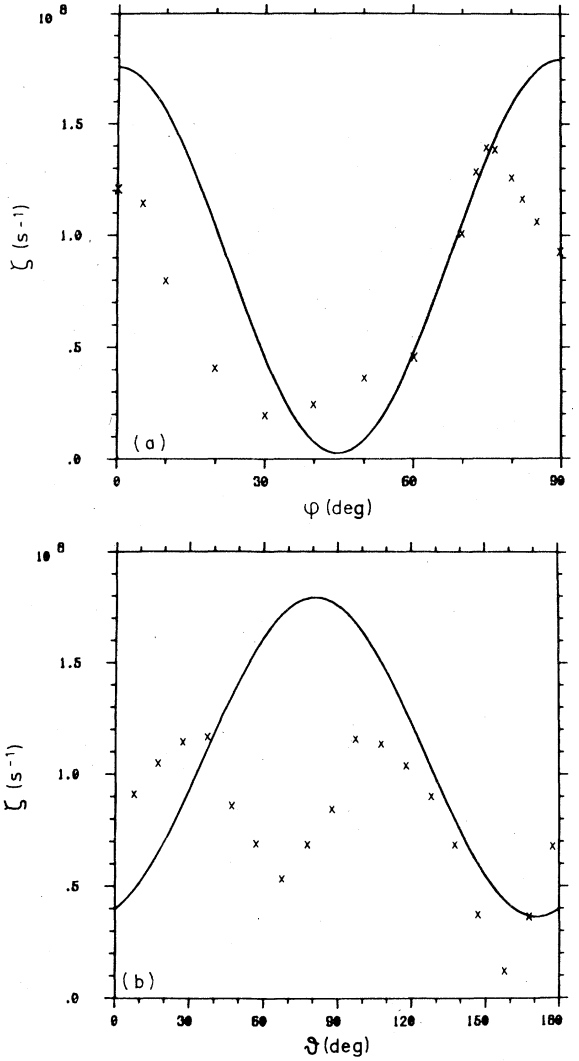

FIG. 6. Anisotropy of the spin-relaxation rate ζ in naphthalene as a function of the magnetic field direction. Solid line: ζ calculated with Reineker's theory for 8 kOe in the crystallographic (a) $\vec{a}$-$\vec{b}$ plane and (b) $\vec{a}$-$\vec{c}$ plane. In (a) the crosses represent the spin-relaxation rates needed for a perfect fit of Suna's theory to the experiment in the crystallographic $\vec{a}$-$\vec{b}$ plane in Fig. 2(a). In (b), the crosses feature the experimental ESR linewidths measured by Haarer *et al.* in the crystallographic $\vec{a}$-$\vec{c}$ plane.

between Suna's theory and the experiment resulted from the spin-relaxation rates calculated by Reineker [Fig. 4(a)]. Figure 6(a) shows the anisotropy of the spin-relaxation rates of naphthalene in the crystallographic $\vec{a}$-$\vec{b}$ plane calculated with Reineker's theory together with a semi-experimental curve of spin-relaxation rates. The latter curve was obtained from the parameters of Eq. (5.3) and the requirement that it should yield a perfect fit of Suna's theory to the anisotropy of the delayed fluorescence in that plane. The difference between the two curves is probably due to contributions to spin relaxation other than the one caused by the motion of the excitons between inequivalent molecules.[17]

There is no doubt that the spin-relaxation rates taken from the ESR linewidths measured by Haarer and Wolf[14] yield the better fit of Suna's theory to the anisotropy of the delayed fluorescence in the $\vec{a}$-$\vec{c}$ plane than the ESR linewidths calculated with Reineker's theory [see Figs. 4(b) and 5]. In Fig. 6(b) these experimental and theoretical ESR linewidths or spin-relaxation rates for the crystallographic $\vec{a}$-$\vec{c}$ plane are compared. A dip at $\vartheta = 65°$ is seen in the experimental curve, which is not obtained with Reineker's theory.

Reineker has compared his theory with Haarer's measurements of the ESR linewidths of anthracene.[17] Particularly in the crystallographic $\vec{a}$-$\vec{c}$ plane the correspondence between theory and experiment is not satisfactory. As in the case of naphthalene [see Fig. 6(b)] the experimental curve displays a dip at $\vartheta = 65°$, which is not seen in the theoretical curve. Rosenthal *et al.*[21] gave an explanation for this discrepancy: They suggest that orientational disorder broadens the magnetic resonance lines inhomogeneously. The disorder was thought of as a distribution of very slightly misoriented domains, each with a volume at least as large as would be traversed by an exciton during its effective lifetime. A more recent measurement by Bizzaro *et al.*[22] of the ESR linewidths of triplet excitons in anthracene is in contrast to the result by Haarer and Wolf but, on the other hand, agrees fairly well with Reineker's theory.

However, the ESR linewidths of naphthalene in the crystallographic $\vec{a}$-$\vec{c}$ plane measured by Haarer and Wolf[14] produce an almost perfect fit of Suna's theory to the anisotropy of the delayed fluorescence in a high magnetic field (Fig. 5). Therefore it seems highly improbable that structural disorder of the type suggested by Rosenthal *et al.* was present in the naphthalene crystals used by Haarer. Such a structural disorder would not give rise to a contribution to spin relaxation. We conclude that another explanation is needed for the poor agreement between the theoretical and experimental anisotropies in the crystallographic $\vec{a}$-$\vec{c}$ plane of the ESR linewidths of triplet excitons in naphthalene. We consider it more probable that a further, up to now neglected process contributes to spin relaxation in addition to the hopping motion between inequivalent molecules.

VII. CONCLUSION

It has been proven that Suna's theory can explain the anisotropy of the delayed fluorescence of pure naphthalene in a high magnetic field, if anisotropic spin relaxation is taken into account. Even the peak along the crystallographic $\vec{a}$ axis seen in the anisotropy curve for the crystallographic $\vec{a}$-$\vec{b}$ plane, the so-called antiresonance, is not in contrast to Suna's theory. The name antiresonance apparently is not appropriate, since its origin is the anisotropy of spin relaxation rather than a resonance phenomenon. It is expected that the experimental results for *p*-terphenyl presented in this paper and for other materials found by different authors agree with Suna's theory, too, if only anisotropic spin relaxation is properly taken into account. From this point of view the anisotropy of the delayed fluorescence of anthracene seems to be the exception rather than the rule, although it has been better understood than the one of other systems. This is a consequence of the relatively small spin-relaxation rate of triplet excitons in anthracene compared to their out-of-plane hopping rate.

Furthermore, we have demonstrated that the ESR linewidths of triplet excitons in naphthalene measured by Haarer and Wolf[14] for the crystallographic $\vec{a}$-$\vec{c}$ plane are in disagreement with the values calculated by Reineker.[17]

We strongly believe that structural defects, an explanation suggested for a corresponding discrepancy found in anthracene, cannot be the reason for this disagreement. We think that beside the hopping motion between inequivalent molecules, an additional process influences the spin-relaxation rate.

ACKNOWLEDGMENTS

We wish to thank P. Reineker for valuable computer programs and R. Voltz for helpful discussions. This research was supported by the Swiss National Science Foundation, whose aid is gratefully acknowledged.

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