# Triplet exciton annihilation in naphthalene at high triplet densities

L. Altwegg, Maria A. Davidovich,* J. Fünfschilling, and Iris Zschokke-Gränacher

*Institute of Physics, The University of Basel, Basel, Switzerland*

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Triplet exciton annihilation in naphthalene has been investigated as a function of triplet exciton density. With increasing triplet density, a change of the magnetic field dependence of the delayed fluorescence as well as of the phosphorescence is observed, which is not expected on grounds of current theoretical models for triplet exciton annihilation. These density effects are studied in detail by varying the triplet exciton density by a factor of $10^5$. Analogous effects have been observed also in p-terphenyl. To explain the experimental findings a theoretical model which includes electron-hole pair production by triplet annihilation is presented.

## I. INTRODUCTION

In an earlier paper on triplet exciton annihilation in naphthalene crystals[1] we outlined that for naphthalene, unlike for anthracene, the magnetic effects on delayed fluorescence cannot be satisfactorily explained with the existing theories.[2,3] First, with regard to the general behavior of the anisotropy of the delayed fluorescence in a magnetic field, there is a difference between anthracene and naphthalene for certain crystallographic planes. Second, and more striking, is the observation that the magnetic effects depend on the density of mobile triplet excitons to a much greater extent than predicted by current theories.[2,3] For example, at high magnetic fields the relative change of the delayed fluorescence in the off-resonance direction is displaced from negative values towards even positive values with increasing triplet density. This means that at high exciton densities the delayed fluorescence intensity is larger when a high magnetic field is applied than without a field.

In the work presented here the triplet-density dependence of the magnetic effects in the delayed fluorescence is studied in detail in naphthalene by varying the triplet exciton density by a factor of about $10^5$. It will be shown that the value of the observed displacement in the high-field delayed fluorescence ratio with increasing triplet density does not depend on the direction of the magnetic field and that it reaches a limiting value at high exciton densities. Moreover, we have also investigated the exciton density dependence of the phosphorescence with and without magnetic field applied. By this means, the relative change of the triplet concentration and of the annihilation rate constant can be studied separately. The experimental results for naphthalene are compared with current theories on triplet exciton annihilation.[2-4]

In the stationary case the density $n$ of triplet excitons is given by

$$\alpha I = \beta n + \gamma_{\text{eff}} n^2 . \tag{1.1}$$

$\alpha$, $I$, and $\beta$ denote the absorption coefficient, the intensity of the exciting light, and the monomolecular decay rate, respectively. Provided the annihilation of two triplets results either in a singlet or triplet exciton or in a ground state, the bimolecular rate constant $\gamma_{\text{eff}}$ is given by

$$\gamma_{\text{eff}} = \tfrac{1}{2}\gamma_T + (1 - \tfrac{1}{2}\xi)\gamma_S + \gamma' , \tag{1.2}$$

where $\gamma_S, \gamma', \gamma_T$ are the rate constants leading to a singlet exciton, a vibrationally excited ground state, and a triplet exciton, respectively. $\xi$ is the quantum yield of the intersystem crossing. The only magnetic-field-dependent rate constants are $\gamma_S$ and $\gamma'$. The field dependence of these rates is described by the theory of Johnson and Merrifield,[2] in a more general form by Suna,[3] and reviewed in the article by Swenberg and Geacintov.[4] This theory, which treats the exciton annihilation in quite general form, has so far been verified in detail only for anthracene at low exciton densities. The delayed fluorescence intensity $\phi$ finally is given by

$$\phi = \tfrac{1}{2}G\eta\gamma_S n^2 , \tag{1.3}$$

where $G$ is the quantum yield of the measuring system and $\eta$ the yield for radiative singlet decay. As for the density of triplet excitons, it will be characterized in the following by the ratio of bimolecular and monomolecular decay rates $\sigma = \gamma_{\text{eff}} n/\beta$. At low densities $\sigma \ll 1$ and $n = \alpha I/\beta$. In the high-density limit $\sigma \gg 1$ and $n^2 = \alpha I/\gamma_{\text{eff}}$, which implies that the triplet density becomes magnetic-field dependent. In naphthalene with a relatively small decay rate $\beta \simeq 7 \text{ sec}^{-1}$, high relative densities can easily be achieved, e.g., $\sigma \simeq 100$ corresponds to approximately $n \simeq 2 \times 10^{14} \text{ cm}^{-3}$.

In order to examine the magnetic field effects, the delayed fluorescence is usually measured with a magnetic field applied to the crystal $[\phi(B)]$ and without $[\phi(0)]$. According to Eq. (3.11) in Ref. 1,

the delayed fluorescence ratio is given by

$$\frac{\phi(B)}{\phi(0)} = p(B)\left(\frac{\{1 + 4r(B)\sigma(0)[1 + \sigma(0)]\}^{1/2} - 1}{2r(B)\sigma(0)}\right)^2, \quad (1.4)$$

with $p(B) = \gamma_S(B)/\gamma_S(0)$, $r(B) = \gamma_{\text{eff}}(B)/\gamma_{\text{eff}}(0)$.

At medium and high densities where $\sigma > 1$, the low-density ratio $p(B)$ is multiplied by the density-dependent expression in the large parentheses. It is readily seen that the two limiting values of the delayed fluorescence ratio are

$$\phi(B)/\phi(0) = p \quad (1.5)$$

in the low-density limit for $\sigma \ll 1$, and

$$\phi(B)/\phi(0) = p/r \quad (1.6)$$

in the high-density limit for $\sigma \gg 1$. Under the assumption[4] that $\gamma' \ll \gamma_S$, and by putting $\gamma_T = c\gamma(0)$ ($c = 3$ for anthracene), the high-density factor becomes

$$r = \frac{\frac{1}{2}c\gamma_S(0) + \gamma_S(B)(1 - \frac{1}{2}\xi)}{\frac{1}{2}c\gamma_S(0) + \gamma_S(0)(1 - \frac{1}{2}\xi)} . \quad (1.7)$$

In Ref. 1 it is shown that, proceeding from the theory,[2,3] at high magnetic field $\phi(B)/\phi(0) < 1$ always; in other words, $p < 1$ as well as $p/r < 1$.

In order to explain the observed exciton-density effects in naphthalene, we have expanded this theory by suggesting an additional magnetic-field-dependent process.

## II. EXPERIMENTAL SETUP

The method of sample preparation, the apparatus, and the measuring procedure, were basically the same as described in Ref. 1. With the following improvements an extension of the accessible range of triplet exciton density to nearly five decades was possible.

At low densities the 476-nm line of a 0.5-W Ar laser was used for triplet excitation. The intensity of the laser beam was especially stabilized in order to minimize the drift during the long data-accumulation times needed. By cooling the photomultiplier the dark current was lowered by more than a factor of 200. To get good statistics and to minimize drift effects, photon-counting techniques were used exclusively.

To reach high triplet densities the crystal was excited with the 472-nm line of a 3-W Ar laser. In naphthalene the absorption coefficient at this wavelength is considerably higher than at 476 nm. In addition, the polarization which is absorbed most strongly was selected with the aid of a polarization rotator. The laser beam was focused onto the crystal by a lens and, being reflected by a mirror behind the crystal, traversed the sample twice. The intensity of the exciting light could be

varied with various neutral-density filters.

As for the delayed fluorescence, we have also measured the magnetic field dependence of the phosphorescence of naphthalene. Since the wavelengths of the phosphorescence and the triplet excitation are very close to each other, the exciting light was interrupted by a mechanical chopper during the measurement of phosphorescence. The speed of the chopper chosen was low enough so that steady-state triplet population was reached during excitation periods. During the period in which the phosphorescence was measured the exciton density did not decay by more than 0.6%. A filter-selector disk was allowed to measure phosphorescence immediately after a delayed fluorescence measurement and vice versa. To avoid overload of the photomultiplier during excitation, low-pass or interference filters were placed in front of the photomultiplier. The intensity of the incident scattered laser light was kept as low as possible by observing the phosphorescence (as well as delayed fluorescence) emitted perpendicularly to the direction of the laser beam.

## III. EXPERIMENTAL RESULTS

Figure 1 shows the anisotropy of the delayed fluorescence intensity of pure naphthalene in the crystallographic $a$-$c$ plane at a magnetic field of 8 kOe. The ratio of the delayed fluorescence intensity measured with and without magnetic field, $\phi(B)/\phi(0)$, is plotted versus the angle $\vartheta$ between the field direction and the crystallographic $c'$ axis. Rectangles and crosses represent, respectively, the low and high triplet-exciton-density limits. The meaning of these limits will be made clear later. Qualitatively the two curves look very similar, with the resonances at exactly the same positions and having approximately the same width and depth. However, the high-density curve is displaced considerably (by about 20%) towards higher values. Such a shift, which is not seen in anthracene, is not to be expected on the grounds of Suna's theory and the commonly used kinetic scheme.[1-5] Yet we have also observed this shift in $p$-terphenyl crystals.

In an earlier paper[1] we have shown that, apart from this shift, the shape of the $a$-$c$ plane anisotropy curve of naphthalene, measured, e.g., at medium density, can be explained fairly well with Suna's theory. However, a few problems arise if a complete fit is performed, as will be shown in a subsequent paper.

The delayed fluorescence intensity ratio $\phi(B)/\phi(0)$ as a function of the magnetic field strength $B$ is presented in Fig. 2 for $\vec{B}$ parallel to the crystallographic $c'$ axis ($\vartheta = 0$) pointing in an off-reson-
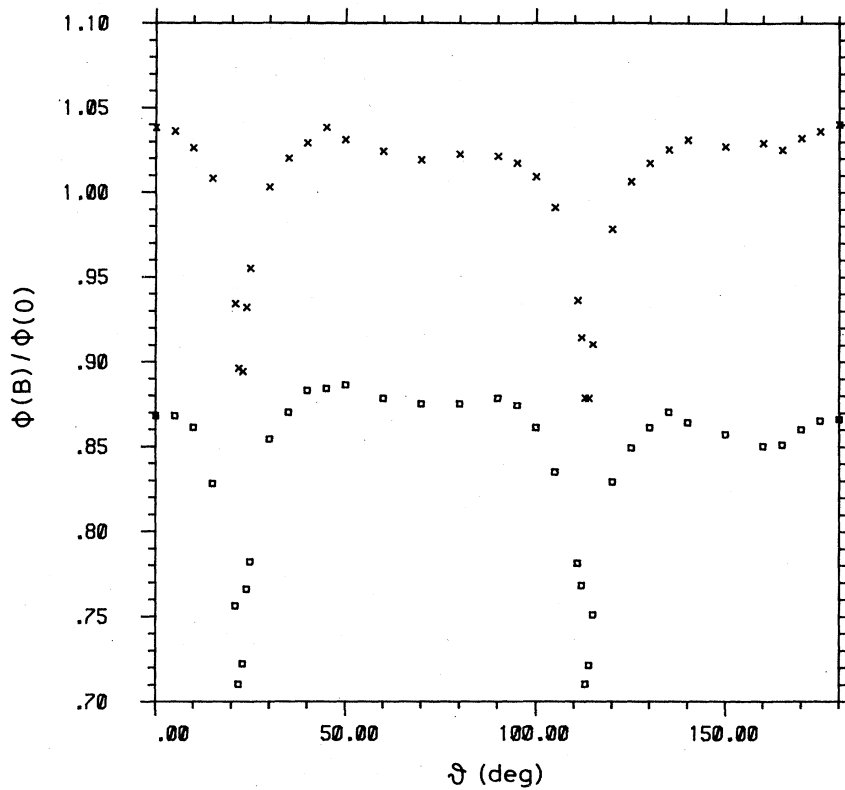
FIG. 1. Ratio of the delayed fluorescence intensities for pure naphthalene with and without magnetic field, $\phi(B)/\phi(0)$, vs the angle $\vartheta$ between the crystallographic $c'$ axis and the magnetic field direction. The field of 8 kOe was rotated in the $a$-$c$ plane. Rectangles: low-triplet-density limit; crosses; high-triplet-density limit.
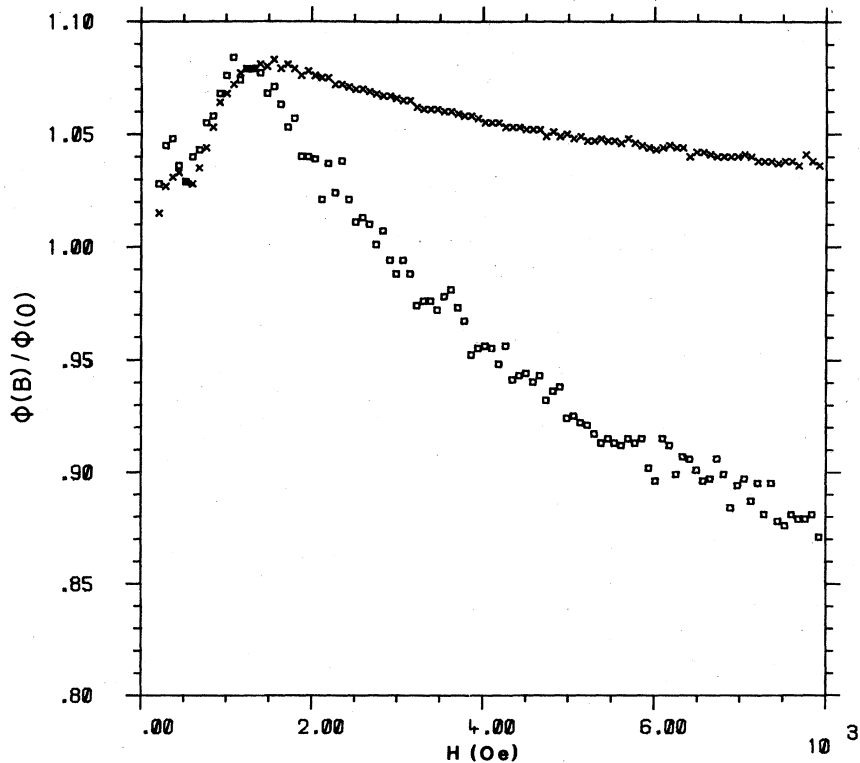


FIG. 2. Ratio of the delayed fluorescence intensities with and without magnetic field $\phi(B)/\phi(0)$ of pure naphthalene as a function of the magnetic field strength $|H|$. $\vec{H}$ parallel to the crystallographic $c'$ axis. Rectangles: low triplet density limit; crosses: high triplet density limit.
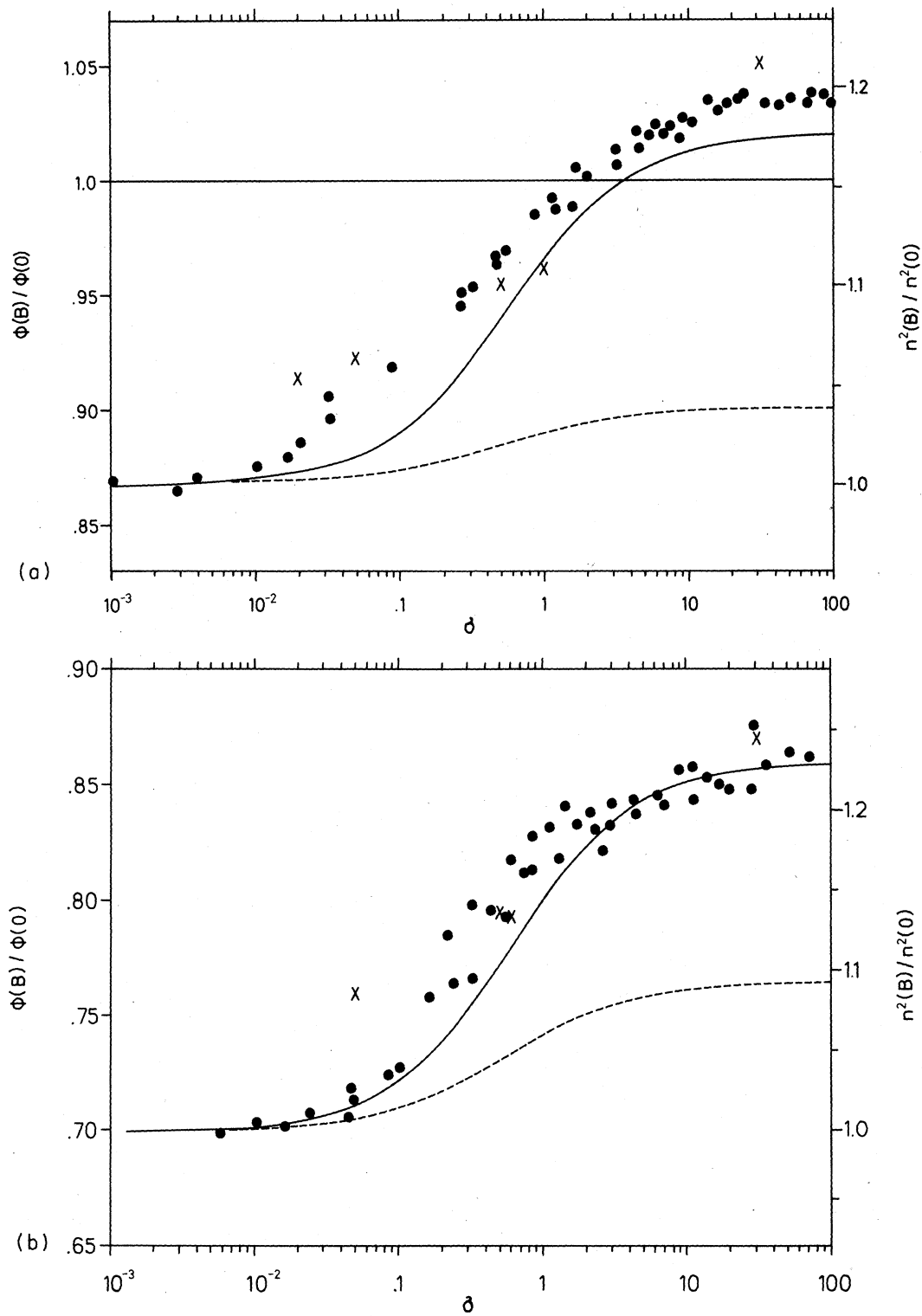
FIG; 3. Ratio of the delayed fluorescence intensities $\phi(B)/\phi(0)$ in a field of 8 kOe together with the corresponding ratio of triplet exciton densities $n^2(B)/n^2(0)$ of pure naphthalene as a function of relative triplet exciton density $\sigma$. Dots: delayed fluorescence measurements; crosses: $n^2(B)/n^2(0)$ from phosphorescence measurements; dashed curve: theory according Eq. (1. 7); solid curve: calculated with the aid of the theory presented in this paper. (a) Off-resonance direction ($\vec{H}$ parallel to crystallographic $c'$ axis). (b) On-resonance direction ($\vec{H}$ in the $a$-$c$ plane $\vartheta = 22°$).

ance direction. At low fields the curve measured at high densities lies slightly below that for low triplet densities. At 1.5 kOe the two curves cross and from there on the difference between high and low density increases monotonically with the field up to a value of about 20% at 8 kOe.

We have also examined the dependence of the delayed fluorescence ratio on triplet exciton density. In Figs. 3(a) and 3(b) the results are shown for the magnetic field $B$ along an off-resonance and an on-resonance direction in the crystallographic $a$-$c$ plane. $\phi(B)/\phi(0)$ is plotted versus $\sigma = \gamma_{\mathrm{eff}}(0)n(0)/\beta$, which is directly proportional to the triplet concentration $n(0)$ at zero magnetic field.

The reduced exciton density $\sigma$ was evaluated from the delayed fluorescence at zero magnetic field $\phi(0)$. As long as Eqs. (1.1) and (1.3) hold, $\sigma = c[\phi(0)]^{1/2}$ where $c$ is a constant. $c$ has been determined separately to an accuracy of $\pm 20\%$ by measuring the reduced triplet lifetime in a transient measurement. The highest value of $\sigma$ we could reach was 100. With $\gamma_{\mathrm{eff}} = 3.5 \times 10^{-12}$ cm$^3$ sec$^{-1}$ from Ref. 6 this corresponds to a triplet density of $n(0) = 2 \times 10^{14}$ cm$^{-3}$.

The existence of the high- and low-density limits, which we refer to in Figs. 1 and 2, is clearly seen in Figs. 3(a) and 3(b): below $\sigma = 0.01$ and above $\sigma = 30$ the ratio $\phi(B)/\phi(0)$ does not depend on $\sigma$. In Fig. 3(a) it is also seen that in the off-resonance direction the value of $\phi(B)/\phi(0)$ changes from smaller than 1 to greater than 1 at high densities. The density dependence as predicted by theory [Eqs. (1.4) and (1.7) with $c = 3$ and $\xi = 0.82$ from Ref. 7] is represented by the dashed curves in Figs. 3(a) and 3(b).

If the fluorescing singlet state is populated by triplet annihilation the delayed fluorescence intensity is quadratic on the triplet concentration $n$:

$$\phi \propto \gamma_S n^2 . \tag{3.1}$$

$\gamma_S$ denotes the bimolecular rate constant for delayed fluorescence. The ratio of the delayed fluorescence intensity with and without a magnetic field is then given by

$$\frac{\phi(B)}{\phi(0)} = \frac{\gamma_S(B)}{\gamma_S(0)} \frac{n^2(B)}{n^2(0)} . \tag{3.2}$$

For low densities $n(B) = n(0)$. At high densities, when the bimolecular decay predominates,

$$\left. \frac{n^2(0)}{n^2(B)} \right|_{\mathrm{hd}} = \frac{\gamma_{\mathrm{eff}}(B)}{\gamma_{\mathrm{eff}}(0)} \equiv r(B) , \tag{3.3}$$

where $\gamma_{\mathrm{eff}}$ is the effective bimolecular decay rate. Thus we get the following expressions for the low-density (ld) and high-density (hd) limits, respectively:

$$\left. \frac{\phi(B)}{\phi(0)} \right|_{\mathrm{ld}} = \left. \frac{\gamma_S(B)}{\gamma_S(0)} \right|_{\mathrm{ld}} , \tag{3.4}$$

$$\left. \frac{\phi(B)}{\phi(0)} \right|_{\mathrm{hd}} = \frac{1}{r} \left. \frac{\gamma_S(B)}{\gamma_S(0)} \right|_{\mathrm{hd}} . \tag{3.5}$$

At intermediate densities the ratio $\phi(B)/\phi(0)$ follows the density dependence given by Eq. (1.4).

By writing $\phi(B)/\phi(0)$ in the form of Eq. (3.2), the important question is whether the ratio $\gamma_S(B)/\gamma_S(0) = p(B)$ changes with the triplet exciton density $n$. In order to separate the density dependences of $p(B)$ and $n^2(B)/n^2(0)$, we have simultaneously measured the density dependence of the delayed fluorescence ratio $\phi(B)/\phi(0)$ as well as of the phosphorescence intensity ratio $\phi_{\mathrm{ph}}(B)/\phi_{\mathrm{ph}}(0)$. Since $\phi_{\mathrm{ph}}$ is directly proportional to the triplet density $n$, we have

$$\phi_{\mathrm{ph}}(B)/\phi_{\mathrm{ph}}(0) = n(B)/n(0) . \tag{3.6}$$

$p$ can therefore be expressed as

$$p \equiv \frac{\gamma_S(B)}{\gamma_S(0)} = \frac{\phi(B)}{\phi(0)} \left( \frac{\phi_{\mathrm{ph}}(0)}{\phi_{\mathrm{ph}}(B)} \right)^2 . \tag{3.7}$$

We have determined $p$ for several densities between $\sigma \simeq 30$ and $\sigma \simeq 0.02$. At all densities the value of $p$ was the same within $\pm 2\%$. $p = 0.86$ in the off-resonance direction $\vec{B} \parallel \vec{c}'$; $p = 0.67$ in the on-resonance direction $\vartheta = 22°$, $\vec{B}$ in the $a$-$c$ plane. These values of $p$ agree also with the low-density-limit values of the delayed fluorescence ratio $\phi(B)/\phi(0)$, as measured, e.g., in Fig. 3. The agreement is quite good for the off-resonance direction. Crystal imperfections and inhomogeneities of the magnetic field might be the reason for the small discrepancy in the on-resonance direction.

Thus the most important conclusion from the phosphorescence measurements is that $p(B)$ does not depend on triplet density. Consequently it is exclusively the unique density dependence of the ratio $n(B)/n(0)$ which is responsible for the density effects observed in the delayed fluorescence of naphthalene crystals. As only this ratio depends on $\sigma$ we now may as well plot $[n(B)/n(0)]^2$ instead of $\phi(B)/\phi(0)$ in Figs. 3(a) and 3(b). The squares of the ratios of $n(B)/n(0)$ from the phosphorescence measurements are also plotted in Figs. 3(a) and 3(b). To decide whether or not $p$ depends on density, $\sigma$ does not have to be measured to high accuracy. Still in Figs. 3(a) and 3(b) the correspondence between $n(B)/n(0)$ from phosphorescence and from delayed fluorescence measurements is satisfactory.

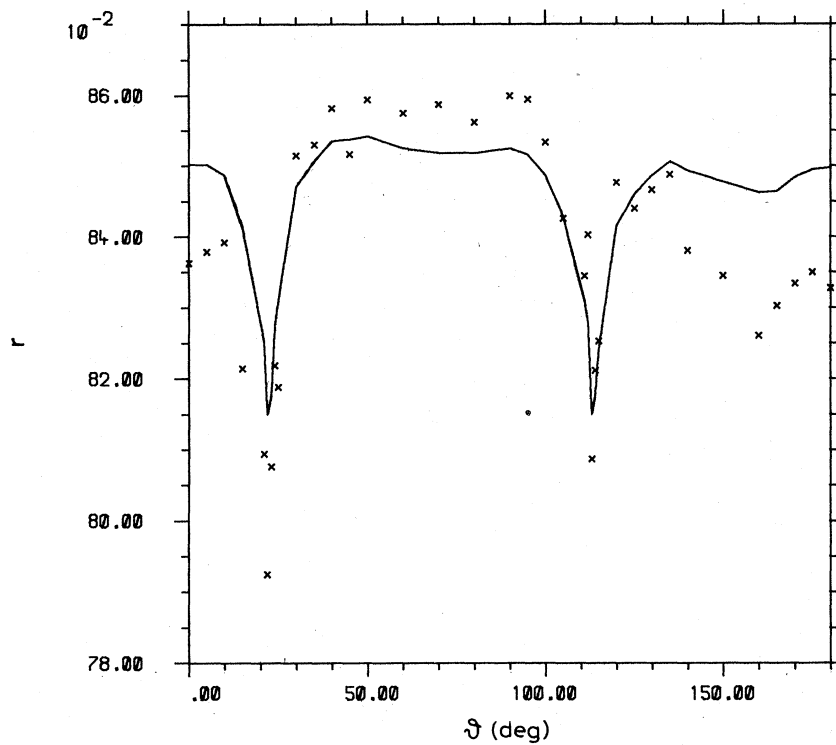As $p$ is independent of $n$, according to Eqs. (3.4) and (3.5) $r$ can be expressed as

FIG. 4. $r(B) = \gamma_{eff}(B)/\gamma_{eff}(0)$ of pure naphthalene as a function of the angle $\vartheta$ between the crystallographic $c'$ axis and the magnetic field direction for a field of 8 kOe rotated in the $a$-$c$ plane. Crosses: experimental points; solid curve: theory presented in this paper.
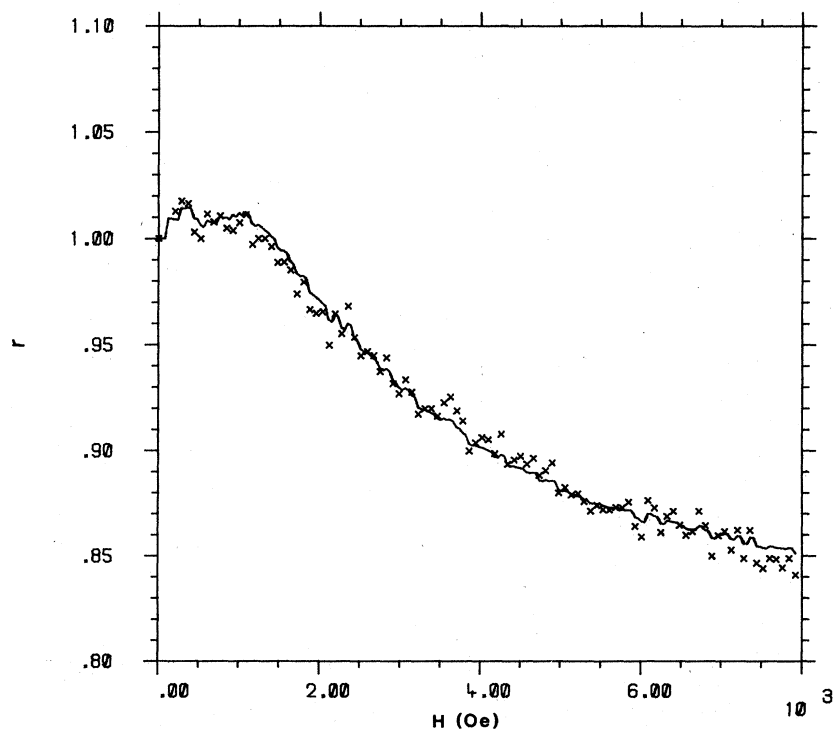


FIG. 5. $r(B) = \gamma_{eff}(B)/\gamma_{eff}(0)$ of pure naphthalene as a function of the magnetic field strength $|H|$ with $\vec{H}$ parallel to the crystallographic $c'$ axis. Crosses: experimental points; solid curve: theory presented in this paper.

$$r = \frac{\phi(B)}{\phi(0)}\bigg|_{ld} \bigg/ \frac{\phi(B)}{\phi(0)}\bigg|_{hd} \, .$$

The anisotropy of $r$ in the $a$-$c$ plane is thus obtained, by dividing the two curves in Fig. 1. In the same way, the field-strength dependence of $r$ for $\vec{B} \parallel \vec{c}'$ is evaluated from the two curves in Fig. 2. The result is shown in Figs. 4 and 5, respectively.

It is generally assumed that the annihilation of two triplets leads either to a singlet or to a triplet exciton. From this assumption it follows[1] that at high fields $p$ must always be smaller than $r$. From a comparison of the low-density curve of Fig. 1 (representing the anisotropy of $p$) with the curve of Fig. 4, it is readily seen that this is violated in naphthalene. Likewise, by comparing the low-density curve in Fig. 2 (representing the field-strength dependence of $p$) with the curve of Fig. 5, it is seen that $r$ is smaller than $p$ at high fields. Furthermore, at around 2 kOe the value of $r$ is smaller than 1 whereas $p$ is greater than 1. This again is in contrast with the current theoretical picture on triplet annihilation.[1]

## IV. THEORY

In the following, we summarize our experimental results for naphthalene:

(i) At fields $> 1.5$ kOe, as the density of triplet excitons increases, $\phi(B)/\phi(0)$ shifts to higher values becoming even greater than 1 in off-resonance directions. This shift increases with field strength and saturates at about 10 kOe.

(ii) At low fields $\phi(B)/\phi(0)$ is almost independent of triplet density, decreasing only slightly as the density increases.

(iii) The anisotropy at high fields, namely, the ratio $[\phi(B)/\phi(0)]_{\text{off res}} / [\phi(B)/\phi(0)]_{\text{on res}}$, decreases slightly with increasing density.

(iv) No directional resonances other than those of the rate constant $\gamma_S(B)$ are observed at high densities.

(v) The density dependence of $\phi(B)/\phi(0)$ is entirely contained in $n(B)/n(0)$.

(vi) An analogous shift of the delayed fluorescence ratio with triplet density has also been observed in $p$-terphenyl crystals but not in anthracene.

On the grounds of these results we conclude that an additional magnetic-field-dependent process must be influencing the triplet exciton density $n$, and this is the subject of this section. The additional process influencing the triplet density should have the following properties: (a) It should be more field dependent than $\gamma_S(B)$ at high fields, (b) it should be approximately field independent at low fields ($B < 1.5$ kOe), and (c) it should either

have no anisotropies or have resonances at the same field orientations as $\gamma_S(B)$. Guided by these properties and by the important fact that the energy of the two annihilating triplet excitons in naphthalene (5.2 eV) is high enough to make the production of charges energetically possible, unlike the case in anthracene, we propose the following model: in naphthalene the annihilation of triplet excitons leads not only to triplet and singlet excitons, but produces also electron-hole pairs. These can dissociate into carriers or recombine to yield triplet and singlet excitons or ground-state molecules. If their lifetime is long enough for significant spin motion to occur in a magnetic field, due to differences in the $g$ factors of electron and hole, the amount of triplets and singlets so formed will be magnetic field dependent. The process involving the charge pairs is sketched as follows:
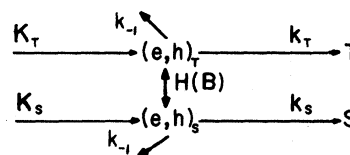


$K_T$ and $K_S$ are, respectively, the rate constants for the formation of triplet and singlet charge pairs, $k_T$ and $k_S$ are the rate constants for recombination of the triplet and singlet charge pairs, respectively, and $k_{-1}$ is the rate constant for dissociation of the pair.

$H(\vec{B})$ is the Hamiltonian which mixes triplet and singlet charge pair states, given by

$$H(\vec{B}) = \mu_B \vec{B} (g_e \vec{S}_e + g_h \vec{S}_h), \qquad (4.1)$$

with $g_e$ and $g_h$ being the $g$ factors for the electron and the hole, $\vec{S}_e$ and $\vec{S}_h$ the spin operators for electron and hole, and $\mu_B$ the Bohr magneton, respectively. In Eq. (4.1) hyperfine interaction can certainly be ruled out. This will be discussed in Sec. VI.

The steady-state equation of motion for the density matrix $\rho$ of the charge pair spin states then has the form

$$K_T P_T + K_S P_S = (i/\hbar)[H(B), \rho] + k_{-1}\rho + \tfrac{1}{2}k_S(P_S\rho + \rho P_S)$$
$$+ \tfrac{1}{2}k_T(P_T\rho + \rho P_T), \qquad (4.2)$$

where the two terms on the left-hand side are the source terms for the triplet and singlet charge pairs, respectively, and the last three terms on the right-hand side represent the decay of the pair states, respectively, by dissociation and recombination into a singlet and into a triplet state. $P_S$ and $P_T$ are projection operators on the singlet and triplet manifold, respectively.

The quantities of interest are the rate of generation of triplet and singlet states by charge pair recombination, which are given by

$$T(B) = k_T \operatorname{Tr}(P_T \rho),  \tag{4.3}$$

$$S(B) = k_S \operatorname{Tr}(P_S \rho).  \tag{4.4}$$

Equation (4.2) is easily solved for $\rho$ by diagonalizing $H(B)$, which mixes only triplet states with $m_S = 0$ and singlet states. In this calculation we have neglected exchange interactions between electron and hole (these are negligibly small if the electron and the hole are not on neighboring molecules). After calculating the matrix $\rho$ we take the trace of $(P_T \rho)$ and $(P_S \rho)$ and obtain

$$T(B) = n^2(B) \left[ \frac{k_T}{k_T + k_{-1}} \frac{\gamma_T'}{3} + \frac{1}{2} \frac{k_T}{k_T + k_S + 2k_{-1}} \right.$$

$$\times \left( \gamma_S'(B) + \frac{\gamma_T'}{3} \right) g(B)$$

$$\left. + \frac{1}{6} k_T (k_S + k_{-1}) \frac{\gamma_T' g(B)}{(\Delta g \mu_B B)^2} \right],  \tag{4.5}$$

$$S(B) = n^2(B) \left[ \frac{1}{2} \frac{k_S}{k_T + k_S + 2k_{-1}} \left( \gamma_S'(B) + \frac{\gamma_T'}{3} \right) g(B) \right.$$

$$\left. + \frac{1}{2} k_S (k_T + k_{-1}) \frac{\gamma_S'(B) g(B)}{(\Delta g \mu_B B)^2} \right],  \tag{4.6}$$

where $\gamma_S'$ and $\gamma_T'$ are the annihilation rates leading to singlet and triplet charge pairs, respectively, $n$ is the triplet concentration, and $g(B)$ is given by

$$g(B) = \frac{(\Delta g \mu_B B)^2}{(\Delta g \mu_B B)^2 + (k_{-1} + k_S)(k_{-1} + k_T)},  \tag{4.7}$$

with $\Delta g = |g_e - g_h|$.

We now add these processes, namely, the additional channels for triplet annihilation leading to charge pairs and the production of triplets resulting from the recombination of these pairs, to the steady-state equation for $n$, Eq. (1.1). Because they are quadratic on $n$, by adding them we actually modify the bimolecular decay rate $\gamma_{\text{eff}}$ in Eq. (1.1): $\alpha I = \beta n + \gamma_{\text{eff}}(B)n^2$ by writing

$$\gamma_{\text{eff}}(B) = \gamma(B) + \gamma_S'(B) + \gamma_T' - T(B)/n^2  \tag{4.8}$$

and

$$\gamma(B) = \frac{1}{2}[(1 + \eta)\gamma_S(B) + \gamma_T],  \tag{4.9}$$

where $\eta$ is the quantum efficiency of fluorescence (the only nonradiative decay term of singlet excitons we consider is intersystem crossing with quantum efficiency $\xi = 1 - \eta$). The annihilation rate constant $\gamma'$ leading to a vibrationally excited ground state has been neglected in Eq. (4.9).

The formation of charge pairs with subsequent annihilation into singlet states would also affect the field dependence of the delayed fluorescence if these singlets contribute to fluorescence. The expression for $\phi(B)/\phi(0)$ is then modified to

$$\frac{\phi(B)}{\phi(0)} = \left[ \frac{\frac{1}{2}\eta\gamma_S(B) + \eta' S(B)/n^2(B)}{\frac{1}{2}\eta\gamma_S(0) + \eta' S(0)/n^2(0)} \right] \frac{n^2(B)}{n^2(0)}$$

$$\equiv f(B) \frac{n^2(B)}{n^2(0)},  \tag{4.10}$$

where $\eta'$ is the quantum efficiency of fluorescence of the singlet states formed by recombination.

The two limiting values of $\phi(B)/\phi(0)$ are now given by

$$[\phi(B)/\phi(0)]_{\text{ld}} = f(B)  \tag{4.11}$$

in the low-density limit $\sigma \ll 1$,

$$[\phi(B)/\phi(0)]_{\text{hd}} = f(B)/r(B)  \tag{4.12}$$

in the high-density limit $\sigma \gg 1$, where

$$r(B) \equiv \frac{\gamma_{\text{eff}}(B)}{\gamma_{\text{eff}}(0)} = \frac{p(B)\left(1 + a - \frac{1}{2} \frac{k_T a}{k_T + k_S + 2k_{-1}} g(B)\right) - \frac{b'}{3} \frac{k_T}{k_T + k_S + 2k_{-1}} g(B)}{1 + a + b + 2b'\left(1 - \frac{1}{2}\frac{k_T}{k_T + k_{-1}}\right)}$$

$$+ \frac{-\frac{b'}{3} k_T (k_{-1} + k_S) \frac{g(B)}{(\Delta g \mu B)^2} + b + 2b'\left(1 - \frac{1}{3}\frac{k_T}{k_T + k_{-1}}\right)}{1 + a + b + 2b'\left(1 - \frac{1}{2}\frac{k_T}{k_T + k_{-1}}\right)},  \tag{4.13}$$

with

$$a \equiv \frac{2}{1 + \eta} \frac{\gamma_S'(0)}{\gamma_S(0)}, \quad b \equiv \frac{1}{1 + \eta} \frac{\gamma_T}{\gamma_S(0)}, \quad b' \equiv \frac{1}{1 + \eta} \frac{\gamma_T'}{\gamma_S(0)}, \quad \frac{\gamma_S'(B)}{\gamma_S'(0)} = \frac{\gamma_S(B)}{\gamma_S(0)} = p(B).  \tag{4.14}$$

The above equations should be substituted for Eqs. (1.5)–(1.7) in Sec. I.

## V. COMPARISON OF THEORY WITH EXPERIMENTAL RESULTS

To check the field and density dependence derived in Sec. IV, we consider the following: (i) the field-strength dependence and the anisotropy of $r(B)$ in Figs. 4 and 5, and (ii) the density dependence of the delayed fluorescence ratio in Fig. 3.

Now we make the assumption that the population of the fluorescing singlet state is not directly affected by the production and recombination of charge pairs. We assume that the recombination of singlet charge pairs, if not negligible, leads to a nonfluorescing state, e.g., a vibronically excited ground state. In this case $\eta' S/n^2 \ll \frac{1}{2}\eta\gamma_S$ and expression (4.10) for the delayed fluorescence is simplified to

$$\phi(B)/\phi(0) = p(B)\, n^2(B)/n^2(0) . \tag{5.1}$$

This assumption is suggested by two facts: First, at low densities the field dependence of the delayed fluorescence (Figs. 1 and 2) is in good qualitative agreement with Suna's theory.[1,3] Second, some preliminary calculations have shown that in order to obtain the observed on- and off-resonance values for $r(B)$ in the high field limit, $\eta'$ in Eq. (4.10) has to be very small.

Before we present the results of quantitative calculations, we will discuss the significance of $b'$ in Eq. (4.14) on the field dependence of $r(B)$. The formation of charge pairs in the triplet state ($b' \neq 0$) only decreases the field dependence of $T(B)$ and consequently of $r(B)$. This decrease becomes less important the smaller the values of the rate constants $k_{-1}$ and $k_S$ are. It reaches a minimum when $k_{-1}$ and $k_S$ are negligible compared to $k_T$, in which case the formation of triplet charge pairs and their subsequent recombination would only add a constant term to $\gamma_{\text{eff}}$. This can be clearly seen by neglecting $k_S$ and $k_{-1}$ compared to $k_T$ in Eq. (4.13). One then obtains

$$r(B) = \frac{p(B)[1 + a - \frac{1}{2}a\, g(B)] + b + b'}{1 + a + b + b'} , \tag{5.2}$$

with

$$g(B) = \frac{(\Delta g\mu B)^2}{(\Delta g\mu_B B)^2 + (k_{-1} + k_S)k_T} . \tag{5.3}$$

As a first trial we have considered the situation which gives the strongest field dependence to $r(B)$; namely, we have fitted Eq. (4.13) with $b' = 0$ to the experimental field-strength dependence for the off-resonance direction. We have taken $\Delta g = 10^{-4}$,[8,9] $\eta = 0.18$,[7] and $\gamma_T/\gamma_S(0) = 3$ as known quantities. For $p(B)$ we have used the experimental curve for $\phi(B)/\phi(0)$ in the low-density limit. The other constants, $a$, $k_T$, $k_S$, and $k_{-1}$ were taken as adjust-

able parameters. It turns out from this fitting that $k_S$ and $k_{-1} \ll k_T$. Obviously, this holds also for $b' \neq 0$. Therefore, when considering the more general case of charge pairs being formed in both spin states, the simplified version of Eq. (4.13), Eq. (5.2), can be used. We have then calculated the field-strength dependence of $r(B)$ given by Eq. (5.2) for the field in an off-resonance direction, taking the constants $a$, $b + b'$, and $k_T(k_{-1} + k_S)$ as adjustable parameters. The result is shown along with the experimental data in Fig. 5. The agreement is good. The noise in the calculated curve appears because we are using for $p(B)$ the experimental curve for $\phi(B)/\phi(0)$ in the low-density limit.

The parameter values which result from these curve fittings are

$$k_T(k_{-1} + k_S) = (7.3 \pm 1.3) \times 10^{12} \text{ sec}^{-2} ,$$

$$\gamma_S'(0)/\gamma_S(0) = 2.4 \pm 1.4 , \tag{5.4}$$

$$(\gamma_T + \gamma_T')/\gamma_S(0) = 11 \pm 7 .$$

The values obtained for $\gamma_S'(0)/\gamma_S(0)$ and $(\gamma_T + \gamma_T')/\gamma_S(0)$ seen to be reasonable. Only the value of the total annihilation rate into the triplet channel $(\gamma_T + \gamma_T')$ can be determined by the fit.

The values obtained for the lifetime of the charge-pair states are longer than expected. For example, if we take $k_S/k_T = k_{-1}/k_T = 0.1$ we get $1/k_T = 10^{-7}$ sec and the lifetime of the singlet charge pairs would be 10 times longer than this. However, the values of these rate constants are quite sensitive to the value of $\Delta g$, which is not known in naphthalene crystals. The value of $10^{-4}$ for $\Delta g$ we have used is the one of anthracene ions in solution.[8,9] We have obtained a fit as good as the one shown in Fig. 5 using $\Delta g = 10^{-3}$. The values of the parameters are about the same as before except for the parameter $k_T(k_{-1} + k_S)$ which gets 100 times greater; thus the charge-pair lifetime is considerably reduced.

Using the set of the parameters of Eq. (5.4), we have calculated the anisotropy curve for $r(B)$ and the density dependence of $\phi(B)/\phi(0)$ for $H = 8$ kOe. The results are shown along with the experimental curves in Figs. 4 and 3. The agreement is quite satisfactory.

## VI. CONCLUSIONS

We have presented more experimental results and a theoretical explanation for the density effects on the delayed fluorescence of naphthalene crystals. By measuring both the delayed fluorescence and phosphorescence, it has been concluded that the unexpected density effects are due to an anomalous field dependence of the triplet exciton

concentration. To explain these observations we have extended the commonly used kinetic schemes to include additional annihilation channels leading to charge pair states. The idea of formation of pairs by annihilation is very attractive because it would explain why this effect is observed in naphthalene and $p$-terphenyl crystals, where the creation of pairs by annihilation is energetically possible, and not in anthracene crystals, where this condition is not satisfied.

The $\Delta g$ interaction that we have assumed to be responsible for the singlet-triplet mixing has been used in the past[10,11] to explain field-dependent intersystem crossing between triplet and singlet spin states. Although the lifetimes we obtain for the charge pair states are longer than expected (because of the small value of $\Delta g$), this was the only interaction which could give the observed field dependence.

We were unable to explain the experimental data by considering other interactions which would also affect the field dependence of the triplet concentration, as, for example:

(i) Triplet-doublet interaction. Triplet excitons could be quenched by trapped electrons and holes formed by triplet annihilation. Since the triplet-doublet interaction constant decreases with field this quenching process would, in fact, increase the triplet concentration ratio $n(B)/n(0)$ at high fields. However, while at high fields the triplet-doublet interaction has resonances at the same field orientations as the triplet-triplet fusion constant $\gamma_S$, at low fields it has resonances at different orientations. Since the delayed fluorescence at high densities does not exhibit any low-field resonances other than the ones of $\gamma_S$ this process can be ruled out. Furthermore it does not have the right field scale since it is more field dependent at low fields, saturating at about 3 kOe.

(ii) In the case of hyperfine interaction the singlet-triplet mixing of our charge pairs could be

due to differences in the electron and hole hyperfine interactions. This can, however, be ruled out—first, because this interaction is probably averaged out by the motion of the electron and hole and second, because it saturates at about 100 G and therefore does not have the field scale observed. In addition, no significant difference has been observed between the measurements of Fig. 2 and analogous experiments in perdeuterated naphthalene.

(iii) We have also unsuccessfully considered the possibility of annihilation in the quintet channel. The quintet states formed could cross to triplet states and therefore would affect the field dependence of the triplet exciton concentration.

(iv) We finally comment on three-particle interactions. As pointed out in Ref. 1, this effect can be neglected in systems in which the exciton diffusion is quasi two dimensional, as long as

$$\gamma_{\text{eff}}\, n \ll \beta_{\text{eff}} , \qquad (6.1)$$

where $\beta_{\text{eff}}$ is approximately given by the out-of-plane hopping rate of triplet excitons. At our highest density, although $\gamma_{\text{eff}}\, n \gg \beta$, condition (6.1) is most probably still satisfied. In fact, the observation that for all densities the delayed fluorescence is exactly quadratic on the triplet concentration indicates that in our experiments these effects can indeed be neglected. Furthermore, within an experimental accuracy of a tenth of a degree we did not observe any shift in the delayed fluorescence resonance positions with increasing triplet density. Such a shift would be expected if additional multiparticle interactions were present at high exciton densities.

*Present address: Departamento de Fisica-PUC, Rua Marquês de Sao Vicente 225, Rio de Janeiro, R. J., Brazil.

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