PHYSICAL REVIEW B VOLUME 22, NUMBER 4 15 AUGUST 1980

Influence of surface effects and temperature on the interaction of triplet excitons in molecular crystals

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(Received 20 February 1980)

The anisotropy of the triplet-exciton annihilation rate in a magnetic field has been investigated in naphthalene and in anthracene as a function of temperature and of the penetration depth of the incident light. In the region between the well-known level-crossing resonances, dips in the delayed fluorescence intensity are observed which are much more pronounced if the triplet excitons are generated near the surface of the crystal than in the volume and which disappear at lower temperatures. It is shown that this difference between the surface and the volume triplet annihilation rate and its temperature dependence is due to the triplet spin-relaxation rate which influences the effective lifetime of the triplet pairs. The anisotropy of prompt and delayed fluorescence in anthracene and of the delayed fluorescence in naphthalene, measured for different ways of exciton excitation, are fitted according to Suna's theory but with the anisotropic spin relaxation taken into account. As a result we get some new information about the temperature dependence of the triplet spin-relaxation rate and its dependence on the molecular environment of the triplet excitons in the volume and at the surface of the crystals.

I. INTRODUCTION

The anisotropy of the delayed fluorescence in a magnetic field of most molecular crystals differs significantly from the well-known anisotropy of the delayed fluorescence in anthracene crystals. In naphthalene crystals,[1] for example, the delayed fluorescence displays dips in the intensity even for certain directions of the magnetic field between the level-crossing resonances. But by close look, in anthracene, too, unexpected magnetic field effects are observed for the triplet-exciton interaction. According to theory, the anisotropy of the prompt fluorescence, due to the dissociation of singlet excitons into two triplet excitons, should be mirror symmetric to the anisotropy of the delayed fluorescence. However, it turns out that in anthracene there are obvious differences observed in the magnetic field dependence of the two processes.[2,3] The dips seen in the anisotropy curve of the prompt fluorescence in anthracene look similar to those in the delayed fluorescence in naphthalene mentioned above.

For the anisotropy of the delayed fluorescence in anthracene the theories by Merrifield and Suna[4,5] explain successfully the magnetic field effects on the triplet-triplet annihilation. At first sight, it seems as if these theories could not explain the observed effects in other organic materials. Even in anthracene, the experimental anisotropy of the singlet fission process cannot fully be explained. Recently, it has been shown for naphthalene[1] that the details in the anisotropy of the delayed fluorescence can be understood in the framework of Suna's theory only if one takes into account the anisotropy of the triplet spin relaxation.

The anisotropy of the triplet-triplet annihilation rate gets very sensitive to the anisotropy of the triplet spin-relaxation rate in a magnetic field if the exciton motion is nearly one or two dimensional. In this case, it is the spin-relaxation rate together with the out-of-plane hopping rate which determine the effective decay rate of the triplet excitons. The influence of the triplet spin-relaxation rate is large provided that it is of the same order of magnitude as the out-of-plane hopping rate. For naphthalene this is indeed the case, whereas in anthracene the spin-relaxation rate is somewhat smaller than the out-of-plane hopping rate. In both cases the spin-relaxation rate is highly anisotropic as it is known from electron spin resonance (ESR) measurements.[6] Changes of the spin-relaxation rate with temperature or due to different molecular environment in the crystal have therefore a perceptible influence on the anisotropy of the triplet-annihilation rate and of the singlet fission rate in a magnetic field.

The aim of this paper is to investigate the influence of temperature and of surface effects on the triplet-triplet interaction in anthracene as well as in naphthalene. This will allow us to draw conclusions about the anisotropy of the triplet spin-relaxation rate and its dependence on temperature and molecular environment in the crystal.

II. THEORY

It has been shown that the anisotropy of the triplet-triplet annihilation rate in a magnetic field usually measured via the delayed fluorescence, can well be described with the aid of Suna's theory on the kinematics of exciton-exciton annihilation in molecular crystals.[5,1] This theory is also applicable for the inverse process, i.e., the singlet-exciton fission, if one bears in mind the different source for the population of the triplet pair state. That means, we have to replace the constant source term $K=(\frac{1}{3}nv)^2$ in the equation of motion of the triplet pair density matrix [Eq. (37) in Suna's paper[5]] by a source term K' which is proportional to the singlet amplitude $\langle l|S|l'\rangle$ of the pair state:

$$K'=-mvG[\beta+(i/2)(E_l-E_{l'})]\langle l|S|l'\rangle\ , \qquad (1)$$

where n, m are the density of the triplet and of the singlet excitons, respectively, v the volume of the unit cell, and G the Green's function defined by Eq. (38) in Ref. 5. Our calculations show that under these assumptions the annihilation rate γ_s and the fission rate γ_s' are indeed mirror symmetric as several authors have assumed before.[3,7]

Altwegg[1] has shown that the observed anisotropy of the delayed fluorescence in naphthalene can only be explained if one takes explicitly into account the anisotropy of the triplet spin relaxation. The triplet annihilation rate as well as the singlet fission rate are quite sensitive to the spin-relaxation rate in crystals where the exciton motion is nearly one or two dimensional.

In molecular crystals with two molecules per unit cell like naphthalene and anthracene, the dominant mechanism causing spin relaxation is assumed to be the motion of the triplet exciton between the two differently oriented molecules in the crystal. In Suna's theory (Appendix C in Ref. 5) the spin relaxation for the one-exciton density matrix takes the form:

$$\left(\frac{d}{dt}\right)_{\mathrm{rel}}\langle n|\rho|m\rangle=-(1-\delta_{nm})\zeta_{nm}^{(2)}\langle n|\rho|m\rangle -\delta_{nm}\left[\left(\sum_j\zeta_{jn}^{(1)}\right)\langle n|\rho|n\rangle -\sum_j\zeta_{nj}^{(1)}\langle j|\rho|j\rangle\right]. \qquad (2)$$

Here $|n\rangle$ is a single-exciton spin state which is an eigenstate of the spin Hamiltonian $\mathcal{H}$ with eigenvalues E_n. $\zeta_{nj}^{(1)}$ are the diagonal relaxation rates and $\zeta_{nm}^{(2)}$ are the off-diagonal relaxation rates.

$\zeta_{nj}^{(1)}$ is given by the following expression [Eq. (D6D) in Ref. 5]:

$$\zeta_{nj}^{(1)}=(16\Psi_d|\langle n|h|j\rangle|^2)/[(8\Psi_d)^2+(E_n-E_j)^2]\ , \qquad (3)$$

where $h=\frac{1}{2}(\mathcal{H}_A-\mathcal{H}_B)$ is half the difference of the Hamiltonians associated with each of the two inequivalent molecules of the lattice. Ψ_d is the nearest-neighbor hopping rate. For magnetic fields large compared to the crystal fine-structure parameters $|E_n-E_j|$ is proportional to B.

Suna has shown that in the case where the exciton hopping rate Ψ_{oop} out of the $\vec{a}\vec{b}$ plane and the spin-relaxation rate ζ are of the same order of magnitude, the spin relaxation of the two-exciton density matrix can be simplified by the following ansatz:

$$\left(\frac{d}{dt}\right)_{\mathrm{rel}}[\rho_2(R)-\tfrac{1}{9}\mathrm{Tr}\rho_2(R)1] =-2\zeta[\rho_2(R)-\tfrac{1}{9}\mathrm{Tr}\rho_2(R)1]. \qquad (4)$$

ρ_2 is the exciton pair density matrix and ζ is an average spin-relaxation rate. In Suna's theory ζ is given by

$$\zeta=\tfrac{1}{3}\sum_n\left(\sum_j\zeta_{nj}^{(1)}\right),\quad n\neq j\ . \qquad (5)$$

This amounts to replacing in the equation of motion of the pair density matrix [Eq. (37) in Ref. 5] the out-of-plane hopping rate Ψ_{oop} by an effective inverse triplet lifetime β_{eff} which is the sum of Ψ_{oop} and an average spin-relaxation rate ζ.

It is important to note that the magnetic field dependent and anisotropic spin-relaxation rate therefore competes with the magnetic field independent out-of-plane hopping rate in determining the effective triplet lifetime. The annihilation or the fission are thus quite sensitive to the relative magnitude of ζ compared to Ψ_{oop}.

Another way to calculate the average triplet spin-relaxation rate is given in the theory of Reineker[8,9] on ESR lineshapes. Reineker has calculated the linewidths $1/T_2$ of triplet excitons in organic crystals on the basis of the Haken-Strobl model. The spin-relaxation rate, which gives rise to transitions between the magnetic sublevels of the triplet exciton, has been identified with the nonsecular part of $1/T_2$.[1] The analytical expression for the spin-relaxation rate in Reineker's theory is restricted to magnetic fields large compared to the exciton fine-structure parameters. Still, the spin-relaxation rate for zero field has therefore to be calculated with Suna's theory. For a known crystal structure and a fixed value for B in both theories the only adjustable parameter is the nearest-neighbor hopping rate Ψ_d.

We have compared the results of Suna's theory about spin relaxation with those obtained by Reineker from the calculation of ESR linewidths. As it is shown in Fig. 1 for the $\vec{a}\vec{c}$ plane of a naphthalene crystal with $\Psi_d=9.75\times10^9$ sec^{-1} and a magnetic field of 12.5 kOe, we find, that the spin-relaxation rates calculated with Suna's and with Reineker's theories are almost the same. Even the dependence of ζ on Ψ_d is the same in both theories. In particular, for a magnetic field B, ζ has its maximum value for $\Psi_d=\frac{1}{8}B$. For larger values of Ψ_d we find

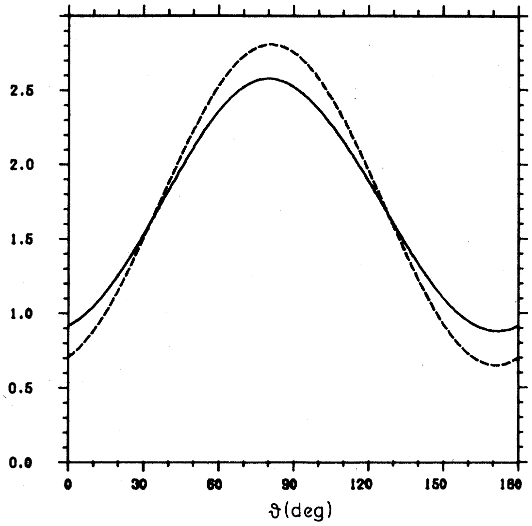

FIG. 1. Anisotropy of the triplet spin-relaxation rate ζ in naphthalene. The magnetic field of 12.5 kOe was rotated in the crystallographic $\vec{a}\vec{c}$ plane. ϑ is the angle of the magnetic field with the crystallographic $\vec{c}'$ axis (see Fig. 2). Solid lines: ζ calculated according to Suna's theory (Ref. 5). Dashed line: ζ calculated with Reineker's theory (Refs. 8 and 9). The nearest-neighbor hopping rate was taken as $\Psi_d = 9.75 \times 10^9$ sec^{-1}.

that ζ is proportional to Ψ_d^{-1}. That means the spin-relaxation rate ζ, and with it the triplet annihilation rate and also the singlet fission rate, are quite sensitive to changes in Ψ_d. This fact allows us to elucidate conclusions about the nearest-neighbor hopping rate Ψ_d from the annihilation rate.

III. EXPERIMENTAL PROCEDURE

The prompt and the delayed fluorescence intensity were measured with the same technique as was earlier described in Ref. 2. In order to generate the triplet excitons near the surface of the crystal we made use of the intersystem crossing from the first excited singlet state. At the various excitation wavelengths chosen within the singlet absorption, the triplet excitons are thus generated within different penetration depths below the surface. In naphthalene as well as in anthracene highly absorbing vibronic singlet states were excited with the 254-nm line of a 6-W glow-discharge mercury lamp. For naphthalene we used in addition the 313-nm line of a 200-W mercury spark arc lamp. The direct triplet excitation in the volume of naphthalene crystals was achieved with the 476-nm line of a 3-W argon laser or with the 436-nm line of the mercury spark arc lamp and in the case of anthracene with a 1.5-mW He-Ne-laser. The crystals were grown by the Bridgman method from zone-refined material. They were cut with a thread saw and polished or cleaved to a size of about $4 \times 4 \times 3$ mm^3. The crystals were mounted on a light guide and placed between the pole pieces of a rotatable permanent magnet providing a field of 5.8 kOe. The light was deflected by a semitransparent mirror and then guided through a light guide onto the crystal. The fluorescence emitted from the crystal passed through the same light guide and the mirror, and was finally measured with a photomultiplier. In the case of singlet excitation a mechanical chopper placed between the semitransparent mirror and the light guide was chopping the signal from the crystal. Thus, alternatively, either the stray light of the lamp or the stray light plus the signal were measured. By electronic subtraction and division of these two signals it was possible to eliminate drifts of the light source and of the photomultiplier. In the case of direct triplet excitation, the delayed fluorescence was measured under steady-state conditions without chopping. In both cases the signal was added up in a signal averager for 20–2000 measurements. By this way a resolution of 0.1–1 per thousand was obtained. To cool the crystal, cold nitrogen or helium gas was pumped through the sample mounting and the temperature was measured with a thermocouple mounted on the crystal.

IV. EXPERIMENTAL RESULTS

In this section we present the anisotropy of prompt and delayed fluorescence in a high magnetic field measured at different temperatures and in different regions of naphthalene and anthracene crystals. We always measured the relative fluorescence intensity $\Phi(B)/\Phi(0)$, i.e., the ratio of the fluorescence with and without magnetic field, as a function of the direction of the magnetic field relative to the crystallographic axes. The magnet was rotated either in the crystallographic $\vec{a}\vec{c}$ plane or in the $\vec{a}\vec{b}$ plane. The angles are measured relative to the $\vec{c}'$ axis or to the $\vec{a}$ axis, respectively. In Fig. 2 a scheme of the crystallographic axes and of the direction angles of the magnetic field relative to these axes is given. All measurements are performed under steady-state conditions. Therefore, in the case where the triplets are generated indirectly by singlet excitation the delayed fluorescence could not be separated from the prompt fluorescence. Because of the superposition of prompt and delayed fluorescence the modulation of the total fluorescence Φ in a magnetic field is much smaller in the case of singlet excitation than in the case of direct triplet excitation, i.e., 0.5% compared to 30%. Under this condition an additional fit parameter which reflects the ratio between

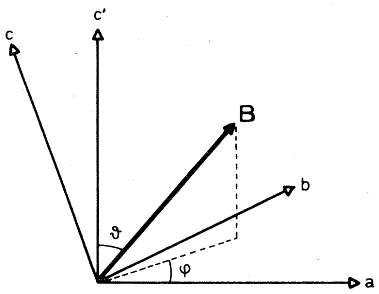

FIG. 2. Orientation of the magnetic field B relative to the crystallographic $\vec{a}, \vec{b}, \vec{c}'$ axes.

prompt and delayed fluorescence is needed to fit the theory to the experiments.

A. Naphthalene

As to the generation of triplet excitons, the triplet absorption coefficient is very weak in crystals like naphthalene and anthracene ($\alpha \sim 10^{-3}$ cm^{-1}). But because in naphthalene more than 80% of the singlet excitons decay by singlet-triplet intersystem crossing,[10] we have the possibility to excite triplet excitons via the first excited singlet state. The advantage of singlet excitation is that the absorption coefficient is many orders of magnitude larger than for triplet excitation. We have made use of the fact that the absorption varies over a wide range ($\alpha \simeq 10^2 - 10^5$ cm^{-1}) (Ref. 11) within the singlet absorption manifold, to select regions of different absorption depth for singlet excitation and thus to generate triplet excitons in different zones below the crystal surface.

In naphthalene, where the triplet diffusion is highly anisotropic, the triplet diffusion coefficient in the crystallographic $\vec{a}\vec{b}$ plane is about 70 times larger than perpendicular to this plane. For this reason the region populated with triplet excitons is larger if we excite parallel to the $\vec{a}\vec{b}$ plane than perpendicular to it.

A disadvantage of triplet population via singlet-triplet intersystem crossing is that the exciton density is not homogeneous throughout the excited region. But although in naphthalene the effect of the triplet-exciton density on the annihilation rate is by no means negligible, its influence on the anisotropy in a magnetic field is quite small.[12] The anisotropy of the delayed fluorescence in naphthalene for direct triplet excitation at room temperature has been very carefully measured earlier.[1]

In Fig. 3(a) the results for naphthalene measured at two different directions of the incident light relative to the crystallographic axes and at two different excitation wavelengths within the singlet manifold are presented. The ratio of the intensities of the fluorescence Φ with and without magnetic field $\Phi(B)/\Phi(0)$ is plotted versus the angle ϑ between

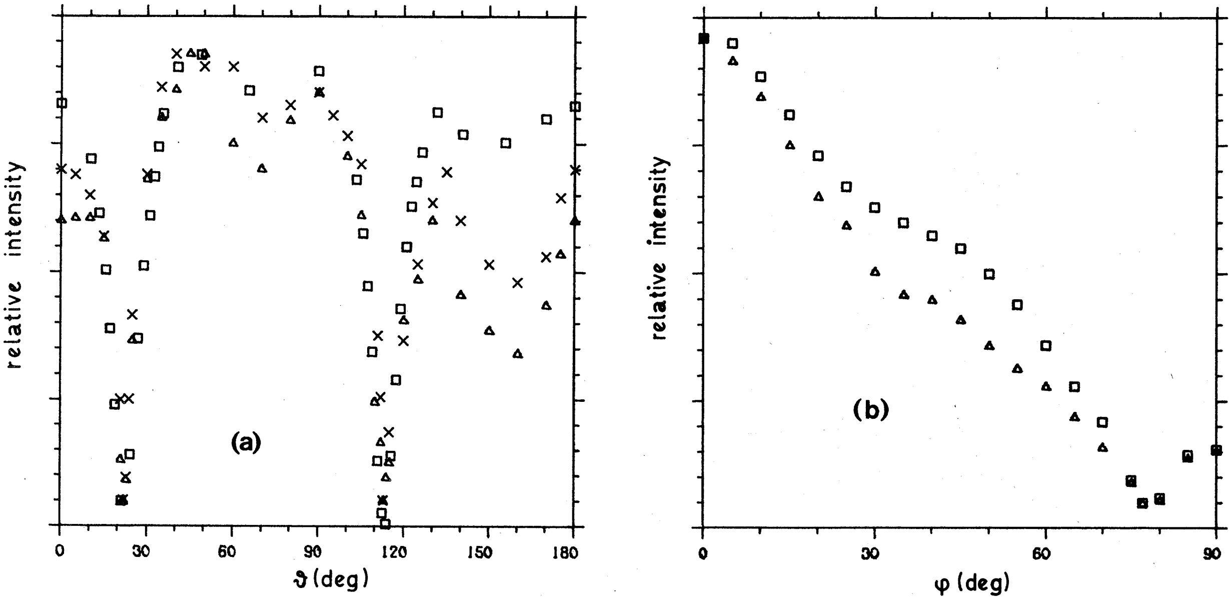

FIG. 3. Naphthalene. Anisotropy of the sum of the prompt and delayed fluorescence intensities measured for different excitation conditions. Excitation wavelength λ and direction of the incident light relative to the crystallographic axes. Rectangles: $\lambda = 313$ nm incident parallel to the $\vec{a}\vec{b}$ plane, i.e., for a singlet absorption coefficient $\alpha \simeq 10^4$ cm^{-1}; crosses: $\lambda = 254$ nm incident parallel to the $\vec{a}\vec{b}$ plane; triangles: parallel to the $\vec{a}\vec{c}$ plane, singlet absorption coefficient $\alpha \simeq 10^5$ cm^{-1}. The magnetic field of 5.8 kOe was rotated (a) in the crystallographic $\vec{a}\vec{c}$ plane and (b) in the $\vec{a}\vec{b}$ plane. ϑ and φ are the angles of the magnetic field with the crystallographic $\vec{c}'$ and $\vec{a}$ axes, respectively.

the field direction and the crystallographic $\vec{c}'$ axis.

The magnetic field of 5.8 kOe was rotated in the crystallographic $\overrightarrow{ac}$ plane. The rectangles correspond to an excitation wavelength of 313 nm which is near the singlet absorption edge of naphthalene and with the excitation perpendicular to the $\overrightarrow{ac}$ plane of the crystal. The crosses represent an excitation wavelength of 254 nm with the excitation also perpendicular to the $\overrightarrow{ac}$ plane, while the triangles correspond to the same wavelength but with the incident light perpendicular to the $\overrightarrow{ab}$ plane. The differences between the three measurements are quite obvious. The curve for 313 nm looks almost as an anisotropy curve measured for direct triplet excitation in the volume of the crystal.[1] At higher excitation energies, however, the dips near $\vartheta = 65°$ and near $\vartheta = 155°$ between the level-crossing resonances get much more pronounced. We see that the depth of these dips varies with the penetration depth of the incident light and also with the diffusion length of the triplet excitons. For the excitation wavelength of 254 nm and the light incident perpendicular to the $\overrightarrow{ab}$ plane the singlet absorption coefficient is $\mathcal{A} \simeq 10^5\ \text{cm}^{-1}$ (Ref. 11) and the triplet diffusion length $L \simeq 10^{-4}$ cm. For 313 nm and the light perpendicular to the $\overrightarrow{ac}$ plane, the depth of the excited surface region is larger because of the smaller absorption coefficient $\mathcal{A} \simeq 10^4\ \text{cm}^{-1}$ and the larger triplet diffusion length $L \simeq 10^{-3}$ cm (Ref. 13).

In Fig. 3(b) the corresponding anisotropy curves, but now for the magnetic field rotated in the $\overrightarrow{ab}$ plane of a naphthalene crystal, are given. Again, the rectangles correspond to an excitation with $\lambda = 313$ nm incident perpendicular to the $\overrightarrow{ac}$ plane and the triangles to an excitation with $\lambda = 254$ nm perpendicular to the $\overrightarrow{ab}$ plane. We get a similar behavior as in Fig. 3(a): The dip at around $\varphi = 30°$ is much more pronounced if the triplet excitons are excited near the surface of the crystal than in the volume. For both crystallographic planes in Fig. 3 these dips are not influenced by different surface treatments as, e.g., cutting, polishing, or putting the crystal in a nitrogen atmosphere.

As it has been shown recently,[1] these off-resonance dips in the delayed fluorescence anisotropy curves are due to the triplet spin-relaxation rate and its anisotropy in a magnetic field. The dips get the more pronounced the larger the anisotropy of the spin relaxation. We therefore conclude from our measurements, that the anisotropy of the triplet spin-relaxation rate must be much larger at the surface of the crystal than in the volume. In Sec. V, where we compare the theory with the experiments, more quantitative statements about the anisotropy of the spin relaxation in the volume and near the surface of the crystal are given.

B. Anthracene

As to anthracene, the selective population of different regions near the surface of the crystal can be achieved, on principle, in the same way as in naphthalene. But because of the much smaller singlet-triplet intersystem crossing rate in anthracene, i.e., only 1% of the singlet excitons decay by intersystem crossing,[14] the modulation of the total fluorescence emission (i.e., the sum of prompt and delayed fluorescence) by a magnetic field is even smaller than in naphthalene and therefore hard to measure. Besides in anthracene, the triplet diffusion is about five times larger and not as anisotropic as in naphthalene.[13] But because the singlet-triplet intersystem crossing rate is so small, another magnetic-field-dependent process which competes with the triplet-triplet annihilation can be observed, namely, the singlet fission. For excitation energies in the singlet manifold larger than twice the triplet energy, i.e., $\lambda < 340$ nm, the excited singlets can dissociate into two triplets. Because of the much smaller diffusion length of singlet excitons (~100 Å) the depth of the excited region, where singlet fission takes place, is given only by the singlet absorption coefficient which for an excitation wavelength of 254 nm is about $\mathcal{A} \simeq 10^5\ \text{cm}^{-1}$.[15]

As pointed out in Sec. II, the anisotropy of the prompt fluorescence due to singlet fission in a magnetic field should be mirror symmetric to the delayed fluorescence resulting from mutual triplet annihilation. In Fig. 4 we have plotted the anisotropy of the prompt fluorescence of anthracene for an excitation with 254 nm and the anisotropy of the delayed fluorescence with direct triplet excitation in the same crystal. In order to compare both curves, the sign of the fission curve has been changed, and its scale has been stretched, i.e., $-\Phi(B)/\Phi(0)$ is plotted versus the angle of the magnetic field relative to the crystallographic axes. Figure 4(a) represents the measurements with the magnetic field of 5.8 kOe rotated in the $\overrightarrow{ac}$ plane and Fig. 4(b) with the magnetic field rotated in the $\overrightarrow{ab}$ plane. The rectangles correspond to the measurements of the delayed fluorescence and the triangles and the crosses to those of the prompt fluorescence at 300 and at 100 K, respectively. It is clearly seen that for both planes the anisotropy of the prompt fluorescence is not mirror symmetric to the anisotropy of the delayed fluorescence. In the $\overrightarrow{ac}$ plane the off-resonance prompt fluorescence intensity is larger at around $\vartheta = -30°$ than at around $\vartheta = 65°$, and in the $\overrightarrow{ab}$ plane there is a dip at around $\varphi = 30°$ as in naphthalene. As it will be shown in

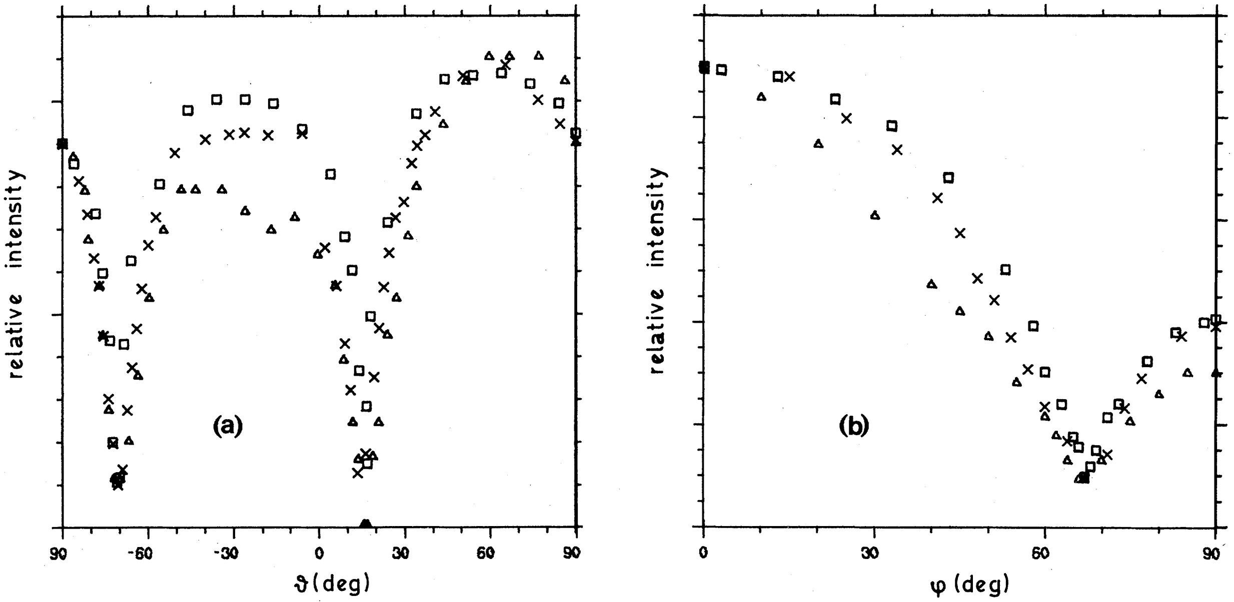

FIG. 4. Anthracene. Anisotropy of prompt and the volume-excited delayed fluorescence, respectively, versus magnetic field direction. Measured at 5.8 kOe in the crystallographic (a) $\vec{a}\vec{c}$ plane and (b) $\vec{a}\vec{b}$ plane; ϑ and φ are the angles of the magnetic field with the crystallographic $\vec{c}'$ and $\vec{a}$ axes, respectively. Rectangles: delayed fluorescence intensity at room temperature; triangles: prompt fluorescence intensity at room temperature; crosses: prompt fluorescence intensity at 100 K. The excitation wavelength was 254 nm for the measurements of the prompt fluorescence. To facilitate the comparison of the three anisotropy curves the sign and the scale of the prompt fluorescence has been changed.

Sec. V again these dips are due to a larger anisotropy of the triplet spin-relaxation rate at the surface than in the volume of the crystal.

C. Temperature dependence of the triplet spin relaxation in anthracene and naphthalene

In Figs. 4(a) and 4(b) the anisotropy of the prompt fluorescence in anthracene at 100 K is shown. The dips are less pronounced than at room temperature although the anisotropy curve is still not mirror symmetric with respect to the volume excited delayed fluorescence. The latter does not change significantly with temperature down to 100 K. Therefore, we conclude that at least in the surface of the anthracene crystal the anisotropy of the triplet spin relaxation changes with temperature and gets smaller with decreasing temperature.

In anthracene the effect of the spin relaxation on the annihilation rate is too small to study the temperature dependence of the anisotropy of the triplet spin-relaxation rate in the volume. This happens because the out-of-plane hopping rate is much larger than the spin-relaxation rate and therefore the effective lifetime of the triplet pairs is determined solely by the out-of-plane hopping rate.

In naphthalene, on the other hand, the effect of the anisotropy of the triplet spin-relaxation rate on the anisotropy of the triplet annihilation rate is large, even in the volume of the crystal, because the out-of-plane hopping rate and the spin-relaxation rate are of comparable magnitude.

We therefore have measured the anisotropy of the delayed fluorescence of naphthalene in a magnetic field with excitation in the triplet manifold at different temperatures. The results are shown in Fig. 5(a) for the crystallographic $\vec{a}\vec{c}$ plane and Fig. 5(b) for the $\vec{a}\vec{b}$ plane. The rectangles correspond to room temperature, the crosses to 180 K, and the triangles to 110 K. In Fig. 5(a) two of the curves have been shifted along the vertical axis with respect to their original positions for clarity reasons.

For naphthalene in Fig. 5 the same temperature effect is observed as in the case of anthracene fission in Fig. 4: In both cases the off-resonance dips at $\vartheta = 155°$ [in Fig 5(a)] and at $\varphi = 30°$ [in Fig. 5(b)] become smaller with decreasing temperature. At 110 K the anisotropy curves look qualitatively the same as the well-known room temperature delayed fluorescence in anthracene. This means that in naphthalene, but at low temperatures, the anisotropy of the spin relaxation of the volume-generated triplet excitons may be neglected. From further measurements of the anisotropy of the total fluorescence with strongly absorbed singlet excitation, it follows that in naphthalene also for surface-generated triplets the anisotropy of the triplet spin-relaxation rate gets smaller

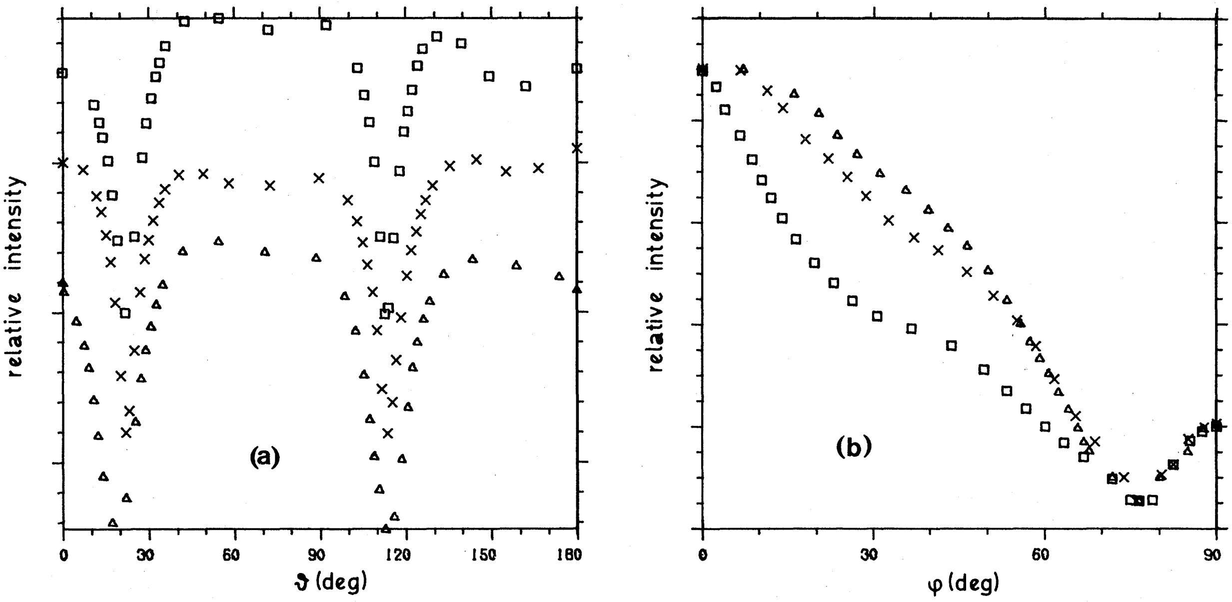

FIG. 5. Naphthalene. Volume-excited delayed fluorescence intensity at different temperatures versus magnetic field direction. Measured in the crystallographic (a) $\vec{a}\vec{c}$ plane, (b) $\vec{a}\vec{b}$ plane, and at 5.8 kOe. ϑ and φ are the angles of the magnetic field with the crystallographic $\vec{c}'$ and $\vec{a}$ axes, respectively. Rectangles: 300 K; crosses: 180 K; triangles: 110 K. In (a) two of the curves have been shifted parallel to the vertical axis for clarity reasons.

with decreasing temperature.

Finally, we summarize our results with regard to the anisotropy of delayed and prompt fluorescence in a high magnetic field as follows:

(1) In anthracene and naphthalene the anisotropy of the triplet-triplet annihilation rate is not the same at the surface and in the volume of the crystal.

(2) The off-resonance dip, in the $\vec{a}\vec{c}$ plane at around $\vartheta = 155°$ relative to the $\vec{c}'$ axis and in the $\vec{a}\vec{b}$ plane at around $\varphi = 30°$ relative to the $\vec{a}$ axis, is more pronounced if the triplet excitons are excited in the crystal surface than in the volume.

(3) By lowering the temperature down to 110 K, these dips get smaller for volume—as well as for surface—excitation of the triplets.

Since we know that these dips are due to the anisotropy of the spin-relaxation rate, we therefore conclude, that the anisotropy of the triplet spin-relaxation rate is larger in the surface than in the volume of the crystal and that it decreases at lower temperatures in the whole crystal. In the following section we will make quantitative statements about the spin-relaxation rate under the different conditions.

V. COMPARISON BETWEEN THEORY AND EXPERIMENT

As we have pointed out in Sec. IV, the anisotropy of the triplet-triplet annihilation rate and of the singlet fission rate in a magnetic field is not the same in the volume and in the surface of the crystal. Furthermore, in naphthalene as well as in anthracene, it is strongly dependent on the temperature. This is mainly due to the anisotropy of the triplet spin-relaxation rate and its temperature dependence. As we have shown in Sec. II the only adjustable parameter to calculate the spin-relaxation rate with Suna's or Reineker's theory for a fixed magnetic field and a known crystal structure is the nearest-neighbor hopping rate Ψ_d.

Usually the values for Ψ_d in anthracene and naphthalene are calculated from the diffusion tensor according to the following expression[5]:

$$D_{ij} = \tfrac{1}{2} \sum_{R} \Psi(R) R_i R_j \,, \tag{6}$$

where R_i, R_j are lattice vectors. The only nonzero hopping rates are taken as

$$\begin{aligned} &\Psi_d = \Psi[\tfrac{1}{2}(\vec{a}+\vec{b})] = \Psi[-\tfrac{1}{2}(\vec{a}+\vec{b})] \,, \\ &\Psi_b = \Psi[\pm\vec{b}] \,, \\ &\Psi_{\text{oop}} = \Psi[\pm\vec{c} \mp \tfrac{1}{2}(\vec{a}+\vec{b})] \,, \end{aligned} \tag{7}$$

where $\vec{a}, \vec{b}, \vec{c}$ are the crystallographic axes.

With the values for D_{aa} and D_{bb} measured by Ern[13,16] at room temperature with direct triplet excitation in the volume of the crystal this yields, for anthracene and naphthalene, respectively, in Oe,

$$\Psi_d/(g\mu_B) = \begin{cases} 2300 \,, \\ 550 \,. \end{cases}$$

The determination of the microscopic nearest-neighbor hopping rate Ψ_d from the macroscopic diffusion tensor, however, implies a value for Ψ_d which is the same in the whole crystal, i.e., surface regions or volume.

As for the temperature dependence, in both materials Ψ_d increases by a factor of 2 if one lowers the temperature to 110 K.[17] In anthracene and in a magnetic field of 5.8 kOe the spin-relaxation rate ζ is proportional to Ψ_d^{-1} and should therefore decrease with increasing hopping rate. On the other hand, in naphthalene at the same magnetic field the spin-relaxation rate should be rather insensitive to the increase of Ψ_d because the dependence of ζ on Ψ_d is weak near $\Psi_d \simeq \frac{1}{8}B$ (compare Sec. II).

Figure 6 shows the measured anisotropy (crosses) of the prompt fluorescence due to singlet fission in anthracene together with a fit with Suna's theory (dashed line). The spin relaxation has been assumed to be isotropic as it always has been done, so far successfully, in the case of anthracene.[5] The magnetic field was rotated in the crystallographic $\vec{a}\vec{b}$ plane. Since in anthracene only vibronic excited singlet excitons can dissociate into two triplet excitons for energetic reasons, the excitation wavelength of 254 nm has been chosen.

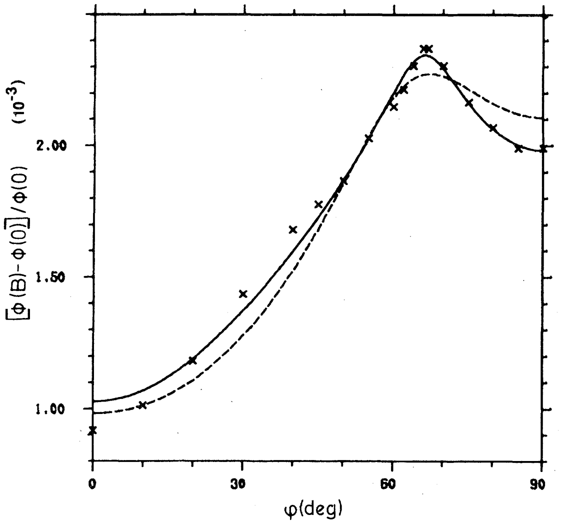

FIG. 6. Anthracene. Ratio of the prompt fluorescence intensities with and without magnetic field $[\Phi(B)-\Phi(0)]/\Phi(0)$ versus the magnetic field direction. Measured in the crystallographic $\vec{a}\vec{b}$ plane and at 5.8 kOe. φ is the angle of the magnetic field relative to the crystallographic $\vec{a}$ axis. Dashed curve: Fit of the experimental points (crosses) with Suna's theory assuming isotropic triplet spin relaxation. Solid curve: Fit with anisotropic triplet spin relaxation which is calculated with Suna's theory as in Fig. 1 but for 5.8 kOe. The kinetic parameters obtained from this fit are listed in Table I.

In this case the fission competes with the thermal relaxation of the vibronic singlets to the vibrationally relaxed first excited singlet state. That means, part of the vibronic singlets decay directly to the vibrationally relaxed first excited singlet state, and the rest dissociates into two triplet excitons which then can again reannihilate to a singlet exciton. The population of the vibrationally relaxed first excited singlet state which determines the measured prompt fluorescence is therefore a sum of the directly relaxed vibronic singlets and the singlets which are due to the reannihilation of two triplet excitons. The ratio of the prompt fluorescence with and without magnetic field is therefore given by the following expression:

$$\Phi(B)/\Phi(0)=[k_r+\gamma_s'(0)n_{s_0}]/[k_r+\gamma_s'(B)n_{s_0}]. \qquad (8)$$

k_r is the thermal relaxation rate of the vibronic singlet excitons, n_{s_0} is the density of the molecules in the ground state, and k_r/n_{s_0} is treated as a fit parameter. The fission rate γ_s' was calculated according to Suna's theory. Additional fit parameters have been the nearest-neighbor annihilation rate λ_s and the sum $\zeta+\Psi_{\text{oop}}$ of the out-of-plane hopping rate Ψ_{oop} and an isotropic spin-relaxation rate ζ. The lattice structure of anthracene and the fine-structure tensor are known.[18,19] The in-plane hopping rates Ψ_b and Ψ_d, are calculated according to Eq. (7) from the diffusion tensor.[13] From Fig. 6 one sees clearly that under the assumptions made the fit (dashed line) is hardly satisfactory. Even the level-crossing resonance is barely recognizable. This is somewhat surprising, because the inverse process, i.e., the anisotropy of the delayed fluorescence in anthracene, is in good agreement with Suna's theory under the above assumption of isotropic spin relaxation.

This big difference between the anisotropy of the prompt and the delayed fluorescence might be due to the fact, that for the two processes the excitons are generated in different regions of the crystal. The in-plane hopping rates calculated from the diffusion tensor, determined for volume-excited triplet excitons, might therefore not be appropriate to describe the fission process which takes place near the surface of the crystal. But as long as we keep the spin relaxation isotropic the value of the in-plane hopping rates $\Psi_{b,d}$ almost does not influence our calculations and the fit does not get better for different values of $\Psi_{b,d}$. However, the nearest-neighbor hopping rate Ψ_d influences the spin-relaxation rate. With decreasing nearest-neighbor hopping rate the spin relaxation increases. Therefore the spin-relaxation rate can then no longer be assumed isotropic. We again fitted the anisotropy of the prompt fluorescence with Suna's theory but this time taking explicitly into account anisotropy of spin relaxation calculated according to Eqs. (3) and (5). The nearest-neighbor hopping rate was taken as an additional fit parameter. The other in-plane hopping rate Ψ_b is thereby calculated from Ψ_d according to $\Psi_b = \Psi_d/2$. This leads to very good agreement between theory and experiment, as is shown in Fig. 6 by the solid curve. The values thus obtained for the fit parameters are listed in Table I. The fraction of the vibronic singlet excitons which undergo fission and which is given by $k_r/[\gamma_s'(0)n_{s_0}]$ is about 8%.

A comparison of the triplet hopping rates from the prompt fluorescence with the values obtained from the diffusion tensor shows that, although the exciton motion is still nearly two dimensional near the surface of the crystal, the in-plane hopping rates are about three times smaller in the surface than they are in the volume of the crystal.

At lower temperatures the hopping rates get larger as it is known from diffusion measurements for volume-excited triplet excitons.[17] This holds also for surface triplets as it is seen from the values listed in Table I obtained from an analogous fit of the anisotropy of the prompt fluorescence at 100 K. The nearest-neighbor hopping rate increases by about a factor of 3 if one lowers the temperature to 100 K.

For anthracene, the anisotropy of the volume-excited delayed fluorescence at room temperature can be satisfactorily described by assuming isotropic spin relaxation. Taking into account the anisotropic spin relaxation leads to a still better and almost perfect fit yielding the parameters listed in Table I. The value obtained for the nearest-neighbor hopping rate is in very good agreement with experimental values given by Ern.[13] From these results we see that in anthracene the nearest-neighbor hopping rate of triplet excitons must be quite different at the surface than in the volume of the crystal and that it is strongly dependent on the temperature.

For the value of the spin-relaxation rate we find that the zero-field spin-relaxation rate ζ is about $\zeta = 7.4 \times 10^7$ sec^{-1} for volume-excited triplet excitons. For surface-excited triplet excitons ζ is about twice as large at room temperature. At 100 K it is of the same order of magnitude as the room temperature value for the volume excitons.

As to naphthalene, it has been shown[1] for the volume-excited delayed fluorescence that a fit with Suna's theory neglecting the anisotropy of the triplet spin relaxation leads to a poor agreement between theory and experiments. For the anisotropy in the crystallographic $\overrightarrow{ac}$ plane the fit does not get better even if one takes into account the anisotropic spin relaxation calculated from Reineker's theory[8,9] together with the value for Ψ_d evaluated from the diffusion tensor.[16]

The correspondence between theory and experiment is still worse for the anisotropy of the delayed fluorescence at 100 K. Using Suna's theory to calculate the spin-relaxation rate ζ improves the results a little bit, because the spin-relaxation rate in Suna's theory is less anisotropic than in Reineker's theory (compare Fig. 1). But with both theories, the calculated anisotropy of the spin-relaxation rate is too large to explain our measurements of the delayed fluorescence for direct triplet excitation. Therefore, we have again, as in the case of anthracene, tried to fit the anisotropy of the delayed fluorescence with anisotropic spin relaxation calculated according to Eqs. (3) and (5) but now treating Ψ_d as a fit parameter.

The results are shown in Fig. 7. The crosses and the rectangles correspond to the measurement at room temperature and at 100 K, respectively, and the solid and the dashed lines are the corresponding fitted theoretical curves. In Fig. 7(a) the magnetic field was rotated in the crystallographic $\overrightarrow{ac}$ plane and in Fig. 7(b) in the crystallographic $\overrightarrow{ab}$ plane. In both cases the triplet excitons

TABLE I. Anthracene. Values of the adjustable parameters λ_s, Ψ_d, Ψ_{oop} in Suna's theory (Ref. 5) obtained from fits to the anisotropy of the prompt and the delayed fluorescence for two different temperatures (see Figs. 4 and 6). For comparison the values for Ψ_d obtained by Ern (Ref. 13) are shown.

	T(K)	Nearest-neighbor annihilation rate λ_s (10^{11} sec^{-1})	Nearest-neighbor hopping rate Ψ_d (10^{10} sec^{-1})	Out-of-plane hopping rate Ψ_{oop} (10^8 sec^{-1})
Prompt fluorescence	300	2.6 ± 0.4	1.5 ± 0.3	4.7 ± 0.9
	100	2.7 ± 0.4	4.3 ± 0.6	3.1 ± 0.5
Delayed fluorescence	300	2.9 ± 0.3	4.9 ± 0.6	1.7 ± 0.6
Diffusion measurements	300		4.1	
by Ern	115		8.2	

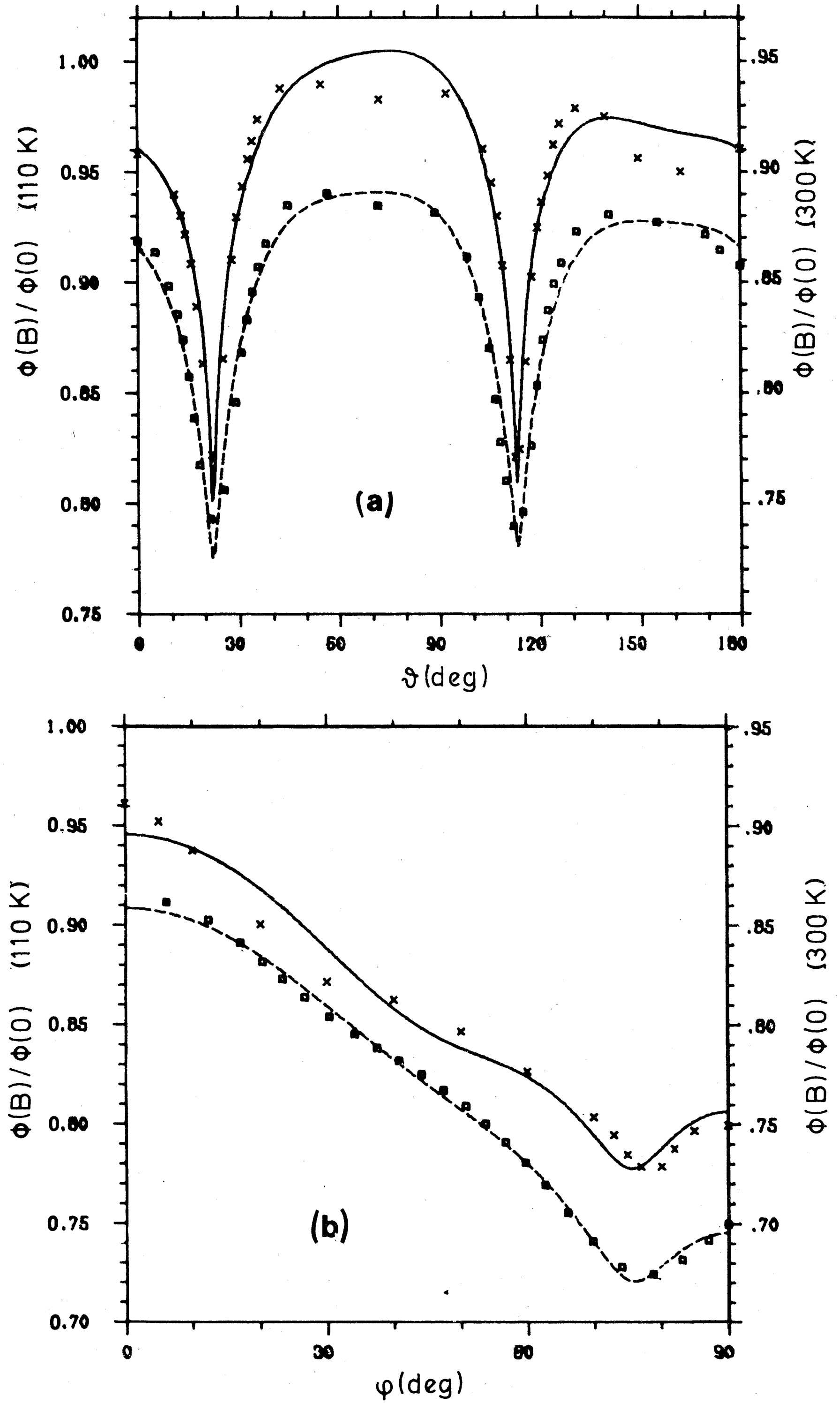

FIG. 7. Naphthalene. Ratio of the volume-excited delayed fluorescence intensities $\Phi(B)/\Phi(0)$ with and without magnetic field versus the magnetic field direction. Measured at 5.8 kOe in the crystallographic (a) $\vec{a}\vec{c}$ plane, (b) $\vec{a}\vec{b}$ plane and at 300 K (crosses) and at 110 K (rectangles). The solid line and the dashed line are the corresponding fitted theoretical curves calculated with Suna's theory taking into account anisotropic spin relaxation. The kinetic parameters obtained from these fits are summarized in Table II. ϑ and φ are the angles of the magnetic field with the crystallographic $\vec{c}'$ and $\vec{a}$ axes, respectively.

were excited directly, that means the excitation is practically homogeneous throughout the volume of the crystal. The fit parameters were again the nearest-neighbor hopping rate Ψ_d, the out-of-plane hopping rate Ψ_{oop}, and the nearest-neighbor annihilation rate λ_s. The agreement between theory and experiments is quite good, especially for the $\overrightarrow{ab}$ plane at 100 K. The values for the fit parameters obtained from the two different crystallographic planes are nearly the same. An average value for the parameters obtained from these fits with anisotropic spin relaxation is summarized in Table II.

Again Ψ_d is somewhat larger at 100 K than at room temperature which is in agreement with diffusion measurements. The value of Ψ_d obtained at 100 K is about two times larger than the low temperature value obtained in Ref. 17.

From the analogous fit of the anisotropy for triplet generation in the surface via strongly absorbed singlet excitation at 254 nm (see Fig. 3), we get a value for Ψ_d which is about two times smaller than in the volume of the crystal (see Table II). In the crystallographic $\overrightarrow{ab}$ plane, the value of the anisotropic spin-relaxation rate ζ of volume-generated triplet excitons varies between $\zeta = 2 \times 10^6$ and 1.9×10^8 sec^{-1} at room temperature, and between 2×10^6 and 1.4×10^8 sec^{-1} at 110 K. In the surface the triplet spin-relaxation rate changes between 2×10^6 and 2.8×10^8 sec^{-1} for the different field directions.

As it is seen in Fig. 7 the agreement between theory and experiment is not perfect, especially in the crystallographic $\overrightarrow{ac}$ plane. The dips at around $\vartheta = 65°$ and 155° cannot be explained with Suna's theory without assuming unreasonably high values for the nearest-neighbor annihilation rate λ_s which would, moreover, not be consistent with the value obtained from the $\overrightarrow{ab}$ plane. These dips get even much deeper for the surface anisotropy curve. There must be an additional magnetic-field-dependent anisotropic process which influences the triplet-triplet annihilation rate and which is larger near the surface of the crystal than in the volume (compare Fig. 3).

In order to decide whether this additional process influences the annihilation rate directly or rather indirectly via the anisotropy of the spin-relaxation rate we can relate to measurements of ESR linewidths in anthracene and naphthalene.[6] The expression for the ESR linewidth consists of a secular and a nonsecular part whereby the nonsecular part corresponds exactly to the spin-relaxation rate. For spin relaxation due to hopping between inequivalent molecules in a monoclinic crystal, the secular part is zero in the crystallographic $\overrightarrow{ac}$ plane because of symmetry reasons. In this plane the measured ESR linewidth give therefore the spin-relaxation rate. With the theory of Reineker for the calculation of ESR linewidths of triplet excitons[8,9] the experimental ESR linewidth measured by Haarer both in naphthalene and anthracene[6] cannot be described unless an additional effect is postulated. Altwegg had pointed out[1] that, on the other hand, with the experimental values for the spin-relaxation rate evaluated from Haarer's measurements the observed anisotropy of the delayed fluorescence in naphthalene at 8 kOe can be fitted perfectly in the $\overrightarrow{ac}$ plane. Therefore we can conclude that the additional anisotropic process influences the anisotropy of the annihilation rate via the spin-relaxation rate.

In order to estimate the magnitude of the addi-

TABLE II. Naphthalene. Values of the adjustable parameters λ_s, Ψ_d, Ψ_{oop} in Suna's theory (Ref. 5) obtained from fits to the anisotropy of the delayed fluorescence measured for triplet excitons generated in the volume and at the surface of the crystal and for different temperatures (see Figs. 3, 5, and 7). For comparison the values for Ψ_d obtained from diffusion measurements (Refs. 16 and 17) are shown.

	T(K)	Nearest-neighbor annihilation rate λ_s (10^{11} sec^{-1})	Nearest-neighbor hopping rate Ψ_d (10^{10} sec^{-1})	Out-of-plane hopping rate Ψ_{oop} (10^8 sec^{-1})
Excitation wavelength 472 nm (volume)	300	4.4 ± 1.4	1.5 ± 0.3	1.6 ± 0.6
	110	4.0 ± 1.0	3.5 ± 0.6	4.4 ± 1.1
Excitation wavelength 254 nm (surface)	300	1.0 ± 0.5	0.8 ± 0.2	1.8 ± 0.6
Diffusion measurements	300		0.97	
	115		1.95	

tional effect which affects the triplet spin relaxation primarily in the surface, we have used semiempirical anisotropy curves of spin-relaxation rates. Suna's theory together with the theoretical anisotropic spin relaxation gives a satisfactory fit to the anisotropy of the delayed fluorescence for volume-excited triplet excitons and in the crystallographic $\overrightarrow{ab}$ plane [see Fig. 7(b)]. Therefore, we have taken the parameters obtained from this fit, and with the requirement that they should yield a perfect fit to the $\overrightarrow{ac}$ plane, we have evaluated the semiempirical curves for the spin-relaxation rates shown in Fig. 8.

The solid line is the spin-relaxation rate calculated with Reineker's theory. The dashed line is the semiempirical spin-relaxation rate we get from a fit to the delayed fluorescence from volume-excited triplet excitons. The third curve is the semiempirical spin-relaxation rate we need to fit perfectly the anisotropy of the fluorescence from triplet excitons in the surface of the crystal.

One sees clearly from Fig. 8 that Reineker's curve, calculated on the basis of the hopping of triplet excitons between inequivalent molecules, gives only one part of the experimental spin-relaxation rate and that the dips at $\vartheta = 65°$ and 155° are due to another process influencing the spin-relaxation rate. The influence of this process must be, however, much stronger at the surface of the crystal than in the volume. Both semiempirical curves show the same anisotropy as the curve measured by Haarer[6] for the ESR linewidths. But the magnitude of the spin-relaxation rates in our experiments is 1.5 and 2.5 times, respectively, larger than in Haarer's experiment. This is most probably just due to the different magnetic fields in which the experiments are done.

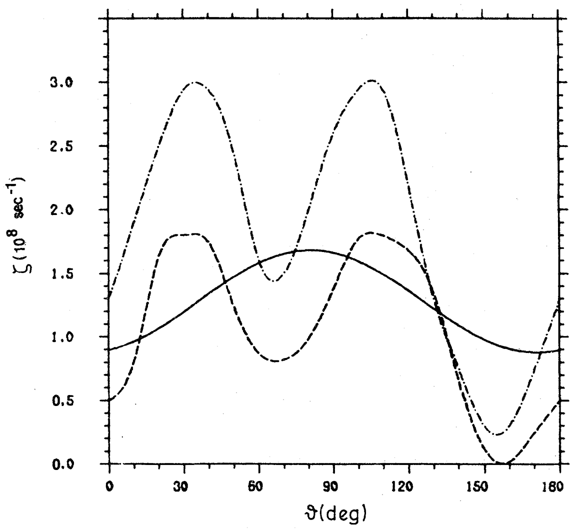

FIG. 8. Anisotropy of the triplet spin-relaxation rate (at room temperature) in naphthalene versus magnetic field direction in the crystallographic $\overleftrightarrow{ac}$ plane. Solid line: ζ calculated with Reineker's theory (Ref. 8 and 9) for 5.8 kOe. Dashed line: spin-relaxation rate resulting from an almost perfect fit of Suna's theory to the experimental anisotropy of the delayed fluorescence for volume-excited triplet excitons [see Fig. 3(a): rectangles]. Dot-dashed line: spin-relaxation rate resulting from an almost perfect fit of Suna's theory to the experimental anisotropy of the fluorescence for triplet excitons generated in the surface of the crystal by intersystem crossing from the singlet state excited at $\lambda = 254$ nm [see Fig. 3(a): triangles].

The question now is which effect causes this additional spin relaxation. Reineker[9] proposes that this additional effect may be due to librations of the molecules whereas Rosenthal[20] gives an explanation for the excess ESR linewidth based on structural defects in the crystal. The second explanation would, however, not lead to triplet spin relaxation and would therefore only influence the ESR linewidth and not the triplet annihilation rate in this way. The librations of the molecules, on the other hand, would not show a surface effect as it is seen in our experiments. We therefore propose the following explanation: In the surface region there are a lot of paramagnetic traps, whether these are paramagnetic impurities (e.g., oxygen) or trapped triplet excitons. During their motion the free excitons would then "perceive" additional fluctuations in the magnetic field which can lead to spin relaxation. At lower temperatures the excitons in the surface could either all be trapped and therefore, their contribution to the delayed fluorescence is strongly reduced, or they would drift away fast from the surface because of their larger hopping rates at low temperatures. The presence of paramagnetic surface traps could also explain the discrepancies between ESR linewidth measurements from Haarer[6] and Rosenthal[20] in anthracene.

VI. CONCLUSION

We have investigated the triplet-triplet annihilation in naphthalene and anthracene for different temperatures and for different excitation conditions. We have shown that the triplet spin-relaxation rate plays a very important role in the kinetic of the triplet-triplet annihilation not only in naphthalene, as it was shown earlier,[1] but even in anthracene. The anisotropy of the annihilation rate in anthracene and naphthalene can only be described with Suna's theory[5] if we take explicitly into account the anisotropy of the triplet spin-relaxation rate. The spin-relaxation rate itself is strongly dependent on the temperature and on the molecular environment of the triplet excitons.

The current theories[5,8,9] which describe the triplet spin relaxation in molecular crystals due to the hopping between inequivalent molecules can only partly explain our measurements, mainly for the magnetic field rotated in the $\vec{a}\vec{c}$ plane. There must be another process which contributes to the triplet spin relaxation and which is much more pronounced near the crystal surface than in the volume. Its contribution to the triplet spin-relaxation rate gets smaller with decreasing temperature. Further investigations on ESR linewidths could possibly give more information about the nature of this additional process.

ACKNOWLEDGMENTS

We would like to thank P. Reineker for stimulating discussions. The authors are indebted to the Schweizerische Nationalfonds for financial support of this work.

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