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MAGNETIC FIELD DEPENDENCE OF SINGLET EXCITON FISSION AND FLUORESCENCE IN CRYSTALLINE TETRACENE AT 300 K

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Abstract. — The magnetic field dependence of singlet exciton fission and fluorescence was studied at 300 K in tetracene crystals in several crystal planes for different field intensities and orientations. The positions of the resonances at high field correspond to those predicted by the zero-field splitting tensor as obtained by EPR, indicating that the outcome of the singlet fission is a pair of free migrating triplet excitons. It is shown that the field dependence and the resonance lineshapes can only be fitted, to within the experimental error, with the kinematic theory of Suna assuming a nearly two-dimensional motion of triplet excitons, restricted to the (a'b) plane. With the assumption of an isotropic triplet exciton diffusion in the (a'b) plane reasonable sets of values can be deduced from the fit for the in-plane hopping rate, for the anisotropy of the diffusion, and for the nearest neighbour triplet-triplet annihilation rate. In many respects, triplet exciton dynamics in tetracene appears to be similar to that in anthracene, as expected from the calculation of the transfer matrix elements and the similarity of the crystal structures. The dependence of the effects on the exciting light intensity are also well accounted for using the usual kinetic equations for the different processes involved during the lifetime of the triplet excitons.

1. Introduction. — The magnetic field (MF) modulation of bimolecular annihilation of triplet excitons and hence of the delayed fluorescence, discovered in anthracene [1], has now been found and studied in a number of pure [2] and doped [3] crystals, as well as in solution [4]. The experimental results and their theoretical interpretation are discussed in several review papers [5-7]. The explanation of these effects is based on the proposal by Merrifield [8], that the probability of fusion of two triplets into one singlet (which may eventually decay radiatively, emitting the so-called delayed fluorescence [9]), is proportional to the square of the singlet amplitude of the spin state of the triplet pair. This idea has been theoretically elaborated in two different ways, by Johnson and Merrifield [10], and by Suna [11], hereafter referred to as theories I and II respectively.

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where almost no experimental information on triplet fusion is available, excitons are localized and move by hopping in the crystal lattice [12]. Triplet fusion then involves two physically different processes: exciton diffusive motion, and interaction of two triplet excitons centered at a distance $R$ from each other.

In theory I [10] a correlated triplet pair ($TT$) is introduced as an intermediate state — whose properties are not further defined — in triplet fusion, and a chemical kinetic-like scheme is written

$$ T + T \xrightarrow{k_{-1}} (TT) \xrightarrow{k_{2}} S^* \quad \{1\} $$

neglecting other decay channels. Three rate constants are introduced as adjustable parameters. As the interaction between the triplets is neglected in the Hamiltonian, $k_1$ and $k_{-1}$ should depend on the spin-independent triplet motion, and $k_2$ on the spin-dependent triplet-triplet interaction. Spin relaxation is not explicitly considered. $k_{-1}$ and $k_2$ can be viewed as determining the lifetime of the triplet pair ($TT$), which is found by curve fitting to be of the order of $10^{-10}$ to $10^{-9}$ s in for instance anthracene or naphthalene [2b, 10], much longer than the triplet hopping times deduced from the known triplet diffusivities [12].

This is apparently a paradox, if no binding energy of the triplet pair is postulated. In theory II [11], no explicit scheme like $\{1\}$ is introduced, but the triplet interaction process is described in terms of parameters corresponding respectively to the exciton motion and the probability of fusion of two triplets. The magnetic field intensities and directions for which the simpler theory I yields results exactly equal to those of theory II have been found [11, 2c]. The large values of $k_{-1}$ can be related to the quasi-two-dimensional character of triplet motion in anthracene, and presumably also in naphthalene [12]. In such systems, the correlation time is limited, either by the hopping of one triplet out of one ($a'b$) plane, or by spin relaxation. The magnetic field effects on delayed fluorescence in quasi-two-dimensional systems is described, in theory II, in terms of three parameters: an interaction rate $\lambda_3(R)$, depending on the distance $R$ of the two interacting triplets, a total hopping rate in the plane $\Psi$ and a parameter $\beta$ corresponding to the combined effect of out-of-plane hopping and spin relaxation (see § 5). The theories will not be further discussed here.

The reader is referred to the original papers or reviews.

Theory II, being mathematically more involved, has seldom been used up to now [2b, 11] and a detailed comparison of the two theories relative to the same experiment is lacking. Most published results can be fairly accounted for using theory I, although theory II is in clearly better agreement with some results. However many points are still not understood (see for instance ref. [2b]).

The above discussion has been concerned only with triplet fusion. The reverse process of triplet pair generation by singlet exciton fission is also well known [13, 14] and has been studied in some detail in crystalline tetracene near room temperature, where the similarity of triplet fusion and singlet fission has been experimentally established [15]. Singlet fission has been described using a kinetic scheme similar to $\{1\}$:

$$ S_0 \xrightarrow{k_{-2}} (TT) \xrightarrow{k_2} T + T \quad \{2\} $$

but there is no detailed study, neither experimental nor theoretical, of magnetic field effects on fission, comparable to those performed on fusion [2, 10].

Both schemes $\{1\}$ and $\{2\}$ are parts of a more general chemical kinetic scheme which can be written as

$$ T + T \xrightarrow{k_{-1}} (TT) \xrightarrow{k_2} S_0 + S^* \rightleftharpoons S_0 + S_1 \quad \{3\} $$

where $S^*$ stands for the excited singlet with an energy equal to that of $(TT)$, $S_1$ for the lowest excited singlet and $S_0$ for the ground state. In triplet fusion experiments on anthracene [1, 10], triplet excitons are generated by the exciting light and the $S^*$ states formed quickly decay into $S_1$; the large energy gap, 0.5 eV, between $S^*$ and $S_1$, makes the equilibrium density $n(S^*)$ negligible, hence also the source term $k_{-2} n(S^*)$ for $(TT)$. Energy flows in scheme $\{3\}$ from left to right, and $\{3\}$ is then equivalent to scheme $\{1\}$. Conversely, for fission in tetracene, the exciting light generates singlets and the thermal equilibrium between $S^*$ and $S_1$, with a small energy difference (0.2 eV) makes $n(S^*)$ large. Also, if the excitation is not too intense, $n(T)$ remains small and the source term $k_1 n^2(T)$ for $(TT)$ is negligible: energy flows in scheme $\{3\}$ from right to left and $\{3\}$ is then equivalent to scheme $\{2\}$.

The important parameters in discussing the relative change of the overall fusion or fission rates with magnetic field $H$ are those corresponding to the destruction of the correlated pair, that is

$$ T + T \xrightarrow{k_{-1}} (TT) \xrightarrow{k_2} S^* \quad \{4\} $$

and only $k_{-1}$ and $k_2$ are important in this respect. In theory I for fusion, for instance, $k_1$ appears, in all formulas for the fusion rate constant, as a multiplicative factor, while $k_{-1}$ appears in a similar way for fission.

Such an approach corresponds to completely neglecting the triplet exciton kinematics, i.e. of the influence of exciton interactions on the triplet exciton distribution functions and correlation, and in general of diffusion processes. In theory II, where these processes are included, absolute values of hopping rates, etc... are required for, or conversely can be obtained from, curve fitting, as shown below.

The equivalence of fission and fusion is clear on scheme $\{3\}$. At the time of the discovery of fission, it was pointed out from thermodynamic arguments,
that if $\gamma_s$ and $\gamma_f$ are the experimental rates of fission and of fusion, into a singlet respectively, then [15]

$$\frac{\gamma_s}{\gamma_f} = 9 \frac{n(TT)}{n(S)} = 9 \exp \left( \frac{E(TT) - E(S)}{kT} \right). \quad (1)$$

The factor 9 comes from the existence of 9 spin states for ($TT$), whereas $S^*$ has only one. Hence, the same theoretical approach and fitting procedure may be used for the MF effect on anthracene delayed fluorescence, due to fusion, or on tetracene prompt fluorescence, due to fission. We return to this problem in § 5.

In this paper, the effect of magnetic fields on the singlet exciton fission in crystalline tetracene at room temperature is studied through the magnetic field modulation of prompt fluorescence. After a description of the experiment (§ 2), the positions of the high-field resonances [10, 11] are reported and discussed, giving information on the nature of the paramagnetic species involved (§ 3).

One purpose of this paper was to compare the same set of results with the predictions of theories I and II. The effect of exciting light intensity of the modulation of total fluorescence by magnetic fields is first studied in § 4, and used to define the low excitation conditions under which all results discussed here were obtained.

Theories I and II are then applied in § 5 to these experimental results, specifically to the modulation with magnetic field intensity and to the anisotropy of the effect at high, low and intermediate fields. A quasi-two dimensional exciton motion as in anthracene is assumed, the transport properties of triplet exciton in tetracene being presently imperfectly known. It is found that resonance lineshapes are poorly accounted for by I, but correctly by II. The fitting using theory II with the above-mentioned assumption of a quasi-two dimensional exciton motion yields reasonable values for the triplet diffusivity tensor and triplet-triplet interaction rate constant.

2. Experimental setup (Fig. 1). — The crystal, illuminated from below by a laser beam, was placed between the pole pieces of an electromagnet, and the magnetic field could be rotated throughout 360° in the horizontal plane. To accurately record an anisotropy curve, as those shown on figures 2, 3, or 6, it is important to rotate the magnetic field, not the crystal, in order to ensure that the sample is excited always in the same region and with constant polarization. The field orientation in the horizontal plane was given by the voltage drop through a precision linear potentiometer driven by the magnet, with an accuracy and a reproducibility better than 1°. The field was measured with a Hall probe.

The crystal was put on a rectangular metallic plate, the laser beam passing through a small central hole; the (001) face was always in contact with the plate, and the light always incident on this face. The plate could be rotated around one of its sides, so that the crystal (001) plane, could be positionned at any angle to the plane of magnetic field rotation, with an accuracy of $\pm 2°$. This is equivalent to the possibility of rotating the magnetic field in any crystal plane, except in planes perpendicular to (001) plane. To achieve this, a second setup was used. The laser beam was reflected horizontally by a reflecting prism placed between the pole pieces, the crystal holding plate was placed in contact with the vertical face of the prism and could be rotated around a horizontal axis, that is perpendicular to the (001) plane. Here the accuracy was $\pm 3°$.

Two wavelengths from an Argon laser (Spectra Physics, model 164) were used : 4 880 and 4 579 Å. They were filtered using a Corning CS5.57 and a Schott BG18 filter for 4 880 and a Corning CS5.58 for 4 579 Å, and attenuated as needed by neutral density filters. In both cases, the incident light is strongly absorbed and the dichroism is small. At 4 880 Å (the wavelength used for most of the measurements) the absorption is between $2 \times 10^4$ cm$^{-1}$ and $6 \times 10^4$ cm$^{-1}$ depending on the polarization $^1$. At 4 579 Å, the corresponding numbers are slightly smaller [16]. Incident light is totally absorbed by the crystal.

The excited region is therefore small : about 1 micron thick and a few mm$^2$ in surface. It may be hoped that crystal inhomogeneities are less important than in fusion experiments where, in order to obtain a large enough delayed fluorescence signal, larger crystals must be homogeneously excited.

$^1$ The tetracene crystal being triclinic [17], the directions of maximum and minimum absorptions for polarized light incident onto the (001) plane are not parallel and perpendicular to the $b \parallel 010$ axis. We have verified that there is indeed, at these wavelengths, a small, but significant, difference of a few degrees. The difference increases at shorter wavelengths.
The fluorescence light was collected by a light guide onto an EMI 9558 QB photomultiplier through a set of filters eliminating stray light: at 4 880 Å we used two Schott OG570 plus one BG18; and at 4 579 Å, used with the prism, where stray light was particularly intense and where filter fluorescence was a problem and fluorescence light collection poor, we had to use two Corning CS4.64, one CS4.106, one Schott OG530 plus one non-fluorescing Corning CS3.144.

The PM output was fed into a Keithley 610B picoammeter, whose output was compared, using a Keithley 660 differential voltmeter, to the signal at zero magnetic field. This difference was measured by the Y channel of a XY recorder, the X channel being either the field intensity (given by the Hall probe) or the field orientation (given by the potentiometer). The amplitude of fluorescence modulation was reproducible within 1% of the total emission.

Tetracene crystals 50 to 100 µ thick were grown by sublimation. The (001) face is always well developed. The shape of the crystal plane varies from sample to sample, however there is always an angle of 55 degrees between two edges of the (001) face, which were determined by X-ray crystallography to be the [0 1 0] (b axis) and [1 1 0] directions. By microscopic observation under polarized light, an extinction direction in yellow light was found 4 ± 1 degree from the crystallographic b axis, and was used for routinely orienting the crystals.

All experiments were performed at room temperature.

3. Analysis of the high-field (5 kG) resonance positions. — By high field, it is meant here any field strength in which the Zeeman energy is much larger (say, by one order of magnitude) than the zero field splitting (ZFS) energies. In the present case, experiments were performed at 5 kG. The discussion in this § refers only to such conditions.

Sharp maxima of fluorescence yield (resonances, corresponding to minima in the fission rate) are observed when the magnetic field direction is such that the energies of the two pair states having a high field singlet character are equal, and a level crossing occurs [8, 10]. Broad maxima can be observed when the energy difference between such pair states varies with the magnetic field orientation but no actual crossing occurs, as in the (bc') plane. Resonance positions were found to be independent of the exciting intensity (see § 4).

Resonance directions can be calculated from the exciton ZFS parameters. Conversely, the determination of these resonance directions yields information of the ZFS parameters of the triplet state involved.

In previous work on tetracene [13, 15], the magnetic field was only rotated in the (001) or (a'b) crystal plane (a' is defined as the direction in (001) perpendicular to the b axis), and only two resonance directions were found, from which an estimation of the ratio $D^*/E^*$ of the exciton ZFS was made. In the present work, the magnetic field was rotated in a number of planes, so that a set of resonances could be compared to theoretical predictions.

The magnetic field (5 kG) was first rotated in the (a'b) plane (Fig. 2). The angle between the two resonance directions is 52 ± 1 degrees. The uncertainty is mainly due to the difficulty in accurately setting the (a'b) plane horizontal. The directions marked $a_1$ and $b_1$ on figure 2 are those of minimum enhancement of the fluorescence in the (a'b) plane. The $a_1$ direction is near, but not coincident with, the a and a' axes. Similarly, $b_1$ is 4 ± 1° from the b axis. To study other planes it was decided to rotate the crystals around these directions as well as the c' (perpendicular to the (a'b) plane) direction as they are easily determinable, so as to facilitate the reproducibility of the experiments.

![Figure 2](image_url)

Figure 2. — Modulation of tetracene fluorescence by a 5 kG magnetic field rotating in the, (a'b), (bc') and (ac') crystal planes. The axes are defined in figure 4.

Figure 3A shows the anisotropy of the high magnetic field effect on prompt fluorescence with the magnetic field rotated in planes obtained by rotating the (a'b) plane in 10° steps around the c' axis. Similar series of curves were obtained when the crystal was rotated around $a_1$ (Fig. 3B) or $b_1$. These results will be now be compared with theoretical calculations and other experimental data. This treatment does not depend on the choice of theory I or II.

The relevant information is summarized in table I: the ZFS parameters of the tetracene molecule were calculated quantum mechanically by Brinen and Orloff [18] and recently measured at 2 K by Clarke et al. [19]. The two set of data are in good agreement. From them and the known crystal structure [17], the triplet exciton parameters $D^*$ and $E^*$ and orient-
Modulation of tetracene fluorescence with a 5 kG magnetic field. The field is rotated in crystal planes obtained:
(A) by rotating an \((a'b')\) plane perpendicular to the field in 10° steps around the \(c\) axis. The angle \(\varphi = 0\) correspond to the \((ac')\) plane. (B) by rotating an \((a'b')\) plane parallel to the field in 10° steps around the \(a\) direction. The angle \(R = 0\) corresponds to the \((a'b')\) plane.

The position of the ZFS tensor can be calculated. The results of such calculations are given on table I (see also ref. [22] and appendix I). From a study of ESR of photoexcited tetracene, Yarmus et al. [20] deduced values of \(D^*\) and \(E^*\) and the orientation of the triplet exciton ZFS tensor as shown on table I (2). The agreement with the values calculated from Clarke's results is not very good. By contrast, in naphthalene or anthracene, the experimental ESR triplet exciton ZFS parameters are in excellent agreement with those deduced from molecular parameters and the crystal structure [21]. One reason for the discrepancy in tetracene may be that the exciton ZFS parameters were deduced [20] from experiments in which the magnetic field was rotated in one crystallographic plane only \((a'b')\). A refinement of the crystal structure would be also welcome.

Also shown on table I are the calculated positions of high-field resonances in the \((a'b')\) plane. In comparison, the distance between the resonances was always found in the present experiments to be between 51.5 and 53 degrees. Experimental values quoted in the literature are similar (Table II) and in good agreement with calculations.

The positions of the high-field resonances depend only on \(D^*/E^*\) and on the orientation of the ZFS tensor. They can be plotted on a polar diagram [3] as on figure 4. The direction \(H\) is defined by the angles \(\theta, \varphi,\) and is plotted on a \((\theta, \varphi)\) plane as point, with \(\theta = (c'H)\) and \(\varphi\) the angle between \(a'\) and projection of \(H\) on the \((a'b')\) plane (see insert of Fig. 4). On such a diagram the \(c'\) axis does not correspond to a point, but to the line \(\theta = 0\).

Any plane containing \(c'\) projects on a straight line \(\varphi = \text{constant}\), and can be directly read on an experi-

A fourth set of data has been given by Tedder [21]. He used molecular \(D\) and \(E\) values deduced by Yarmus et al. [20] from their crystal study, to calculate the exciton parameters \(D^*\) and \(E^*\) and orientation of the ZFS tensor, and obtained data quite different from Yarmus' values. This is quite surprising, as it is apparently a cyclic procedure. We have repeated the calculation, and from the molecular parameters given by Yarmus, we deduce crystal parameters which differ only insignificantly from Yarmus' crystal values, as expected. Tedder has recently published an erratum (Chem. Phys. 24 (1977) 287) and his revised data now agree with our and with Yarmus' results.

### Table I

<table>
<thead>
<tr>
<th>Reference</th>
<th>Molecule</th>
<th>Exciton</th>
<th>Position of predicted high-field resonances in ((a'b')) plane (degrees from (b) axis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Brinen [18]</td>
<td>0.063</td>
<td>—0.004 6</td>
<td>—0.009 45 0.028 8 —0.328 23° 32°</td>
</tr>
<tr>
<td>Clarke [19]</td>
<td>0.057</td>
<td>—0.004 3</td>
<td>—0.008 55 0.026 1 —0.327 23.8° 31.2°</td>
</tr>
<tr>
<td>Yarmus [20]</td>
<td>0.052</td>
<td>—0.005 2</td>
<td>—0.006 2 0.024 8 —0.25 21.5° 29°</td>
</tr>
</tbody>
</table>

Underlined numbers are those quoted in the original papers.

### B - Director cosines of the triplet exciton ZF axes

<table>
<thead>
<tr>
<th>(a')</th>
<th>(b)</th>
<th>(c')</th>
</tr>
</thead>
<tbody>
<tr>
<td>(X)</td>
<td>0.964 0</td>
<td>—0.027 2</td>
</tr>
<tr>
<td>(Y)</td>
<td>—0.263 3</td>
<td>0.254 9</td>
</tr>
<tr>
<td>(Z)</td>
<td>—0.042 0</td>
<td>0.966 5</td>
</tr>
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</table>

Deduced from [18] (*)

<table>
<thead>
<tr>
<th>(a')</th>
<th>(b)</th>
<th>(c')</th>
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<tr>
<td>(X)</td>
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<td>—0.283 3</td>
</tr>
<tr>
<td>(Y)</td>
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</tr>
<tr>
<td>(Z)</td>
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<td>0.968 0</td>
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Deduced from [19] (*)

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<th>(c')</th>
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<tbody>
<tr>
<td>(X)</td>
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<td>—0.026 9</td>
</tr>
<tr>
<td>(Y)</td>
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<td>0.246 3</td>
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<tr>
<td>(Z)</td>
<td>—0.037 2</td>
<td>0.971 4</td>
</tr>
</tbody>
</table>

Measured in [20]

(*) Using the rigid-lattice crystal structure [17].
TABLE II

Experimental positions of high-field resonances in (a'b)
plane (in degrees)

<table>
<thead>
<tr>
<th>Reference</th>
<th>This work</th>
<th>[13a]</th>
<th>[13b]</th>
<th>[20]</th>
<th>[15]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angular positions on either side of b axis</td>
<td>22  18  23  23.5  20</td>
<td>30  34  30  30  30  30  30  30  30  30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distance</td>
<td>52  52  53  53.5  53  53  53  53  53  53</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(*) Value read on figure 3 of ref. [15], not given in text.

\[
\cos \theta = \sin \alpha \sin R \quad (2)
\]

and

\[
\cos \alpha = \sin \theta \cos (\varphi - A) \quad (3)
\]

giving \(\theta, \varphi\) as a function of \(\alpha, R\). A similar calculation should be performed for planes obtained by rotations around \(b_1\).

From experimental results, the projection of experimental high-field resonance directions in various planes have been calculated in this way, and are plotted (open and filled circles) on figure 4. The accuracy is similar to that for rotation around \(c'\).

Using the ZFS triplet exciton parameters (Table I), the theoretical positions of the resonances have been calculated and are plotted (curves) on figure 4. They are given by the equation (3, 7):

\[
(d - 1)(H \cdot X)^2 + (d + 1)(H \cdot Y)^2 = \frac{2}{3}d 
\quad (4)
\]

where \(d = D^*/E^*\). When the reference axes are the crystal axes (as on Fig. 4) and not the ZF axes, \(X, Y, Z\), the corresponding equation becomes fairly complicated [22].

Taking into account the experimental uncertainties, our experimental results are in excellent agreement with the calculation. We take this as a strong indication that the fission process produces two free triplet excitons. A trapped triplet would have different ZFS parameters: for instance, if the trap were a displaced tetracene molecule, its parameters would be those obtained by Clarke [19], that is \(D/E = 13.3\) and the ZF axes oriented along the axes of the displaced molecule. In this instance of heterofission [23], the resonance positions would not fit as on figure 4. In addition, in heterofission more than two resonances are expected in most planes, which is not the case here. Our results also indicate that the triplet exciton does not involve significant lattice distortion (polaron formation), which would influence the ZFS parameters.

It is worth noting that these results are equivalent to ESR measurements, but can be obtained with a number of triplets much smaller (down to \(10^7\) here) than is needed for ESR and that a 10-fold increase in accuracy could be possible if the samples were mounted on a goniometer.

4. Influence of excitation intensity on the amplitude of magnetic field modulation of fluorescence. — The incident flux \(I\) at 4 880 Å was varied over almost 5 orders of magnitude from about 30 mW/cm² down to 0.5 µW/cm². The relative shapes of the fluorescence anisotropy curves are unchanged throughout but the absolute magnitude of the magnetic field effect is smaller at high flux as shown on figure 5.
This reduction, already noted in [24a], is readily explained: it has been shown that, as the excitation is increased, delayed fluorescence is an increasing fraction of the total emission, culminating to about 2/3 of the total [24b], and that, at room temperature, it is almost independent of the magnetic field, since the effects on the fission rate $k_S$ and the fusion rate constant $\gamma$ are just opposite [15].

More precisely, in the low intensity limit, neglecting singlet diffusion, the singlet density at depth $x$ below the illuminated surface is given by

$$aI \exp(-ax) = k_S n_S$$

and the total number of singlets present in the sample is

$$N_S = Slk_S^{-1}$$

for an incident beam cross-section $S$. The total emission rate is then

$$F = Sk_r k_S^{-1}$$

where $k_r \ll k_S$ is the singlet radiative rate constant. The absorption coefficient here is $\alpha = 2 \times 10^4 \text{cm}^{-1}$, that is a penetration depth of 5 000 Å, compared to which the singlet diffusion length $\lambda_S \sim 100$ Å is indeed negligible [25]. In this limit, the magnetic field dependence of $F$ is only due to $k_S$

$$\frac{\Delta F}{F(0)} = \frac{F(H) - F(0)}{F(0)} = \frac{k_S(0) - k_S(H)}{k_S(0)} = -\frac{\Delta k_S}{k_S(0)} \left( 1 + \frac{\Delta k_S}{k_S(0)} \right)^{-1}.$$  

Experimentally, at resonance $\Delta F/F(0) = 0.35 \pm 0.01$, hence $\Delta k_S/k_S(0) = 0.26 \pm 0.01$.

In the high intensity limit, on the other hand, delayed generation of singlets is important. If the intensity is high enough, triplets will disappear mainly by bimolecular annihilation; their lifetime, hence their diffusion length, will be short, so that both monomolecular decay and diffusion will be negligible in the kinetic equation for triplets.

$$2k_S n_S = (\gamma_S + \gamma_T) n_T^2 \equiv \gamma_{tot} n_T^2$$  

$$aI \exp(-ax) + \frac{1}{2} \gamma_S n_T^2 = k_S n_S$$

$\gamma_S$ and $\gamma_T$ are the rate constants for fusions leading to singlet and triplet respectively, and the factors 2 and 1/2 account for the fact that one singlet generates two triplets in the fission process—assumed to be the dominant singlet decay channel—and two triplets generate one singlet in fusion. Then

$$N_S = Slk_S(1 - f)$$  

$$F = S(k_f)/k_S(1 - f)$$

$$f(H) = \frac{\gamma_S H}{\gamma_T + \gamma_S H}.$$  

$f$ also is magnetic field sensitive since only $\gamma_S$ is magnetic field sensitive (according to our calculations in § 5 the conditions for this are met in theories I and II). Now, considering fission and fusion as thermodynamically reciprocal processes $k_S \ll \gamma_S$ and $k_S(1 - f) \ll (\gamma_T/\gamma_T + \gamma_S)$, so that $\Delta F/F(0)$ at high field is, compared to its low intensity value, multiplied by $(1 - f(0))$. The present experiments yield a lower limit of $(1 - f(0)) = 0.39$ or $f(0) = 0.61$ off resonance, and $(1 - f(0)) < 0.44$ or $f(0) > 0.56$ on resonance, in agreement with the value obtained in § 5 and with the previously measured $f(0) = 0.66 \pm 0.06$ [24b]. In all our experiments, singlet-triplet (ST) annihilation remains negligible, since, even at 30 mW/cm², $n_T < 2 \times 10^{13}$ cm⁻³ everywhere, or $\gamma_{ST} n_T < 4 \times 10^8$ s⁻¹ using $\gamma_{ST} \sim 2 \times 10^{-7}$ cm³ s⁻¹ [24b] a value which according to a recent experiment [26] might be overestimated. As $\gamma_{ST} n_T < k_S$, the singlet-triplet interaction term may indeed be neglected in the kinetic equation for singlets.

For excitation just above the low intensity limit, the term $1/2 \gamma_S n_T^2$ is no longer negligible in the singlet kinetic equation, but the triplets still disappear mainly monomolecularly, and their diffusion may not be neglected. Hence one can use eq. (10) and

$$2k_S n_S = \gamma_T n_T - D \frac{d^2n_T}{dx^2} \equiv 2aI \exp(-ax),$$

where $D$ is the diffusion coefficient of triplet excitons in the direction of their density gradient, that is, in the present case the c' direction. $D = D_{out}$ used in § 5 and in table III.

The solution of the latter approximate equation, with the boundary condition $n_T(0) = 0$, is

$$n_T(x) = \frac{2aI}{1 - cD\alpha^2} \left( e^{-ax} - e^{-\alpha x} \right)$$

where $\alpha$ is the magnetic field sensitive constant for fusions leading to singlet and triplet respectively, and the factors 2 and 1/2 account for the fact that one singlet generates two triplets in the fission process—assumed to be the dominant singlet decay channel—and two triplets generate one singlet in fusion.
TABLE III
Examples of parameters used and computed in various fits, and comparison with anthracene (ref. [11])

<table>
<thead>
<tr>
<th>Set</th>
<th>$\omega_0$ (s$^{-1}$)</th>
<th>$D_0$ (cm$^2$/s)</th>
<th>$\xi$ (s$^{-1}$)</th>
<th>$\beta$ (s$^{-1}$)</th>
<th>$\omega_{int}$ = $\beta - \xi$</th>
<th>$D_{out}$ (cm$^2$/s)</th>
<th>$-G(\beta)$ (s)</th>
<th>$\lambda_0$ (s$^{-1}$)</th>
<th>$K$</th>
<th>$\gamma_0$ (cm$^3$/s)</th>
<th>$\gamma_{tot}$ (*) (cm$^3$/s)</th>
<th>$k_{-1}$ (**) (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>$6 \times 10^{12}$</td>
<td>$4 \times 10^{-10}$</td>
<td>$1.5 \times 10^6$</td>
<td>$6 \times 10^6$</td>
<td>$6 \times 10^7$</td>
<td>$6 \times 10^7$</td>
<td>$10^{-6}$</td>
<td>$4.9 \times 10^{-12}$</td>
<td>$5 \times 10^{-14}$</td>
<td>$122$</td>
<td>$1.8 \times 10^{-10}$</td>
<td>$6 \times 10^{-10}$</td>
</tr>
<tr>
<td>(B)</td>
<td>$7 \times 10^{11}$</td>
<td>$4 \times 10^{-8}$</td>
<td>$10^7$</td>
<td>$1.2 \times 10^8$</td>
<td>$\sim 10^8$</td>
<td>$2 \times 10^{-6}$</td>
<td>$3.4 \times 10^{-12}$</td>
<td>$2.5 \times 10^{-12}$</td>
<td>$4.3$</td>
<td>$2 \times 10^{-11}$</td>
<td>$6 \times 10^{-11}$</td>
<td>$8 \times 10^9$</td>
</tr>
<tr>
<td>(C)</td>
<td>$10^{11}$</td>
<td>$6 \times 10^{-5}$</td>
<td>$9 \times 10^7$</td>
<td>$10^8$</td>
<td>$10^{-7}$</td>
<td>$1.8 \times 10^{-11}$</td>
<td>$1.7 \times 10^{-11}$</td>
<td>$1.5$</td>
<td>$3 \times 10^{-12}$</td>
<td>$10^{-11}$</td>
<td>$3 \times 10^9$</td>
<td></td>
</tr>
<tr>
<td>S(*)</td>
<td>$2 \times 10^{12}$</td>
<td>$1.5 \times 10^{-4}$</td>
<td>$8 \times 10^7$</td>
<td>$2.8 \times 10^8$</td>
<td>$2 \times 10^{10}$</td>
<td>$1.7 \times 10^{-6}$</td>
<td>$6.6 \times 10^{-12}$</td>
<td>$3 \times 10^{-11}$</td>
<td>$1$</td>
<td>$5 \times 10^{-12}$</td>
<td>$1.2 \times 10^{-11}$</td>
<td>$8 \times 10^9$</td>
</tr>
</tbody>
</table>

(*) Using for tetracene $\gamma_0/\gamma_{tot} = 0.6$ (see text and ref. [24b]) and for anthracene $\gamma_0/\gamma_{tot} = 0.4$ [27].
(1) Using the approximate formula (33) in text.

with $d^{-2} = rD$. Hence

$$\alpha e^{-axx} + \frac{2 \alpha^2 I^2 \gamma_0 \tau^2}{(1 - rD \alpha^2)^2} (e^{-axx} - e^{-ax})^2 = k_S \eta_D(x)$$

(16)

and by integrating over $x$:

$$I = \frac{\alpha}{k_S} \frac{1}{D^2 d(d + \alpha)^3} \frac{\gamma_0}{k_S} I^2 = \frac{1}{k_S} + \frac{\alpha^2 \gamma_0}{(1 + \alpha/d)^3} I^2 = N_S$$

(17)

where the $I^2$ term is independent of $H$.

This relation may also be expressed as a fluorescence quantum yield

$$\eta \propto N_S I = \frac{1}{k_S} \left(1 + \frac{\alpha^2 \tau \gamma_0}{(1 + \alpha/d)^3} I\right) = \frac{1}{k_S} (1 + mI).$$

(18)

The effect of a magnetic field $H$ is now

$$F(H) - F(0) = \frac{k_S(H) - k_S(0)}{k_S(H)} (1 + m\gamma_0 I)^{-1}$$

(19)

and is therefore changed, from the low field limit, by the factor $1 + m\gamma_0 I$. The experimental results of figure 5 are not very accurate. With $\tau = 1$ to $2 \times 10^{-4}$ s as experimentally measured on these crystals, and $\alpha = 2 \times 10^6$ cm$^{-1}$, they are compatible with eq. (19) if $D_{out} = 1$ to $2 \times 10^{-6}$ cm$^2$ s$^{-1}$ and $\gamma_0 = 2$ to $20 \times 10^{-11}$ cm$^3$ s$^{-1}$, that is with sets of parameters (A) and (B) obtained below (see Table III). Set (C) is more difficult to reconcile with the results displayed on figure 5.

The analysis offered here is therefore internally consistent. In the discussion of the results of figure 5, it has been assumed that $\gamma_T$ is not magnetic field sensitive. This has been demonstrated only for triplet exciton fusion in anthracene [27]. Results such as those of figure 5, could provide information on possible field dependence of $\gamma_T$ in tetracene, by comparing results obtained on resonance and off resonance; but this would imply an improvement of at least one order of magnitude in experimental accuracy.

No anomalous high intensity effect as reported for naphthalene [2] has been found here and all results are compatible with the predictions of theory II.

5. Variation of fluorescence yield with magnetic field strength and orientation. — The experimental results to be analyzed are summarized on figures 6 to 9. Figure 6 shows the fluorescence intensity observed (under constant and low excitation) when magnetic fields of respectively 5 kG, 700 G and approximately 150 G are rotated in the $(a'b)$ crystal plane: when $H$ decreases, the amplitude of the high field resonances decreases, they become more unequal and other broad resonances appear inbetween. These are the so-called low-field resonances, which correspond to individual triplet level crossings and are in directions of the individual triplet ZF tensor principal directions, as found here. Since tetracene is triclinic, these axes

TABLE IV

<table>
<thead>
<tr>
<th>Reference</th>
<th>$\gamma_{tot}$ (cm$^3$/s$^{-1}$)</th>
<th>Method used</th>
</tr>
</thead>
<tbody>
<tr>
<td>[24a]</td>
<td>$1.6 \times 10^{-9}$</td>
<td>Temperature dependence of fluorescence yield</td>
</tr>
<tr>
<td>[15]</td>
<td>$1.5 \times 10^{-9}$</td>
<td>Variation of fluorescence yield with excitation intensity</td>
</tr>
<tr>
<td>[24b]</td>
<td>$5 \times 10^{-10}$ (*)</td>
<td>From fit of magnetic modulation of fluorescence</td>
</tr>
<tr>
<td>This work A</td>
<td>$6 \times 10^{-10}$</td>
<td></td>
</tr>
<tr>
<td>This work B</td>
<td>$6 \times 10^{-11}$</td>
<td></td>
</tr>
</tbody>
</table>

(*) Taking into account the corrected value of $\epsilon (3 \ 250 \ \Lambda)$. 
are not related to crystallographic directions, therefore the resonances in the \((a'b)\) plane are of unequal amplitude and do not bissect the high field resonance directions, contrary to anthracene. Figure 7 shows the change of fluorescence as a function of magnetic field strength when \(H\) is increased from 0 to 5 kG, in several fixed directions: high field resonance and the two off resonance directions \(a_1\) and \(b_1\). Analysis of this dependence yields information on the kinetic aspects of the interaction. The results were analysed with both theories I and II.

These theories were developed for triplet fusion, whereas the results presented here correspond to singlet fission. The connection between the two processes was already qualitatively discussed in the introduction. For both processes a density matrix equation can be written. In the basis which diagonalizes the spin pair Hamiltonian for instance, one obtains in theory I

\[
\begin{align*}
\{ i(E_m - E_n) + k_{-1}\} & \rho_{mn} + \frac{1}{2} k_2 \times \\
& \times \sum_l (S^*_m S_l \rho_{ln} + S^*_l S_n \rho_{nm}) = Q
\end{align*}
\]  

with \(E_m\) and \(S_m\) the energy and singlet character of state \(m\) (see eqs. 87 and 104 of ref. [7]). \(Q\) is the source term, different for both processes:

- for fusion:
  \[
  Q = \frac{1}{2} k_1 n^2 \delta_{mn}
  \]

- for fission:
  \[
  Q = k_{-2} n_5 S^*_m S_n.
  \]

The experimental fusion (bimolecular) rate constant \(\gamma_f (\text{cm}^3 \text{s}^{-1})\) is obtained as

\[
\gamma_f n^2 = k_2 \sum_m S_m S^*_m \rho_{mn}
\]

and the (monomolecular) fission rate constant \(k_f (\text{s}^{-1})\) as

\[
k_f n_5 = k_{-1} \sum_m \rho_{mn}.
\]

The equivalence of fission and fusion [7, 15, 27, 28] implies that eqs. (23) and (24) yield the same relative dependence of fluorescence on magnetic field strength and direction. We have verified this equivalence numerically for several field directions at all field strengths and all field directions in several planes at high, intermediate and low field strengths.

It is known [11] that theories I and II yield the same values of \(\gamma_f\) at resonance and infinitely far from resonance. Using eqs. (20), (22) and (24), these values are, for triplet fission

- on resonance
  \[
  k_f^m = k_{-2}(1 + k)^{-1}
  \]

- in zero field
  \[
  k_f(0) = k_{-2} \left(1 + \frac{k}{3}\right)^{-1}
  \]
where $k = k_2/k_{-1}$ in scheme (2). In our experiments, we measure the relative fluorescence change $\Delta F/F(0)$ from which the relative change of fission rate (see eq. 5) $\Delta k_s/k_s(0)$ can be calculated (see eq. 8). Fission and fusion being assumed reverse processes, from (4) and (5)

$$\frac{\Delta k_s}{k_s(0)} = -0.265 = -\frac{2}{3} \frac{k}{1 + k} \tag{27}$$

or $k = 0.66$. Theory also yields an expression for the value toward which $k_s$ would tend at infinite angle from resonance

$$k_s^\infty = k_{-2} \left(1 + \frac{4k}{9}\right) \left(1 + \frac{k}{3}\right)^{-1} \left(1 + \frac{2k}{3}\right)^{-1} \tag{28}$$

which, with the value of $k$ obtained above gives

$$\frac{k_s^\infty}{k_s(0)} = 0.9$$

This is not very different from the ratio deduced from the experimental minimum and maximum value of $\Delta F/F$. This only means that fitting the results with theory I or II is not an a priori impossible task.

Further fitting must resort to computer calculations. Using the ZFS parameters of the triplet excitons as discussed in § 3, $k = 0.66$ and with a value of the adjustable parameter $k_{-1} = 2.2 \times 10^{-5}$ s$^{-1}$, we can reproduce within the framework of theory I, the main features of the effect (Figs. 6 and 7). However the lineshape of the resonances is not correctly reproduced (Fig. 8). No other set of parameters gives a general improvement. Moreover, outside the range

$$k = 0.68 \pm 0.08 \quad k_{-1} = 2.2 \pm 0.3 \times 10^9$$

the fit becomes clearly worse. These values are then considered to be the best possible fit of our results in the Johnson-Merrifield theory I.

Two properties of the high field resonances are conspicuous on figure 2: they are highly cusped and have different widths. This is more clearly seen on figure 8 which shows one resonance at higher angular resolution: the full widths at half maximum—measured above the minimum close to the $b$ axis—are about 7º and less than 5º for the two resonances in the $(a'b)$ plane. Clearly, these lineshapes cannot be fitted in the Johnson-Merrifield theory [10] where a Lorentzian lineshape is assumed. This is not special to tetracene nor to fission. A similar lineshape is found for triplet exciton fusion in crystalline anthracene [11], naphthalene [2], and 1,4 dibromonaphthalene [29], where linewidths also are of the order of 5 to 10 degrees. This cusped lineshape is indeed predicted by Suna’s theory [11]. However, these resonances may be inhomogeneously broadened and can lose their cusped character. This will occur when the orientation of the ZFS tensor of the exciton and/or its $D^*$ and $E^*$ values spatially fluctuate, as would be the case in a slightly strained and distorted crystal. Indeed, the difficulty of obtaining large perfect single crystals increase from naphthalene through anthracene to pyrene. In this respect, the experimental situation chosen here has two advantages: the excited region is very small, of the order of $10^{-8}$ cm$^3$, and the short lifetime of the singlet makes it less likely that it will accumulate preferentially in distorted regions, as may be the case with long-lived triplet excitons.

We turn now to theory II. In Suna’s treatment of exciton interactions, triplet transport properties appear explicitly, so that, when the diffusivity tensor is known, there is only one adjustable parameter, namely the strength $\lambda_s$ of triplet-triplet annihilation into a singlet. Suna [11] considered the case of triplet fusion in anthracene, where triplet motion was known to be nearly two-dimensional, and the diffusivity in the $(a'b)$ plane is reasonably isotropic [12], so that an average in-plane diffusion constant $D_{in}$ and an average in-plane hopping rate $\gamma$ could be used. and a good fit with experimental results was obtained with two adjustable parameters, $\lambda_s$ and the out-of-plane hopping rate $\beta$, since only an upper limit of $\beta$ had been experimentally obtained [30]. In naphthalene [2b], it was assumed that because of the similarity between the crystal structures of naphthalene and anthracene, triplet motion is nearly two-dimensional. $D_{in}$ is known [12] and again is almost isotropic, and Suna’s approach was used again with the same two adjustable parameters $\lambda_s$ and $\beta$. In this case, however, some experimental observations, namely the resonances in the $(a'b)$ plane, could not be fitted.

In tetracene, the triplet diffusivity tensor is not known. One value only is quoted in a recent paper [31]: $D_{in} = 4 \times 10^{-3}$ cm$^2$ s$^{-1}$, about 20 times larger than in anthracene or any other known organic crystal [12]. The anisotropy has not been studied. It was felt useful to investigate the influence of the magnitude of the diffusion coefficients on the magnetic field effects, so no numerical value of $D$ was a priori introduced.
The calculation cannot however be performed without some assumptions. A preliminary one is that the gross features of triplet motion in tetracene are, as in anthracene, a quasi two-dimensional motion in the (a'b) plane, and isotropic diffusion in this plane. Such assumptions are supported by the similarity of crystal structures, the triclinic structure of tetracene [17] being only a slight deformation of the monoclinic structure of anthracene [32], the relative positions of the molecules in the unit cell being very similar. The assumption is also supported by the calculation of transfer integrals [33].

The parameters used are then: a total in-plane hopping rate $\Psi$, or equivalently an average in-plane diffusivity $D_{in}$ (1), a triplet-triplet annihilation rate $\lambda_s$, and a triplet decay rate $\beta$. This decay rate $\beta$ should not be confused with the monomolecular decay rate of an isolated triplet $\beta_T$ (essentially by intersystem crossing to the ground state). $\beta$ in theory II is the sum of the rates of all processes by which the conditions of interaction of a given triplet with the others are changed. First, it may be due to simple deactivation (rate $\beta_T$). Secondly, if triplet motion is very anisotropic, for instance quasi two dimensional, and if (as assumed by Suna for anthracene [11] and in the present work for tetracene) it is assumed that two triplets can annihilate only if they are in the same plane, then hopping of a triplet from one plane to a neighbouring one changes the conditions of interaction, since the triplet has left the population of a given (a'b) plane; this out-of-plane motion is characterized by a hopping rate $\psi_{out}$ or equivalently a diffusion coefficient $D_{out}/D_{in}$. A third process changing the conditions of interaction may be spin relaxation of an isolated triplet, which changes the spin of any pair this triplets might form (cross relaxation within a triplet pair has no such consequence and should not be considered for the calculation of $\beta$). Spin relaxation is believed to be due to excitation hopping between inequivalent sites [34, 35, 11], so that its rate is known once $\Psi$ is given, and is characterized in [11] by an average rate $\zeta = A \Psi^{-1}$. The factor $A$ was calculated by the method first used in [11]. For tetracene one gets $A = 9 \times 10^{11}$ s$^{-2}$. Since $\beta_T \approx 10^4$ s$^{-1}$ [24b] whereas $\psi_{out}$ or $\zeta$ are orders of magnitude larger,

$$\beta \approx \beta_T + \psi_{out} + \zeta \approx \psi_{out} + A \Psi^{-1}.$$

Hence the problem is completely defined by three independent parameters, for instance $\Psi$, $\psi_{out}$ and $\lambda_s$. As in all previous work [2b, 11] $\lambda_s$ is assumed to be non-zero only when the two triplets are on neighbouring sites. This allows us to use the so-called smooth approximation in theory II. The energy $E_n$ and singlet character $S_n$ of each of the nine pair states of a triplet pair are first calculated. The density matrix elements $\rho_{mn}$ are then obtained by solving a steady state equation similar to (20):

$$G(\beta) G(\beta) + i \left( \frac{E_m - E_n}{2} \right) \rho_{mn} +$$

$$+ \frac{1}{2} K \sum_{\ell} \left[ S^*_m S_\ell \rho_{\ell n} + S^*_n S_\ell \rho_{\ell m} \right] = 2 \delta_{mn} - \frac{1}{9} n^2 v^2 \text{ is the source term, } n \text{ is the exciton density and } v \text{ the molecular volume. } K = -\frac{1}{2} \lambda_s G(\beta) \text{ plays a similar role as } k = k_2/k_{-1} \text{ in theory I, but the fits do not necessarily lead to equal numerical values of } K \text{ and } k \text{ : indeed Suna found in anthracene [11] (he used the notation } k \text{) } K = 1.0 \text{ whereas from theory I } k = 0.4 \text{ [10]; this point is further discussed below.}

Eq. (29) is obtained from eq. (37) of ref. [11] which is, changing $l, l'$ into $m, n$:

$$\rho_{mn} = \frac{n^2 v^2}{9} \delta_{mn} + \frac{1}{4} G \left( \beta + i \frac{E_m - E_n}{2} \right) \times$$

$$\times \langle m | A \rho_2 + \rho_2 A | n \rangle$$

(30)

projecting $A = \lambda_s | 0 \rangle \langle 0 |$ where $| 0 \rangle = \sum_{i} S_i | l \rangle$ and $\langle 0 | = \sum_{i} S_i^* | l \rangle$, the index $l$ running over the nine states, the last term of eq. (30) becomes

$$\sum_{l} \left[ \langle m | 0 \rangle S_i^* \rho_2 | n \rangle + S_i^* \langle m | 0 \rangle \rho_2 | l \rangle \langle 0 | n \rangle \right] =$$

$$= \lambda_s \sum \left[ S^*_m S_\ell \rho_{\ell n} + S^*_n S_\ell \rho_{\ell m} \right]$$

and multiplying both sides of eq. (30) by $G(\beta)/G(\beta + i \frac{E_m - E_n}{2})$

$$\text{eq. (29) is obtained. Note that if in eq. (29) one substitutes in the left hand side the factor representing a Lorentzian lineshape }$$

$$\left( 1 + i \frac{E_m - E_n}{k_{-1}} \right) \text{ (see eq. (39) of ref. [11]), then eq. (20) for theory I is obtained with } k_2 \text{ and } k_{-1} \text{ having their meaning as on scheme } \{1\}. \text{ Within the smooth approximation and in a reasonable range of parameter values }$$

$$G \left( \beta + i \frac{E_m - E_n}{2} \right) \approx g \left( \frac{R \beta + i \frac{E_m - E_n}{2} }{R^2} \right)$$
the Green's function for the diffusion equation, which is approximated in the quasi-two dimensional case by the zero-order Hankel-Bessel function

\[
g\left(\overline{R}, \beta + i \frac{E_m - E_n}{2}\right) \approx \frac{v_{ab}}{2\pi D_{in} K_0} \left[ \frac{R}{\overline{D}_{in}} \right]^{1/2} \left( \beta + i \frac{E_m - E_n}{2} \right)
\]

\(v_{ab} = 23.77 \times 10^{-16} \text{ cm}^2\) is the area per molecule in the \((a'b)\) plane, that is the cell volume in two dimensions. \(R\) is the average of the module of the six vectors \(\pm b, \pm 1/2(a + b), \pm 1/2(a - b)\). \(R = 5.32 \text{ Å}\) and it was checked that \(g(R, \beta)\) does not differ by more than 4 \% from the values of \(g\) obtained with each of the six vectors. The smooth approximation is therefore, in tetracene, at least as good as in anthracene. This approximation also allows \(g(0, \beta + i \frac{E_m - E_n}{2})\) to be computed which is a necessary step in the calculation of \(G\left(\beta + i \frac{E_m - E_n}{2}\right)\). See the original work \[11\] for further details.

From the density matrix \(\rho\), the rate constant can be obtained as

\[
\gamma_S = \frac{1}{2} \frac{\nu \lambda_S}{\alpha} \sum_{m,n} S_m S_n^* \delta_{mn}
\]

and its variation with magnetic field can be compared to experiment.

For numerical calculation, a value of \(\Psi\) is chosen, corresponding to a value of \(D_{in}\) which sets a lower limit for \(\beta > \lambda S \Psi^{-1} = 9 \times 10^{18} \Psi^{-1}\) (which would correspond to \(\psi_{out} = 0\)) if the method used by Suna to take into account the effect of spin relaxation is followed. A value of \(\lambda_S\) is then chosen, and \(\beta\) is varied from its lower limit up to about \(10^{-2} \Psi\), which is taken to be the upper limit compatible with our assumption of quasi-two dimensional triplet motion. A set of parameters \((\Psi, \lambda_S, \beta)\) was said to fit the results if the following conditions were met: a) that the set, to within experimental accuracy, gives the correct values of the relative modulation \([F(H) - F(0)]/F(0)\) at resonance and in the off-resonance directions \(a_i\) and \(b_i\) in \((a'b)\) plane (Fig. 2), and b) that the set reproduces the lineshape of the resonance; in particular, the predicted lineshape near the maximum should not be rounder than the experimental lineshape; lines slightly narrower than the experimental one (less than 1\% throughout) are not rejected, to allow for a possible slight contribution of inhomogeneous broadening in the experiment.

It is found that, when a fit as defined above is at all possible, only one set \((\lambda_S, \beta)\) becomes acceptable (within 50 \% for \(\lambda_S\), less for \(\beta\)) for a given \(\Psi\). However the range of values of \(\Psi\) for which an acceptable fit can be found spans more than one order of magnitude. Table III shows an example of three such sets of parameters, labeled \((A), (B)\) and \((C)\) which are compared to Suna's best fit for anthracene \[11\]. Sets \((A)\) and \((C)\) correspond, approximately, to the upper and lower limits of the acceptable range of \(\Psi\). For \(\Psi < 10^{11} \text{s}^{-1}\) no fit is possible with \(\beta > 9 \times 10^{18} \Psi^{-1}\).

For \(\Psi \geq 10^{13} \text{s}^{-1}\), the calculated modulation amplitude at resonance is never large enough. For large \(\beta\) also, the predicted resonance amplitude remains small. For instance \(\beta = 10^{10} \text{s}^{-1}\), \(\Psi = 6 \times 10^{12} \text{s}^{-1}\), \(\lambda_S = 10^{15} \text{s}^{-1}\) yields a maximum field modulation of 1 \%.

Table III shows that the optimum value for \(\beta\) is almost independent of \(\Psi\) and \(\lambda_S\), and is such that the anisotropy of diffusion is always very large. It becomes infinite for set \((C)\) \((D_{out} \rightarrow 0)\), and is extremely large for \(\Psi \geq 10^{13} \text{s}^{-1}\) \((D_{out}\) is increasingly large). It is a minimum around set \((B)\), where the ration \(D_{in}/D_{out}\) is still \(\sim 200\), comparable to the value found in anthracene by a similar analysis \[11\]. The order of magnitude of \(D_{out}\) found here is not in contradiction with the value which can be inferred from indirect evidence gained from the study of surface generated photocurrents, which would lead to \(D_{out}\) somewhere in the range \(2 \times 10^{-6} \text{ to } 2 \times 10^{-5} \text{ cm}^2/\text{s}\) \[36\]. \(\alpha(\beta)\) remaining almost constant, \(K = -1/2 \lambda_S G(\beta)\), which is a kind of branching ratio between reaction or scattering of the two triplets, is proportional to \(\lambda_S\) and becomes very large for set \((A)\) \(K > 10^{2}\), whereas \(K = 0.68\) was found above with theory I.

The last line of table III shows a value for \(k_{-1}\). This is not a parameter of theory II, but it can be estimated using the relation \[11\]

\[
k_{-1} \approx 2.24 R^{-1} (\beta D_{in})^{1/2}
\]

which yields in anthracene a value \[11\] about three times larger than the best-fit value in theory I \[10\]. The best-fit value of \(k_{-1}\) in tetracene deduced from eq. \(33\) is always larger than \(2.2 \times 10^9 \text{s}\), the value

![Fig. 9. — Complete anisotropy in the \((a'b)\) plane for (A) \(H = 5 \text{kG}\), (B) \(H = 750 \text G\), (C) \(H = 150 \text G\). Solid lines: experiment. Dots: fit with theory II using the set of parameters (B) in table III.](image-url)
obtained with theory I, by a factor which reaches 10 for set (A). If one tries to fit the results with theory II, using the value of $B D_{\text{in}} \sim 2.8 \times 10^3 \text{cm}^2 \text{s}^{-2}$ deduced from $k_{-1} = 2.2 \times 10^9 \text{s}^{-1}$, the lines are always too narrow, and increasingly so from set (C) to set (A).

The value of $\zeta$ is always small enough to justify neglecting triplet-triplet fusion leading to an excited triplet, that is, neglecting magnetic field effects on $\gamma_T$.

6. Discussion and conclusions. — The set (C) of parameters in table III can probably be rejected, by considering evidence from other work on tetracene. Intermolecular exchange or charge transfer interaction are calculated to be larger in tetracene than in anthracene, by a factor of 2 to 3 [33], so that $D_{\text{in}}$ is expected to be 5-10 times larger in tetracene, and $\Lambda_s$ also larger. In addition, very small values of $D_{\text{out}}$ are physically unrealistic. The present discussion will therefore be limited to sets (A) and (B), considered as the two extreme cases; the true values may well lie inbetween.

Set (A) would agree with the published value of $D_{ab}$ [31] and the more commonly found value of $\gamma_T$ or $\gamma_{T0}$ (see table IV and discussion below). The small value of $\zeta$ would also be consistent with the large spin polarization observed in ESR [20]. However it implies a very large value of $\Lambda_s$, hence of $K$, which is then two orders of magnitude larger than $k$ in theory I. There is also a large difference between the approximate value of $k_{-1}$ inferred (eq. (33)) and the best-fit value of $k_{-1}$ in theory I. If set (A) is the correct one, these discrepancies raise more questions as to the actual connexion between the two theories, and to the physical meaning of parameters $k$ and $k_{-1}$.

Set (B) does not agree with published values of $D_{ab}$ or $\gamma_T$ but leads to less extreme values of $\Lambda_s$ and $K$, and to more similarity between tetracene and anthracene.

It should not be forgotten, however, that isotropic triplet motion was assumed in the $(a'b)$ plane. The next step would be to discard this assumption (at present necessary for practical calculations) since it is possible that the more general theory II could fit the experimental results with smaller values of $\Lambda_s$.

The value of $\gamma_{T0}$ deserves further discussion. A number of determinations of $\gamma_{T0}$ are found in the literature (Table IV). In all cases but one

$$\gamma_{T0} \sim 10^{-9} \text{cm}^3 \text{s}^{-1},$$

but the latest measurement [24c] yielded

$$\gamma_{T0} \sim 2 \times 10^{-11} \text{cm}^3 \text{s}^{-1},$$

although the experimental procedures in [24b] and [24c] were almost identical. The absorption coefficient at 3 250 Å — the wavelength used in [24b] — has been recently remeasured in this laboratory [37] and found to be $e_{\text{max}} = 2.7 \times 10^3 \text{cm}^{-1}$ and $e_{\text{min}} = 1.3 \times 10^3 \text{cm}^{-1}$. $\gamma_{T0}$ was therefore overestimated by a factor 2 to 4 in [24b], and the corrected value should rather be $5 \times 10^{-10}$ to $10^{-9} \text{cm}^3 \text{s}^{-1}$ as given on table IV. Set (A) in table III yields good agreement with this value, whereas set (B) would give an order of magnitude difference. Obviously, remeasurement of $\gamma_{T0}$ and $\Delta$ would be useful, and this is currently being undertaken in our laboratory. From the present fitting, one may only presently conclude that triplet motion in tetracene is likely to be at least as anisotropic as in anthracene, with faster diffusion in the $(a'b)$ plane.

The present study leads to other conclusions.

Concerning tetracene, no evidence of crystal distortion associated with triplet exciton formation has been found: the ZFS parameters obtained from these results, and which complement EPR measurements, are consistent with those calculated from molecular ZFS and the crystal structure. Tetracene in this respect is comparable to the hydrocarbons, naphthalene, anthracene or pyrene.

On the other hand, the ratio of rate of singlet formation by fusion to total annihilation rate is confirmed to be $\approx 0.6$. Here, tetracene behaves differently from anthracene [27] and pyrene [2c] where this ratio was $\approx 0.4$, which is the expected value if only the spin degrees of freedom are important.

More generally, the present study experimentally shows that the theoretical approach as proposed for triplet fusion can be used to fit the properties of singlet exciton fission, further supporting the idea that both are basically the same microscopic process. It offers the first detailed comparison of the two theoretical approaches [10, 11] and shows that the influence of triplet diffusion on annihilation must be explicitly taken into account, as in [11]: only theory II (provided $D$ is known or some of its general properties are assumed) yields a good general fit, and particularly of the high field resonance lineshape (Fig. 8). With the sets of parameters given in table III, the fit is almost always within the uncertainty of the experiment itself. It also shows that the so-called triplet pair correlation time $1/k_{-1}$ of theory I is not a well defined quantity and that the value obtained from a best fitting with theory I should not be taken literally. It would be interesting to investigate in more details the temporal decay of excited states, associated to the strongly non-lorentzian resonance lineshapes observed.

The one feature of the experimental results which is not accounted for is the unequal heights and widths of the two high-field resonances. Similar observations have been made in homofusion [2b] and heterofusion [3] and are as yet unexplained. Since this occurs in pure naphthalene where in-plane triplet motion is known to be isotropic [12], the assumption of isotropic in-plane motion in tetracene made above is not likely to be the origin of the disagreement. This problem deserves further consideration. One can think of two possible reasons: the very much averaged way in which spin relaxation is taken into account, although it is known to be anisotropic [34], and the neglect of
triplet-triplet interaction potential in the hamiltonian [10, 11]. In order to initially better define the discrepancies with Suna’s theory, accurate results should be obtained on a well characterized system and carefully fitted to the theory. Tetracene could be a good candidate for this.

One may hope to be able to extend in this way the theory of magnetic field effects on exciton interactions beyond the present limitations of Suna’s approach.

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Appendix I. — COMPUTATION OF THE EXCITON FINE STRUCTURE PARAMETERS. — Since the exciton hopping time is shorter than the spin precession time at all magnetic field used, the exciton spin hamiltonian is taken as the average of the molecular spin hamiltonian of the two non-translationally equivalent molecules in the unit cell.

\[ X = \frac{D}{3} - E, \quad Y = \frac{D}{3} + E, \quad Z = -\frac{2D}{3} \]

are the diagonal elements of the diagonal matrix \( P \). Likewise, \( X^*, Y^*, Z^* \) and matrix \( P^* \) are defined for the exciton fine structure. Let \( A_1, A_2, A^* \) represent the matrices of the direction cosines corresponding respectively to the fine structure tensors of the two molecules in the unit cell, and of the crystal triplet exciton. Diagonalization of the matrix

\[ H = \frac{1}{2} \{ A_1 P A_1^{-1} + A_2 P A_2^{-1} \} \]

yields \( A^* \) and \( P^* \), from which \( D^* \) and \( E^* \) can be deduced.

References

   b) ATKINS, P. W. and EVANS, G. T., Mol. Phys. 29 (1975) 921; or


[35] In high field resonance directions, the conditions are met for rapid cross relaxation in a triplet pair. But this does not alter the total spin of the pair and can be neglected here, although it may be important if spin relaxation of the individual triplets is considered, for instance as a function of triplet density and magnetic field direction.


[37] BERREHAR, J., unpublished results.