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MAGNETIC FIELD MODULATION
OF TRIPLET-INDUCED DELAYED FLUORESCENCE
AND PHOTOENHANCED CURRENTS IN CRYSTALLINE PYRENE

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Résumé. — L’effet d’un champ magnétique (0-6 kG) sur la fluorescence retardée et les courants photoassistés dans le cristal de pyrène à 300 K s’explique qualitativement à l’aide des théories déjà développées pour l’anthracène. Le triplet mobile a la même structure fine en champ nul que l’exciton monomère. En fluorescence retardée, la formation d’une paire de triplets est limitée par la diffusion sans interaction au-delà des plus proches voisins (constante de vitesse $2.7 \times 10^{-10}$ cm$^3$ s$^{-1}$) et la durée de vie de la paire est de l’ordre d’un temps de saut (environ $10^{-10}$ s) sans indice de stabilisation de la paire.

Dans l’étude des photocourants, on trouve suivant les cas des effets de champ magnétique de signes opposés. Si le courant est limité par la charge d’espace, les triplets agissent sur le rapport charge libre/charge piégée, et le champ magnétique module l’interaction triplet-charge piégée et diminue le photocourant. La constante de vitesse pour la formation de la paire ($1.7 \times 10^{-9}$ cm$^3$ s$^{-1}$) est beaucoup plus grande que la valeur limitée par la diffusion sans interaction à distance, et implique une distance d’interaction de plusieurs dizaines d’Å. Pourtant, la réaction de la paire pour former un singulet n’a lieu que dans environ 10 % des cas. Si le courant est limité par l’injection, le champ magnétique module (augmente) la durée de vie du triplet, via son effet sur l’interaction triplet-charge piégée, et donc augmente la densité de triplets près de la surface, et le flux de triplets vers l’électrode.

Abstract. — The effects of magnetic fields (0-6 kG) on the delayed fluorescence and photoenhanced currents in crystalline pyrene at 300 K can be explained qualitatively using the theories already used for anthracene. It is found that the moving triplet exciton has the same zero-field fine structure as the monomer exciton. In delayed fluorescence, triplet pair formation is diffusion limited with no long range interaction (rate constant $2.7 \times 10^{-10}$ cm$^3$ s$^{-1}$) and pair lifetime is of the order of one hopping time, or $10^{-10}$ s, with no evidence of pair stabilization.

In the study of photocurrents, two magnetic field effects, of opposite sign, are found. If the current is space-charge limited, triplets alter the ratio of free charge to trapped charge; and the magnetic field acts through modulation of the triplet-trapped charge interaction rate constant. The rate constant for pair formation ($1.7 \times 10^{-9}$ cm$^3$ s$^{-1}$) is found to be much larger than diffusion limited for nearest neighbour interaction, and implies a distance for pair formation of several tens of Å. Yet reaction of the pair thus formed to generate a singlet occurs only in about 10 % of cases. If the current is injection limited, triplets enhance the injection ability of the electrode, and the magnetic field acts through modulation of the triplet lifetime (by interaction with trapped charges), hence of the triplet density near the surface and the triplet flux to the electrode.

1. Introduction. — Small magnetic fields (less than 10 kG) modulate the triplet-triplet interaction rate constant $\gamma$ in anthracene, and therefore the delayed fluorescence, in a characteristic way [1]. To account for these effects, Merrifield proposed that the rate of singlet generation by annihilation of the triplet pair is proportional to the singlet amplitude of the pair, which is determined both by Zeeman interactions and the triplet exciton fine structure [2a]. In particular, in high field, only two pair states have a non-zero singlet amplitude, and a sharp decrease of the annihilation rate occurs when the field direction is such that these two pair states are degenerate. The reaction scheme used is sketched on figure 1a. It is not meant that (TT) is any kind of stable biexciton, but simply that triplets can be put into two classes, the free and the interacting...
Fig. 1. — Kinetic schemes for triplet-triplet (a), and triplet-doublet (b), interactions.

ones, without any physical assumption about the interaction process. As pairs are short-lived entities, and degeneracy occurs in various cases, interferences among the pair spin states should be considered. For this purpose, Johnson and Merrifield used the full density matrix of the pair spin states \([2b]\), from which they obtain an expression for \(\gamma\), for arbitrary orientation and magnetic field strength; the parameters \(k_1, k_2, k^{-1}\) (Fig. 1a) and the zero field splitting parameters \(D^*\) and \(E^*\) of the crystalline triplet exciton may then be computed. However, the kinetics of exciton-exciton interaction was not considered in [2]; this was done by Suna [3] who explicitly determined the limits of applicability of earlier theory [2] and the physical meaning to be associated with the various parameters of figure 1a. Of special interest to us is the emphasis put on the one-, two-, or three-dimensional character of triplet motion.

Likewise, magnetic field modulation of triplet-doublet — TD — interactions is expected and found when doublets are free radicals [4]. Charge carriers being doublets, both the triplet lifetime in the presence of charges, and the photoenhanced currents when photogenerated triplets detraps charges, are modulated by magnetic fields. Recently, Merrifield’s theory has been extended to the TD case (Fig. 1b), and triplet-hole interaction in anthracene studied in this way [5].

The effects are of course general and not restricted to anthracene. Other aromatic crystals have now been shown to emit magnetic field sensitive delayed fluorescence. Among them is crystalline pyrene [6].

In the course of a study of triplet excitons in pyrene, it has been shown that triplets are very efficiently quenched by trapped holes [7]. In this paper, modulation of delayed fluorescence and photoconductivity of pyrene by magnetic fields is studied and interpreted in the framework of existing theories. Pyrene may be an interesting test of Suna’s theory [3], since triplet diffusion appears to be essentially three-dimensional in this material [8], contrary to anthracene where it is markedly two-dimensional [9].

2. Experimental set-up (Fig. 2). — Pyrene crystals, 300 to 800 \(\mu\) thick, cut and polished generally with large \((a, c)\) plane faces, were sandwiched between conducting glass electrodes; in some of the experiments, Cu had been evaporated on one surface, then treated with I\(_2\) vapor to prepare a hole-injecting Cu-I electrode [10]. The samples, properly shielded and protected against stray-light, were placed between the pole pieces of an electromagnet whose field was continuously measured and recorded using a Bell 120 Hall-effect gaussmeter.

Crystals were excited by the 5 145 A of an \(\text{A}^+\) laser (Spectra-Physics mod. 165) through a Schott OG 4 filter, and the delayed fluorescence was detected by an EMI 9558 QB photomultiplier through Schott BG 12 and Corning CS 5.58 filters. The photomultiplier was magnetically shielded by two mumetal sheets, and its insensitivity (less than 0.2 %) to the magnetic fields applied to the crystal was checked.

Crystal photocurrent and PM current were measured using Keithley picocommeters and recorded.

3. Delayed fluorescence. Results and discussion. — Magnetic fields, up to \(H \approx 10\) kG, have qualitatively similar effects on delayed fluorescence in pyrene and in anthracene [1-2]: in pyrene, the intensity, at
constant incident flux, first increases with \( H \) up to 500 G, then decreases and saturates in high fields \((H > 6 \text{ kG})\) to a value smaller than the zero-field value (Fig. 4a); the high-field value depends on the relative orientation of \( H \) and the crystal axes. Figure 3a shows the anisotropy of the delayed fluorescence intensity when a field \( H = 6 \text{ kG} \) is rotated in the crystal \((a, c)\) plane, with pronounced dips for directions making an angle of 113 ± 2°.

![Magnetic Field Effect on Triplet Interactions in Pyrene](image)

For discussion of these results we shall use Suna’s theory [3] whenever possible. For clarity and completeness, some of its main results are recalled first. Assuming TT interaction takes place when the two triplets are on nearest neighbour molecular pairs, since molecules are assembled in pairs in the pyrene crystal lattice [11] and triplet motion is by hopping, it makes sense to think of them as localized on lattice units. Let \( \lambda_s \) be the rate for singlet generation from two neighbouring triplets, and \( v \) the molecular volume, the macroscopically measured rate \( \gamma_s \) is (eq. (42) of ref. [3])

\[
\gamma_s = \frac{1}{3} v \lambda_s \sum_{l} A_l \tag{1}
\]

where the \( A_l \) are six complex quantities, obeying six coupled equations (eq. (43) of ref. [3]), which are, neglecting spin relaxation

\[
A_l \left\{ 1 - \frac{1}{4} \lambda_s \sum_{l'} \left| \left< s / l' \right> \right|^2 G \left( \beta + i \frac{\Delta E_{ll'}}{2} \right) \right\} = \left| \left< s / l \right> \right|^2 \left\{ 1 + \frac{1}{4} \lambda_s \sum_{l'} A_{l'}^* G \left( \beta + i \frac{\Delta E_{ll'}}{2} \right) \right\} \tag{2}
\]

where \( \Delta E_{ll'} = E_l - E_{l'} \) is the energy difference between pair states \( l \) and \( l' \); and the summation is over the six pair states, including \( l \), which may have, but do not necessarily have, non zero singlet amplitude \( \left< s / l \right> \). The function \( G \) is defined in terms of the

Green’s function for the diffusion equation (eq. (38) and (11) of ref. [3]), and \( \beta \) is the triplet decay rate, whose exact meaning depends on triplet diffusion dimensionality (see below).

In Merrifield’s form of the theory, where the details of the kinematics of the interaction, and the effect of near-degeneracies on the description of the pair in terms of occupation-number of stationary states, were neglected [2a], \( \gamma_s \) is simply given by

\[
\gamma_s = \frac{1}{9} k k_s \sum_{l} \left| \left< s / l' \right> \right|^2 \frac{1}{1 + k \left| \left< s / l' \right> \right|^2} \tag{3}
\]

which takes simple forms in three experimentally well-defined situations. For \( H = 0 \) in the absence of accidental degeneracies

\[
\gamma(0) = \frac{1}{3} k k_s (1 + \frac{1}{3} k)^{-1} \tag{4}
\]

at high field in a resonance direction

\[
\gamma_{\text{off}} = \frac{1}{3} k k_s (1 + \frac{1}{3} k) (1 + \frac{1}{3} k)^{-1} (1 + \frac{3}{3} k)^{-1} \tag{5}
\]

and infinitely far from a resonance direction (so that no near-degeneracy needs to be considered)

\[
\gamma_{\text{off}} = \frac{1}{3} k k_s (1 + \frac{1}{3} k) (1 + \frac{1}{3} k)^{-1} (1 + \frac{3}{3} k)^{-1} \tag{6}
\]

If all \( \Delta E_{ll'} \) are large enough, in a sense specified below, then

\[
G(\beta + i \frac{1}{3} \Delta E_{ll'}) \approx \delta_{ll'} G(\beta) \tag{7}
\]

and in eq. (2) the \( A_l \)’s are separated, they are now real quantities referring to state \( l \) and eq. (1) reduces to eq. (3). Therefore, \( \gamma_{\text{off}} \) is also given by (6) in a more correct treatment, as well as \( \gamma(0) \) by (4) if there is no accidental degeneracy.

As pointed out in [2b, 3], another interesting case is that where only one \( \Delta E_{ll'} \) is small, and there is nearly resonance between two levels, while the other four are decoupled from one another and from the two near-resonance ones. In this case, \( \gamma_s \) obtained by a perturbation treatment, is given by the rather complicated eq. (45) to (47) of [3] which are eq. (A.1) and (A.2) of the appendix. In particular, when resonance occurs between the only two states bearing a non-zero singlet amplitude, as in a high field resonance direction, the result of the theory of [2b] is recovered (and eq. (5) is therefore also correct). Moreover, with the assumption of a Lorentzian shape,

\[
G(\beta) \approx \frac{1 + i \Delta E_{ll'}/k}{1 + i \Delta E_{ll'}/k} \tag{8}
\]

the anisotropy at high field is found to be, as in reference [2b]

\[
\gamma(\text{H}) = \gamma_{\text{off}} - (\gamma_{\text{off}} - \gamma_{\text{off}})(1 + \omega^2 \Delta^{-2}) \tag{9}
\]
where \( \omega = \Delta E/k_{-1}, \Delta \) is the resonance width

\[
\Delta^2 = \frac{(1 + k)(1 + \frac{1}{3} k)^2}{(1 + \frac{1}{3} k)(1 + \frac{2}{3} k)}
\]  

(10)

and \( \gamma_{\text{eff}} \) and \( \gamma_{\text{on}} \) are given by (6) and (5).

The exact lineshape is not Lorentzian, but crystalline imperfections are expected to smear out the non-Lorentzian details, as is indeed observed [2b-3].

Having recalled the results of the simpler theory and some of the conditions for them to hold, we now proceed to the numerical analysis of the results (see Appendix B).

The directional resonances (Fig. 4) are a consequence of the degeneracy of the two pair states which in high field have non-zero singlet amplitude, and are determined by the zero-field splitting parameters \( D^* \) and \( E^* \) of the interacting triplet species. In the \((a, c)\) plane, for the crystal structure of anthracene or pyrene [2b], the relation is especially simple and the resonances occur at angles \( \pm \alpha_0 \) from the \( x \) axis of the fine-structure tensor such that

\[
\cos 2\alpha_0 = D^*/3E^* .
\]  

(11)

From the known fine-structure parameters of the pyrene molecule dissolved in crystalline fluorene [11] and the known crystal structure [12], it is possible to calculate the fine-structure parameters of a triplet exciton localized on one molecule and moving by random walk in an undistorted lattice:

\[
D^* = 0.040 \text{ cm}^{-1}
\]

and \( E^* = -0.0366 \text{ cm}^{-1}, \) \( D^*/E^* = -1.10, \) and the \( x \) axis of the tensor is at \( 26^\circ \) from the \( a \) axis [13].

Experimentally, \( 2\alpha_0 = 113 \pm 2\circ \), hence

\[
D^*/E^* = -1.17 \pm 0.1
\]

and the acute bisector of the resonance directions (this should be the \( x \) axis) is at \( 30 \pm 3\circ \) from the \( a \) direction (which was not determined with high accuracy).

The experimental anisotropy in other planes, such as the \((b, c')\) plane [6], is also compatible with the same \( D^*/E^* \). It appears therefore that the mobile species responsible for T-T annihilation and delayed fluorescence at \( 300 \text{ K} \) in pyrene is the triplet monomer exciton. This assumption is further substantiated by the phosphorescence spectrum, particularly the absence of Stokes shift of the origin [14].

In the following, the \( D^* \) and \( E^* \) calculated above will therefore be used as those of the moving triplet exciton expressed in \( \text{s}^{-1} \).

\[
D^* = 7.576 \times 10^9 \text{ s}^{-1}
\]

and \( E^* = -6.881 \times 10^9 \text{ s}^{-1}. \) For \( H = 0, \) the energy differences between pair states whose \( S_n \neq 0 \) are \( 2(D^* \pm E^*) \) or \( 1.39 \times 10^9 \text{ s}^{-1} \) and \( 28.9 \times 10^9 \text{ s}^{-1}. \)

Using eqs. (4)-(6) one would find \( k_{-1} \approx 7.5 \times 10^9 \text{ s}^{-1}. \) Therefore, two of the three zero-field levels of interest are nearly degenerate and one may not use eq. (4). This is further discussed in the appendix. In high field, the direction farthest from resonance is \( \alpha = 0 \) (Fig. 4a), where the energy difference of the two levels whose \( S_n \neq 0 \) is \( D^* - E^* = 28.2 \times 10^9 \text{ s}^{-1}, \) therefore eq. (5) and (6) are correct and Merrifield’s theory may be used for the analysis of the high field anisotropy (Fig. 4a).

However, what is actually measured is not \( \gamma_{\text{eff}} \) and \( \gamma_{\text{on}}, \) but a minimum, \( \gamma_{\text{min}}, \) and maximum, \( \gamma_{\text{max}}, \) value of \( \gamma, \) respectively.

It is often assumed that \( \gamma_{\text{min}} \equiv \gamma_{\text{on}}, \) which amounts to assuming that crystal imperfections play no role in T-T annihilation. But it has not been proved yet that annihilation takes place at random sites in the lattice. If the singlets responsible for delayed fluorescence are generated preferentially at distorted sites, the anisotropy may be modified in two ways. If the crystal axes in these regions are not aligned with respect to those of the main part of the crystal, the peaks are displaced, generating a kind of “inhomogeneous” broadening. If on the other hand, spatial variation of the triplet band energy constrains the triplets to move, for a certain number of hops say 10 to 100, in a very limited region of the crystal, the pair lifetime is increased, and the peak becomes sharper, unless the pair lifetime is limited by the spin lattice relaxation time, which will also destroy correlation [15].

On the other hand, \( \gamma_{\text{max}} \) corresponds to \( \alpha = 0 \) and \( \omega \) remains finite, its maximum possible value being \( (D^* - 3E^*)/k_{-1}. \)

Hence from eq. (9)

\[
\gamma_{\text{eff}} = \gamma_{\text{max}} + (\gamma_{\text{max}} - \gamma_{\text{on}})\Delta k_{-1}^2/(D^* - 3E^*)^2
\]  

(12)

and the correcting term contains \( k_{-1}. \) Taking this into account, the best fit to experiment is obtained with

\[
k = 0.27 \pm 0.07 \text{ cm}^{-1}
\]

\[
k_{-1} = 8.2 \pm 2.2 \times 10^9 \text{ s}^{-1}
\]

and \( k \approx 0.4. \) But \( bc' \) plane is less favourable than the plane chosen here for accurate analysis [2], as shown by the large uncertainty in \( D^*/E^*. \) In anthracene, the values found by Johnson and Merrifield are [2] :

\[
k_{-1} \text{ (anthr.)} = 2.8 \times 10^9 \text{ s}^{-1}
\]

and \( k = 0.4. \)

The absolute value of \( \gamma \) has been measured [16] and

\[
\gamma_{\text{on}} = 6.4 \pm 4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}
\]

whence

\[
k_1 = 2.7 \pm 1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}. \]

This is a large value. As triplet diffusion in pyrene is clearly three-dimensional [8], an order of magnitude for the diffusion-limited TT pair formation rate may be obtained as \( 8 \pi D \delta R. \) The rate obtained by replacing the average of \( D \delta R \) by its value in the direction of fastest diffusion, with \( \delta R \) the nearest neighbouring distance, is \( 2.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}, \) which implies that
triplet pair formation is indeed diffusion limited with a capture distance comparable to, and at least equal to the nearest neighbour distance.

In Suna’s theory, the half-width $\Gamma$ of

$$\text{Re } G(\beta + i \frac{1}{2} \Delta E)$$

in an isotropic medium where the triplet diffusivity is $\mathcal{D}$ and the interaction distance $\lambda$, is:

$$\Gamma = 1.17 \mathcal{D} \lambda^{-2}$$

when no specific interaction between triplets is assumed, and the lifetime of the correlated pair (TT) of figure 1a is limited by the free triplet hopping rate $\Psi$. From the known triplet diffusion tensor, $\mathcal{D}$ varies from about $5 \times 10^9$ s$^{-1}$ between translationally non-equivalent molecules, to about $1.3 \times 10^{10}$ s$^{-1}$ between molecules related by a $\mathbf{b}$ translation. These values are consistent with the experimental value of $k$.

The following picture of TT annihilation in pyrene is therefore in fair agreement with the results obtained here and elsewhere [6-8-16] : free triplets moving by hopping in an essentially undisturbed lattice, diffuse toward each other, each hop being separated from the preceding or the following one by c.a. $10^{-10}$ s. When two triplets occupy near-neighbour positions, they may annihilate to generate a singlet exciton, and the probability of this process is given by Merrifield’s or Suna’s theories. If no reaction occurs, the two triplets separate and there is no further interaction between them : the TT pair formation is diffusion-limited, and its lifetime is about a hopping time (Fig. 1a). There is no evidence of any specific interaction stabilizing the pair [17]. In retrospect this adds support to the assumption made in analyzing the results that annihilation occurs at random sites in the lattice.

Pyrene may then be a typical example for application of Suna’s theory to a three-dimensional system, completing the already known examples of a two-dimensional material, anthracene [9], and a one-dimensional one, 1,4-dibromonaphthalene [18].

However, as discussed in the Appendix A, there remains a discrepancy between the experimental value of $\gamma$ in zero-field and the value expected from the current theories. This points to the necessity for further work on this problem.

In a three-dimensional system, $\beta$ is the ordinary time decay rate into the ground state by monomolecular intersystem crossing (in 1- or 2-dimensional systems it would be the hopping rate out of a line or plane), and the conditions for (7) to be valid are $\vert \Delta E_{\text{int}} \vert \gg \beta \sim 3 \times 10^2$ s$^{-1}$ which is always true except very near to a resonance and $\vert \Delta E_{\text{int}} \vert \gg \Psi$ which, as we have seen, is at least approximately valid in large regions of figure 4.

Spin lattice relaxation was neglected throughout. Although no investigation of pyrene triplets by ESR has yet appeared, it is doubtful that $T_1$ could be short enough to significantly alter the model obtained here.

It could be included in the discussion [3] at the expense of a more complicated numerical treatment.

We found no evidence for triplet excimers. If they coexisted with the monomer in appreciable concentration, even as immobile trapped excimers, one would see evidence of monomer-excimer heterofusion, which is not observed. Alternatively the excimers have the same $D^*$ and $E^*$ as the monomers, and are not visible in such experiments. This appears to us unlikely.

4. Photocurrent. Results. — Two different hole injecting electrodes were used : CuI and SnO$_2$ (conducting glass) and from I-V characteristics the injection conditions were found to be different for these two types of electrodes (Fig. 6). In all cases, the photoenhanced current is modified by application of a magnetic field, but in different ways.

Case A. — If holes are injected from CuI, the photoenhanced current $I$ at 5 145 Å is much larger than the dark current $I_0$, typically $I/I_0 \sim 10^3$ and $I \propto \nu^{2+a}$ where $0 < a < 0.3$ (Fig. 6a). In this case, a magnetic field always decreases $I$, there is no inversion at low field (Fig. 4b) but the effect is small, 2 % at resonance for 6 kG. The high field anisotropy could not be obtained with high accuracy, but is very similar to the anisotropy found for delayed fluorescence, the resonance directions are the same, and the linewidths seem larger. The effect decreases linearly with $\nu$ (Fig. 7).
Case B. — On the other hand, if holes are injected from conducting glass, dark currents are slightly smaller and photoenhancement much smaller \( I/I_0 \approx 10 \) or less; \( I \) departs more strongly from a \( V^2 \) dependence, being \( \propto V^{1.5} \) at low voltages and \( \propto V^{2.7} \) at high voltages (Fig. 6b). In this case, \( I \) increases on application of a magnetic field, up to 5% at high field. Except for this change in sign and magnitude, the effect shows the same magnetic field intensity as in the previous case (Fig. 4c) and an orientation dependence similar to that of delayed fluorescence, but with wider peaks (Fig. 3b).

5. Photocurrents. Discussion. — In a previous paper, the effects of magnetic fields on photoenhanced current in anthracene were studied [5]; it was found that the triplet-trapped hole interaction rate constant is decreased by application of a magnetic field, in the same way as the rate constant of interaction of triplets with free radicals [4], where the overall relative decrease is \( \leq 0.1 \). The results were analyzed using an extension of Merrifield’s theory for TT interaction (see Appendix B).

The important parameters in TD interaction are the projections \( D_i \) of the six TD pair spin states of the pure doublet, the TD rate constant can only decrease upon application of a magnetic field, as in zero field all these projections are equal, \( |D_i|^2 = \frac{1}{6} \).

We shall analyze the present results on pyrene in the same way, in the light of the discussion of § 3 above. As \( I \) in case A is much larger than in case B, for the same crystal and the same values of \( \Phi \) and \( V \), photoenhanced current in case B cannot be a SCL current, but it must be limited by the injection capability of the electrodes, not by the bulk space charge, which is therefore \( \ll CV \). The current in case A, on the contrary, has all the characters of a photoenhanced SCL current, in particular \( I \) is nearly proportional to \( V^2 \). In this case, the average space charge density is

\[
\overline{N} = \frac{1}{2} e \xi V/eL^2
\]

and it was shown previously that in the present case the triplet decay rate is increased proportionally to \( V/L^2 \) [7], that is to \( \overline{N} \), by the presence of trapped holes.

Therefore, in case A, a space charge density \( \overline{N} \) is present in the crystal. The actual density is only weakly variable with depth in the crystal, diffusion effects will be neglected and only average densities will be considered below.

At dynamic equilibrium, the triplet density in the presence of carriers is given by

\[
\alpha \Phi = (\beta_0 + Rn_p) n_+ + \gamma n_T^2
\]  \hspace{1cm} (13)

where as usual, \( \alpha \) is the \( S_0 \rightarrow T_1 \) absorption coefficient, here at 5145 Å \( \alpha(\lambda = 5145 \text{ Å}) = 8 \times 10^{-4} \text{ cm}^{-1} \) [16]; \( \Phi \) is the photon flux exciting intensity; \( \beta_0 \) is the monomolecular triplet lifetime in the charge-free crystal; \( R \) is the rate constant for triplet annihilation on trapped holes.
\[ R = 4.5 \times 10^{-11} \text{ cm}^3 \text{s}^{-1} \] [7]; \( n_p \) and \( n_T \) are the trapped hole and triplet exciton densities respectively; and \( \gamma \) is the total (radiative plus non-radiative) TT annihilation rate constant,

\[ \gamma = 7.5 \times 10^{-12} \text{ cm}^3 \text{s}^{-1} \] [16].

In eq. (13), free holes are neglected since their density is at most \( 10^{-3} n_p \) and the rate constant for triplet annihilation on free holes is only

\[ 1.3 \times 10^{-10} \text{ cm}^3 \text{s}^{-1} \] [19].

In all the present experiments, \( \Phi \) is small enough for \( \gamma n_T^2 \) to be only a small correction term in eq. (13). It then suffices to take for \( n_T \), not the exact solution, but the first order correction to the purely monomolecular regime, that is

\[
n_T = \frac{\alpha \Phi}{\beta_0 + R n_p} \left( 1 - \frac{\gamma \alpha \Phi}{(\beta_0 + R n_p)^2} \right). \tag{14}
\]

The free charge density \( n_e \) is given by

\[
n_e / \tau = \eta R n_T n_p + \sigma n_p n_T = \eta \gamma \Phi \xi (1 + \xi) \left( 1 - \frac{\gamma \alpha \Phi}{\beta_0 (1 + \xi)} \right) + \sigma \Phi n_p \tag{15}
\]

with \( \xi = R n_p / \beta_0 \), where \( \eta \) is the efficiency of carrier detrapping by triplets \( \sigma \) the cross section for hole photodetrapping and \( \tau \) the hole trapping time. In eq. (15), \( \xi \) — through \( R \) — and \( \gamma \) are magnetic field dependent. From the results of the preceding paragraph, \( \Delta \gamma / \gamma \leq 0.15 \) and by extrapolation of the Anthracene results, it is expected that \( \Delta R / R \lesssim 0.10 \). Indeed it will be found below that \( \Delta R / R = 0.05 \).

At \( V = 1000 \text{ V} \), the highest voltage applied, \( \theta = n_p / n_p = 10^{-3} \), \( n_p \leq 10^{12} \text{ cm}^{-3} \) and \( \xi \leq 0.15 \). As in addition, \( \Phi \leq 10^{18} \text{ cm}^{-2} \text{s}^{-1} \), \( \gamma \Phi / \beta_0^2 < 0.1 \). Therefore, including these small quantities, eq. (15) gives, assuming the yield \( \eta \) independent of \( H \)

\[
\frac{\Delta n_e}{n_e (1 - \sigma \Phi \theta^{-1})} \approx \frac{\Delta R}{R} \left( 1 - \frac{R n_p}{\beta_0 + R n_p} + \frac{2 \gamma \alpha \Phi R n_p}{(\beta_0 + R n_p)^2} \right) - \frac{\Delta \gamma}{\gamma} \frac{\alpha \Phi \gamma}{(\beta_0 + R n_p)^2} - \frac{\alpha \Phi \gamma}{\beta_0^2} \left( 1 - \frac{\sigma \Phi}{\theta} \right) \tag{16}
\]

or again to first order only

\[
\frac{\Delta I}{I} \approx \frac{\Delta n_e}{n_e} \approx \frac{\Delta R}{R} \left( 1 - \frac{\sigma \tau \Phi}{\theta} \right) \times \left[ 1 - \frac{R n_p}{\beta_0} \right] \left( 1 - \frac{2 \alpha \Phi \gamma}{\beta_0^2} \right) - \frac{\Delta \gamma}{\gamma} \frac{\alpha \Phi \gamma}{\beta_0^2} \left( 1 - \frac{\sigma \Phi}{\theta} \right). \tag{17}
\]

Eq. (17) shows that magnetic field effect on TT interaction increases the photocurrent, \( \Delta \gamma \) being negative. As the net effect is negative, \( \Delta R / R \) is negative as required, and large enough to overtake \( \Delta \gamma / \gamma \).

Experimentally (Fig. 3) \( \Delta I / I = -2 \% \) in a resonance at 100 V with \( \Phi \approx 5 \times 10^{17} \text{ cm}^{-2} \text{s}^{-1} \). As

\[
\Delta \gamma / \gamma = -0.15,
\]

the second term in eq. (17) is of the order of 0.5%.

At 1.5 kG, \( \Delta \gamma / \gamma = 0 \) and the effect is due solely to \( \Delta R / R \). It is found to be 1.4%. These numbers imply a value of \( 1 - \sigma \tau \Phi \theta^{-1} \approx 0.6 \) or

\[
\sigma \tau \approx 8 \times 10^{-22} \text{ cm}^2 \text{s}^{-1}.
\]

With \( \tau \approx 5 \times 10^{-5} \text{s} \) one has \( \sigma \approx 1.6 \times 10^{-17} \text{ cm}^2 \), a value similar to those found in anthracene for photons of comparable energies [20].

As \( n_p \propto V \) in case A, eq. (17) may be rewritten

\[
\frac{\Delta I}{I} \approx \frac{\Delta R}{R} (a - b V) - c \frac{\Delta \gamma}{\gamma} \tag{18}
\]

and the effect should decrease linearly with increasing voltage, as found (Fig. 7). The slope leads to \( R \approx 10^{-10} \text{ cm}^3 \text{s}^{-1} \) in agreement with [7].

In case B, the density of space charge, is \( \ll N \) and unknown. Here the magnetic field will not affect the photoenhanced current simply by changing the balance between free and trapped holes, as the current is limited by the availability of holes at the electrode. A magnetic field will then modulate the current through modulation of the mechanism of injection from the surface region into the bulk, in which, according to the experimental results, the TD interaction should also be involved.

Current injection in the bulk, due to triplets, should be either proportional to the triplet density in the surface region, \( n_T \), or to the triplet flux through the surface, where they annihilation and can assist the injection of a hole. This flux is again proportional to \( n_T \).

The following model is therefore proposed: trapped holes are held near the electrode in a barrier where their density \( n_p \) is large. If

\[
\frac{\alpha \Phi}{\beta_0} \lesssim 10^{13} \text{ cm}^{-3}.
\]

Near the surface, intersystem crossing from \( T_1 \) to the ground state may be faster than in the bulk, due for instance to the presence of additional impurities acting as quenchers. \( \beta_0 \) in eq. (13) should then be replaced by \( \beta \). The hole density in the barrier will vary with depth in an unknown manner, as the shape of the barrier is unknown. The density will, in general, increase steadily toward the surface. Everywhere where \( n_p \geq \beta / \gamma \), the term \( R n_p \) becomes dominant in eq. (13), and the corresponding effective triplet lifetime is

\[
\beta = \beta_0 + R n_p + (\alpha \Phi \gamma)/\beta_0.
\]
including a small correction for bimolecular TT interaction, and the corresponding triplet density is

\[ n_T = \alpha \Phi / \beta \]  

As \( I \) is proportional to \( n_T \) at some depth

\[ \frac{\Delta I(H)}{I} = \frac{\Delta n_T(H)}{n_T} \]  

which shows that the actual details of barrier shape or variation of \( n_p \) or \( n_T \) with depth are not important as soon as \( n_p > \beta_p / R \) in a thick enough region, and as long as only relative changes of \( I \) with \( H \) are considered. Then, from eq. (19),

\[ \frac{\Delta I}{I} = \frac{\Delta \beta}{\beta} = - \frac{\Delta R}{R} \]  

where the small term due to the variation of \( \gamma \) with \( H \),

\[ - \frac{\alpha \Phi \gamma}{R^2 n_p^2} \frac{\Delta \gamma}{\gamma} \]

is omitted, as it is calculated to be negligible.

As found experimentally, \( I \) should increase in a magnetic field, and \( - \Delta I / I \) have all the properties of \( \Delta R / R \).

In the cases most often studied, electrode limited currents are true saturation currents, where all the carriers available at the interface are injected in the bulk, such as in many injecting electrolytic contacts [21], and the saturation current is independent of the voltage. Such a situation was, for instance, found in our recent work on anthracene, when aqueous solution of Iodine was used as anode [5]. Here \( I \) increases with \( V \) (Fig. 6b), and this suggests that the injection ability of the contact is not limited by the ability of the hole to cross the interface, but by the existence of a barrier which becomes thinner and shallower at higher voltage.

The high field anisotropy can be analyzed in case A as well as case B but difficulties similar to those encountered above are possible in the zero field case. The actual calculation has been conducted for the results obtained in case B, which are more precise (Fig. 3b). In high fields, adaptation to the TD case of eq. (9) is [5]:

\[ R = R_{\text{off}} - \frac{1}{2} \left( R_{\text{off}} - R_{\text{on}} \right) \times \left[ \left( 1 + \Delta^{-2} \omega_{23}^2 \right)^{-1} + \left( 1 + \Delta^{-2} \omega_{45}^2 \right)^{-1} \right] \]  

where \( R_{\text{off}} \) and \( R_{\text{on}} \) are the values of \( R \) infinitely far from resonance and at resonance respectively. \( \Delta \) is the resonance linewidth and \( \omega_{ij} \) are energy differences between pair states involved in the resonance as follows (Fig. 8):

\[ k_{-1} \omega_{23} = E(|1 + 1, -1/2>) - E(|0, + 1/2>) \]  

\[ k_{-1} \omega_{45} = E(|0, -1/2>) - E(|1 - 1, +1/2>). \]  

The resonance positions for the photocurrent coincide exactly with those for delayed fluorescence, as expected (Fig. 3). However, the linewidth is greater.

But this may reflect some inhomogeneous broadening (see above): the best anisotropy curves are obtained in case B, where \( \Delta I / I \) is larger; the effect is then a surface effect, and the surface region may be distorted. As in the case of delayed fluorescence, \( k' \) and \( k'_{-1} \) were calculated from the anisotropy to be

\[ k' = 0.08 \pm 0.02 \]  

\[ k'_{-1} = 5.4 \pm 2 \times 10^9 \text{s}^{-1} \]

hence \( k_2 = 4.3 \pm 2 \times 10^8 \text{s}^{-1} \).

These values are quite different from the corresponding \( k \), \( k_{-1} \) and \( k_2 \) : \( k'_{-1} < k_{-1} \) and \( k' \ll k \).

From \( R(0) = 4.5 \times 10^{-11} \text{cm}^3 \text{s}^{-1} \) [7]

\[ k_1 = 1.7 \times 10^{-9} \text{cm}^3 \text{s}^{-1}. \]

The diffusion limited value, for TD pair formation at nearest neighbour approach of T to D, is only \( 1.2 \times 10^{-10} \text{cm}^3 \text{s}^{-1} \). As the measurement value is obtained from experimental conditions where crystal imperfections are not important in triplet displacement, it suggests that pair formation is certain as soon as the triplet approaches to \( \sim 50 \text{Å} \) from the trapped hole.

This does not correspond to long-range annihilation through a kind of resonance process, since the pair thus formed reacts to form an excited doublet in only c.a 10% of the cases. It may however, simply mean that the hole trap is in a distorted region of \( \sim 50 \text{Å} \) radius, which is also a shallow triplet trap. In such a case, \( k'_{-1} \) may be interpreted as the escape frequency of the triplet from the trap, or, from detailed balance [22]

\[ k'_{-1} = N_s S v \exp(-\Delta E/kT) \]
where $N_v$ is the valence band density of state $\sim 5 \times 10^{21}$, $S$ the capture cross section $7.5 \times 10^{-13}$ cm$^2$ ($\pi \times (50 \text{ Å})^2$), $v$ the triplet thermal velocity $\sim 3 \times 10^6$ cm$^2$ [23], hence a triplet trap depth of 2 000 cm$^{-1}$ [24].

The above considerations could be tested by the study of temperature dependence of $k^{-1}$, and on crystals of different origins. A weakness of the present work is that, as is almost always the case, the exact physical or chemical nature of the hole trap is unknown. A further step of the present work will be the study of crystals intentionally doped with known substitutional impurities.

6. Conclusion. — Following previous work, where the absolute value of the total triplet-triplet annihilation rate constant $\gamma = 7.5 \times 10^{-12}$ cm$^3$ s$^{-1}$ [16], and of the rate constant of annihilation of triplets on trapped holes — trapped on unknown centers — $R = 4.5 \times 10^{-11}$ cm$^3$ s$^{-1}$ [7], were measured, we have studied in detail the effect of magnetic fields on $\gamma$ and $R$, through delayed fluorescence and photocurrents.

The moving triplet entity has the same $D^*/E^*$ ratio as the triplet monomer exciton would, and is very likely this monomer.

TT annihilation to generate excited singlets may take place when two triplets happen to be on neighbouring lattice sites during their independent, three-dimensional, random walk, into the lattice. The probability of this reaction is approximately 0.3.

Photo-enhanced currents may be influenced by a magnetic field through modulation of the triplet-trapped carrier interaction rate constant $R$, hence of the free to trapped carrier ratio, or through modulation of the triplet lifetime near the electrode, hence of the injection efficiency of this electrode. In both cases, results agree reasonably well with the adaptation of Merrifield's theory [2] to the triplet-doublet case [5].

The quantitative analysis of the effect of magnetic field and the large value of $R$, lead to a very large rate constant for TD pair formation in the case studied here, implying a capture distance of $\sim 50$ Å. Possible explanations of this finding through extrinsic effects have been discussed. Once formed, the lifetime of the pair is $\sim 0.2$ ns; the probability of excited doublet formation is only 0.1.

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Appendix A. — Influence of near (accidental) degeneracy of two of the pair zero-field levels on the magnitude of zero-field TT annihilation rate constant. — In zero-magnetic field, the differences of energies of the pair states having singlet character are $\Delta E = 2(D^* \pm E^*)$, and in crystalline pyrene $2(D^* + E^*) = 1.39 \times 10^9$ s$^{-1}$. This is certainly much less than $k_{-1}$ or $I$, whatever the exact value of this parameter, and there is near degeneracy of these two levels. On the other hand

$$2(D^* - E^*) = 28.8 \times 10^9 \text{ s}^{-1},$$

which is a few times $k_{-1}$, and the third level cannot be considered infinitely distant from the two nearly degenerate ones. Estimating $\gamma (H = 0)$ in this case is somewhat difficult. In fact, the experiment gives only the ratio of $\gamma (H = 0)$ to $\gamma_{\text{max}}$ and for the field direction corresponding to $\gamma_{\text{max}}$ in (a, c) plane, the energy difference between the two high-field levels having singlet character is $D^* - 3 E^*$ which in pyrene is almost (within 2 %) equal to $2(D^* - E^*)$.

If $D^*$ were equal to $- E^*$, the two degenerate zero-field levels could be linearly combined with only one combination having non-zero singlet character, $S^2 = \frac{1}{2}$, and one would have almost exactly $\gamma (H = 0) = \gamma_{\text{max}}$ both quantities differing from $\gamma_{\text{att}}$ by the same small amount (see eq. (12)).

Experimentally however $\gamma_{\text{max}}/\gamma (H = 0) = 0.95$ in the (a, c) plane. As $D^* + E^*$ is not strictly zero, it is indeed expected that this ratio is less than 1. The order of magnitude to be expected for $\gamma_{\text{max}}/\gamma (0)$, due to the non-exact degeneracy is estimated in this appendix.

In the present case, $\gamma$ is written, using the notations of eq. (45)-(47) of [3].

\[
\left( \frac{1}{9} \psi_{\text{max}} \right)^{-1} \gamma = \frac{1}{1 + k/3} + \frac{2/3 + 2 k/\beta(1 - f(E))}{1 + 2 k/3 + k^2/9 (1 - f(E))} (A.1)
\]

\[
f(E) = \text{Re} \left[ \frac{1 + k/3}{G(\beta) + i \frac{1}{2} D} \right] + \frac{k}{3} (A.2)
\]

where $A = 2(D^* + E^*)$. $G$ is given by the equations (also taken from Suna)

\[
G(\beta) = \frac{g(R, \beta)}{1 + \beta g(0, \beta)} (A.3)
\]

\[
g(R, \beta) = - \frac{v}{4 \pi D R} \exp - \frac{\beta}{\sqrt{D}} (A.4)
\]

$g(0, \beta)$ is not given by the above equation but implicitly by

\[
1 + \beta g(0, \beta) = \psi \left| g(R, \beta) - g(0, \beta) \right| (A.5)
\]
where \( \psi \approx 1.17 D/R^2 \). As \( \bar{R} \), is of the order of the near-neighbour molecular distance, \( v \), the molecular volume, is of the order of magnitude of \( R^3 \), hence \( v/4\pi D\bar{R} = (l\psi)^{-1} \) where \( l \) is not known exactly, but is between 1 and 10. In addition, \( \sqrt{\beta/D} \ll 1 \) hence:

\[
g(\bar{R}, \beta) \simeq -1/\psi
\]

\[
g(0, \beta) = \frac{\psi}{\psi + \beta} \, g(\bar{R}, \beta) - \frac{1}{\psi + \beta} \simeq \left( -\frac{1}{l} - 1 \right) \frac{1}{\psi} = -\frac{1}{m\psi}
\]

(A.6)

where \( m \) is also between 1 and 10, hence

\[
\beta g(0, \beta) \simeq \beta / \psi \ll 1
\]

and therefore

\[
G(\beta) \simeq g(\bar{R}, \beta) \simeq -1/\psi . \quad (A.7)
\]

Similarly \( \beta \ll \Delta \) and we assume \( G \) to be smooth enough so that

\[
G(\beta + \frac{1}{2} i\Delta) \simeq G\left(\frac{1}{2} i\Delta\right) = \frac{g\left(\bar{R} + \frac{1}{2} i\Delta\right)}{1 + \beta g\left(0 + \frac{1}{2} i\Delta\right)} \quad (A.8)
\]

\[
g\left(\bar{R} + \frac{1}{2} i\Delta\right) = -\frac{1}{h\psi} \exp -\frac{\bar{R}}{D} \frac{\Delta}{1 + i} = \frac{e^{-\pi \left(1+i\right)}}{h\psi} \quad (A.9)
\]

where, using \( \Delta \approx 1.4 \times 10^9 \text{s}^{-1}, D \approx 5 \times 10^5 \text{cm}^2 \text{s}^{-1} \) an average value, and \( \bar{R} \approx 4.8 \times 10^{-8} \text{cm} \), \( \alpha \) is of the order of 1.3 to 0.2 i.e. being smaller than \( -1/\psi \), \( 1 + \beta g(0, \beta) \) is again \( \# 1 \), and

\[
G\left(\beta + \frac{1}{2} i\Delta\right) \simeq g\left(\bar{R} + \frac{1}{2} i\Delta\right) .
\]

Hence

\[
f(E) = \Re \frac{1 + k/3}{e^{\pi(1+i)} + k/3} = \frac{(1 + k/3)(e^\pi \cos \alpha + k/3)}{(e^\pi \cos \alpha + k/3)^2 + (e^\pi \sin \alpha)^2} \quad (A.10)
\]

which allows exact calculation of \( \gamma \) for given \( \alpha, k \). As from \( \gamma_{\min} \) and \( \gamma_{\max} \), \( k \approx 0.3 \), and \( \alpha \) is expected to be \( \leq 0.3 \), \( (\gamma(0) - \gamma_{\min}) / \gamma_{\max} \) is calculated to be \( \leq 2 \% \). To reach

the experimental value of 5 \% one would need \( x \approx 1 \) or an interaction distance \( R \) much larger than the nearest neighbour distance, and of the order of 15 Å.

Therefore, Suna’s theory as applied here does not allow us to reach complete agreement with experiment. The origin of the discrepancy is not clear. The deviation of triplet exciton diffusion from isotropy has been neglected; spin-lattice relaxation also was neglected, assuming that \( \psi / T_1 \gg 1 \) which seems reasonable but is unproved. Fast relaxation would mix the pure triplet pair states with the other six. It may be that the origin of the discrepancy should be sought elsewhere, for instance in another, as yet unknown effect of magnetic fields on triplet populations in the experimental situations used here.

**Note added in proof.** — Among the approximations used, eq. (7) seems not to give quantitatively good results, so that to settle the question an exact solution of eqs. (2) would be needed. We are grateful to Dr. A. Suna for useful correspondence on this question.

**Appendix B. — Hamiltonians.** — In the calculation of TT or TD pair energies, the one-triplet exciton spin hamiltonian is written as

\[
H_{ss} = D^*(S_z^2 - \frac{1}{2} S^2) + E^*(S_x^2 - S_y^2) \quad (B.1)
\]

where \( x, y, z \) are three mutually orthogonal quantisation directions. For a discussion of different possible choices for \( H_{ss} \) see [25].

For TT pairs, the hamiltonian used was simply the sum of the spin-spin and Zeeman hamiltonians for the two separate triplets, with no inclusion of interaction terms [2-3], that is

\[
\mathcal{H}^{(TT)} = H_z^{(T)} + H_z^{(T)} + H_{ss}^{(T)} + H_{ss}^{(T)}
\]

where \( D^*[(S_{x}^{(T)} - S_{y}^{(T)}) - \frac{1}{2}(S_{x}^{(T)} + S_{y}^{(T)})] + E^*[(S_{x}^{(T)} - S_{y}^{(T)}) - (S_{x}^{(T)} + S_{y}^{(T)})] \) (B.2)

For \( g_T \) we used the average value \( g_T = 2.0023 \) obtained from the known \( g \) tensor [11].

For TD pairs, similarly [5]

\[
\mathcal{H}^{(TD)} = g_T \beta \mathbf{H} \cdot \mathbf{S}^{(T)} + g_D \beta \mathbf{H} \cdot \mathbf{S}^{(D)}
\]

where \( g_D \) we used the free electron value, which does not differ much from those of the isolated positive or negative ions, in the case of hydrocarbon ion radicals [26]. Possible magnetic field effects due to orientation-dependent differences between \( g_T \) and \( g_D \) tensors were neglected, as there is no evidence of such effects.
References

[13] The optical axis x is at 26°8 from a axis.
[15] To avoid such errors, one should investigate line shapes in processes occurring truly at random sites. One may think of using fission into two triplets from non-relaxed singlets as in KLEIN, G., VOLTZ, R. and SCHOTT, M., Chem. Phys. Lett. 16 (1972) 340 and 19 (1973) 391; MOLLER, W. M. and POPE, M., J. Chem. Phys. 59 (1973) 2750, but here again it is not proved that, following photon absorption, energy localization occurs at random sites, or at sites having a small enough binding energy for excited singlets.
[23] v is not known, but should be comparable to the anthracene value, see reference [1].
[24] Such a situation would make easier to understand the relatively low value — compared to R — of the triplet-free hole interaction rate constant Rf = 1.3 x 10^-16 cm^2 s^-1 [19]. If the formation of the pair is limited by diffusion of the hole to the triplet, k_1 ~ 5 x 10^-8 cm^-3 s^-1 and from the theoretical expression of Rf, k_2 ~ 0.01 only. Indeed, if neither a net attractive interaction (which would immobilize the hole) nor a dimensional effect stabilizes the triplet-free hole pair, it would survive only approximately one hole hopping time hence k_1 ~ 10^8 to 10^11 s^-1, which implies k_2 ~ 10^6 to 10^9 s^-1 for free holes, as for trapped holes. This is reasonable if the hole trap is a displaced pyrene molecule, or molecule pair, as the matrix elements should be similar in both cases.