Mechanism of the Effect of a Resonant Microwave Field on Triplet-Triplet Annihilation Between Unlike Triplet Species*

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The intensity of the DF-ODMR spectrum has been derived when unlike triplets contribute to the annihilation process (heterofusion). Resonant microwave transitions that perturb the spin levels of the triplet pair and of the species diffusing separately (free species) were considered. In the latter case the DF-ODMR signals are negative at any orientation of the magnetic field. The spectra of single crystals of the Diphenylacetylene(DPA)-TCNB complex support the theoretical expectations.

Introduction

In molecular crystals, triplet excitons are generated by intersystem crossing (ISC) from the low-lying excited singlet state after optical excitation inside the singlet manifold. During their random walk motion excitons deactivate mainly through two pathways: (i) trapping at an impurity center of the crystal and (ii) triplet-triplet annihilation.

In the annihilation process two triplets meet and form an interacting triplet pair having some levels with singlet admixtures. Escape from a level of the pair is allowed according to its singlet character giving rise to a singlet exciton that decays to the ground state by emission of a photon of delayed fluorescence (DF). Triplet pairs can be formed either between two identical species (homofusion) or between different triplets such as an exciton and a trap (heterofusion). In the latter case a direct population of singlet states of the traps is possible with DF spectra due to these species. The main features of the exciton interactions in solids have been reviewed by Swenberg and Geacintov [1].

As is known [2], the intensity of delayed fluorescence is affected by a magnetic field in that it can produce variations in the rate constant of triplet annihilation. Extensive investigations [1] have been performed concerning the dependence of the DF intensity upon the strength and the direction of the magnetic field with respect to the crystal.

More recently it has been shown that the exciton annihilation rate can be changed by resonant microwave transitions. This is the basis of the detection method known usually as DF-ODMR or RYDMR [3]; it has been applied with or without the presence of a static magnetic field which causes the mixing of the zero field wavefunctions.

In our recent study [4] of the DF-ODMR spectra of single crystals of Anthracene-1,2,4,5-Tetracyano-benzene (A-TCNB) and Biphenyl-TCNB (B-TCNB) CT complexes we have found that variations in the DF intensity can be produced by microwave transitions that affect the triplet pair levels as well as the levels of the separately diffusing triplet excitons (free species). The former case occurs only if the triplet pair lifetime is long enough to be comparable with the inverse of the rate at which resonant transitions are induced inside the pair.

The polarization (absorption or emission) and the intensities of the resonant transitions occurring between levels of an intermediate triplet pair, are determined by the populations of the pair sublevels. When the populations of the triplet excitons substates obey the equilibrium distribution, the levels of the triplet pair are populated at the same rate. Resonant transition induced by a microwave field from a pure quintet state to a singlet-containing state increases the population of the latter and gives a positive variation of the DF intensity. In the case that the exciton sublevels are spin polarized by virtue of the spin selection of the ISC process, the microwave transitions could decrease the DF intensity, provided that the singlet-containing states of

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the triplet pair are more populated than the pure quintet states.

With spin polarized species one expects a variation of the DF-ODMR signal intensity by rotating the single crystal in the magnetic field $B$. In fact, the populating rates of the pair spin states are given by products of the populations of the triplet spin levels, and the latter are affected by the direction and the strength of $B$. The eigenfunctions of the total spin Hamiltonian (Zeeman and fine structure interactions) are admixtures of the ZFS eigenfunctions with coefficients that depend on $B$. An angular dependence of the DF-ODMR signal intensity by rotating $B$ is expected also when the resonant transitions act on the free exciton levels. In this case, however, the optically detected signal intensity displays the peculiar feature that its sign changes at those orientations of $B$ where a change in the phase of the EPR signal occurs [4].

In this paper we report the results of an investigation concerning the effect of the microwave field when unlike triplets contribute to the annihilation. In particular, we will discuss the case in which the partners of the triplet pair are a polarized triplet exciton and a polarized triplet trap generated from the former by trapping. This situation was met in the crystal of Diphenylacetylene (DPA)-TCNB. Experimental features of the DF-ODMR spectra will be presented in which two excitons or an exciton and a trap are involved in the annihilation process. The traps present in the crystal consist of 1:2 CT complexes of t-Stilbene (tS)-(TCNB)$_2$ where the tS molecule substitutes two DPA molecules in the crystal lattice [7].

Theory

The annihilation process is called heterogeneous (heterofusion) when the two constituents A and B of the reactive pair belong to different species. Their difference can arise either from the different values of the ZFS parameters, or from the relative orientation of the principal directions of the fine structure tensor, or from both causes. The latter case usually occurs when the pair is formed by a triplet exciton and a deep trap.

The annihilation by heterofusion is described by the following kinetic scheme [5]:

$$
T^j_A + T^j_B \xrightarrow{k_{jA+}^{A,B}} [T^j_A \cdots T^j_B]^j \xrightarrow{k_{jS}^{A,B}} S_{A,B} + G_{B,A},
$$

where $T^j_A$ represents the $J$ molecule in its $k$-th triplet sublevel. As distinct from the case of homofusion we must consider here two different rate constants $k_{jS}^{A,B}$ and $k_{jS}^{B,A}$ for the processes of formation of the singlet excited species A or B, respectively. They are expressed by

$$
k_{jS}^{A,B}(ij) = k_{jS}^{A,B} |\langle T^j_A, T^j_B | S \rangle|^2,
$$

where $|T^j_A, T^j_B \rangle$ is a state of the pair. $S \rangle$ a pure singlet state and $k_{jS}^{A,B}$ is independent of spin.

Following the derivation given for homofusion [4], we have calculated the variation $\Delta \gamma$ in the delayed fluorescence yield by distinguishing case 1: microwaves acting on the free triplet sublevels (either exciton or trap), from case 2: microwaves acting inside the heterogeneous pair.

In case 1 we derived the relation

$$
\Delta \gamma_{1 \pm}^{A,B} = -\Gamma_1 (R_{A,B}^{1 \pm} - 1) (R_{B,A}^{1 \pm} - 1),
$$

valid for low microwave fields. The coefficient $\Gamma_1$ is given by

$$
\Gamma_1 = k_1 k_{-1} k_{c} \sigma \pi \rho_0 \rho_B (e^A + e^B) (e^A + e^B + 3)
$$

with $e_{A,B} = k_{A,B}^{A,B}/k_{-1}$ and $k_{c} = \frac{1}{2} (g \beta B/2)^2$, while the quantities $R_{A,B}^{1 \pm}$ represent the ratios

$$
R_{A,B}^{1 \pm} = n_{A,B}^{1 \pm}/n_{B}^{1 \pm}
$$

For unpolarized triplets the population ratios $R_{A,B}^{1 \pm}$ and $R_{B,A}^{1 \pm}$ are smaller and larger than unity, respectively, for each orientation of the magnetic field, and $\Delta \gamma_1$ of (3) is always positive. When one or both triplet species A and B display spin polarized substates, the values of $R_{A,B}^{1 \pm}$ and $R_{B,A}^{1 \pm}$ can both be greater than unity for certain orientations of the magnetic field, and thereby $\Delta \gamma_1$ has a negative sign.

In the case 2, when the sublevels of the heterogeneous pair are involved, the major difference with respect to the case of the homofusion stems from the fact that now we must consider three distinct pair states, $|00\rangle$, $|+ - \rangle$ and $|- + \rangle$, that have singlet character, instead of two, degeneracy of the $|+ - \rangle$ and $|- + \rangle$ states being lost. Our derivation gives the expression

$$
\Delta \gamma_{2 \pm}^{A,B} = \Gamma_2 [(R_{A,B}^{2 \pm} - e_1) + R_{B,A}^{2 \pm} (1 - R_{A,B}^{2 \pm} e_1)],
$$

where

$$
e_1 = 1/[1 + \frac{1}{2} (e^A + e^B)]
$$

and

$$
\Gamma_2 = \frac{5}{2} k_{c} k_{-1} k_k \pi \rho_0 \rho_B (e^A + e^B) e_1/(2 + e^A + e^B)
$$

(8)
For thermalized triplets, \( A_{72} \) has a positive sign as in the case of the homofusion. When the triplets are polarized, the sign of \( A_{72} \) as well as that of \( A_{71} \) depends on the values of \( R^A \) and \( R^B \) which can be calculated by solving the set of kinetic equations for the triplet populations under steady-state conditions (\( n_i = 0 \))

\[
\dot{n}_+ = (-k_+ - w_1 - w_3) n_+ + w_1 e_1 n_0 + w_3 e_3 n_- + P_+ n_s ,
\]

\[
n_0 = w_1 n_+ + (-k_0 - w_1 e_1 - w_2) n_0 + w_2 e_2 n_+ + P_0 n_s ,
\]

\[
\dot{n}_- = w_3 n_+ + w_2 n_0 + (-k_- - w_3 e_3 - w_2 e_2) n_- + P_- n_s .
\]

\( P_i \) and \( k_i \) are the populating and depopulating rate constants of the Zeeman levels \(+, 0, -\), and they are related to those of the ZFS levels by the equation

\[
P_u = \sum_{u} C_{iu}^2 P_u \quad (u = x, y, z) ,
\]

an analogous equation holding for \( k_i \). The coefficients \( C_{iu} \) express the eigenvectors of the total Hamiltonian

\[
H = H_{\text{Zeeman}} + H_{\text{ZFS}}
\]

in terms of the eigenfunctions of the ZFS hamiltonian and depend on the strength and direction of the magnetic field with respect to the ZFS principal axes. The quantities \( w_i \) and \( e_i \) are the relaxation rate constants and the Boltzmann factors concerning the level pairs \((+, 0)\) and \((+,-)\), respectively, while \( n_s \) indicates the population of the excited singlet state precursor of the triplet. In general the steady-state \( n_i \)'s of [9] depend on a set of nine parameters. However, as mentioned above, it has been proved that for triplet excitons that deactivate by triplet-triplet annihilation or by trapping processes, the decay rate constants are almost independent of the orientation of the magnetic field [8, 9]. The same can be done for the relaxation frequencies \( w_i \) [6]. Therefore the independent parameters are \( P_x, P_y, P_z \) and \( k/w \) (ratio of the decay rate over the relaxation rate constant).

**Experimental**

The emission spectrum of the crystal of the DPA-TCNB CT complex doped with t-Stilbene was detected at room temperature and at 77 K, and no spectral change was observed. The spectrum exhibits a maximum at 18690 cm\(^{-1}\), as shown in Figure 1. The room temperature emission spectrum of the crystal of tS-(TCNB)\(_2\) consists of a broadband emission with a maximum at 17540 cm\(^{-1}\) while the onset of the 0-0 band starts at 18690 cm\(^{-1}\). This implies that the light collected by a narrowband optical filter centered at 19160 cm\(^{-1}\) (Schott 211314) is emitted only by the DPA-TCNB complex while that conveyed through the filter centered at 16780 cm\(^{-1}\) (Schott 155121) results from the superposition of the exciton and trap emission.

The decay of the delayed emissions was investigated in a microsecond time scale by using a nitrogen pulsed laser (Lambda Physik mod. K 600) as light source. The signals were detected by a Boxcar averager (EG and G mod. 162). The intensity of the exciton emission singled out at 18690 cm\(^{-1}\) and detected at 100 K decays exponentially with a lifetime \( \tau = 20 \mu s \). At room temperature the trap emission centered at 17540 cm\(^{-1}\) in the DPA-TCNB crystal gave too weak a signal to be analyzed. We measured the emission intensity of the tS-(TCNB)\(_2\) x-trap in the tS-(TCNB)\(_2\) crystal which decays exponentially with a lifetime of 2 ms.

The EPR and DF-ODMR measurements were performed by mounting the crystal on a goniometer quartz rod which served also to collect the DF emitted light. Details of the experimental setup have already been reported [4]. The crystal of DPA-TCNB was rotated inside the microwave cavity of the EPR spectrometer (JEOL PE-3X) with the magnetic field \( B \) being in the crystallographic
planes $a, b, c$ ($c = a \times b$). The DF-ODMR spectra were monitored in correspondence to the microwave resonant transitions between the exciton as well as the trap sublevels. They were obtained by singling out the fluorescence light conveyed onto the photomultiplier through the narrow-band (400 cm$^{-1}$) filters centered at 19 160 cm$^{-1}$ and 16 780 cm$^{-1}$.

Both sites of the trap and the exciton have the same $z$ axis whereas the in-plane axes $x$ and $y$ of the localized triplets are displaced by a rather large angle of $\pm 34.5^\circ$ from the corresponding principal directions of the exciton. Details on the crystal structure of DPA-TCNB and on the triplet EPR spectra are reported in [7]. The above analysis made it easy to identify the positions of the EPR lines of the exciton and of the trap, and selective perturbations of the spin levels of the two species could be accomplished by microwave transitions.

When the optical filter was centered at $v_e = 19 160$ cm$^{-1}$, firstly we detected the DF-ODMR signals due to the perturbation of the triplet exciton populations. Although the weakness of the signals did not allow their detection in a wide range of the crystal orientations, this was possible for significant orientations. In Fig. 2 the DF-ODMR spectra with the magnetic field parallel to the crystallographic axes $a$ and $b$ are reported. Measurements in the $ab$ plane (likewise in the $ac$ plane) are of interest in that the EPR spectra exhibit inversion in the signal phases when $B$ is rotated from $B \parallel a$ to $B \parallel b$. The important feature presented by the DF-ODMR spectra is that the signal is negative when $B \parallel a$ and positive when $B \parallel b$. The signal intensity becomes considerably stronger when the microwave transition is tuned to the trap spin levels. In this case the signal corresponds to a decrease of DF for each orientation of $B$ in the crystallographic planes.

When the filter centered at $v_T = 16 780$ cm$^{-1}$ is used, the DF-ODMR signals are negative for each orientation of $B$ in both cases of microwave transitions involving the exciton or the trap spin levels. The spectra reported in Fig. 3 for $B \parallel a$ and $B \parallel b$ refer to the latter case.

Before we start to discuss the different routes that lead to a variation in the yield of DF, induced by microwave transitions, there is a point that deserves a comment. Since the energy levels of the singlet and the triplet excited states of the trap are fairly close, the light emitted at $v_T$ might contain in part radiation due to the emission of the triplet trap by phosphorescence. However, the microwaves tuned to one transition between the trap spin levels produce a change in the phosphorescence yield (ODMR signal) only if a substantial anisotropy exists in the decay rates from each spin level.
The angular dependence of the spin polarization carried by the EPR lines of the exciton and the trap was found to be very similar in the crystal of DPA-TCNB [7]. Since for excitons the decay, caused by trapping or by triplet-triplet annihilation, has rate constants fairly independent of the spin level [8, 9], the above results indicate that also the spin levels of the trap decay with almost equal decay rate constants. In addition, the general feature of the ODMR signal should be to change its sign at those orientations of the crystal where a change in the phases of the EPR lines is observed. Our experimental evidences of the RYDMR spectra do not support such an expectation. For these reasons we will not consider further the contribution to the spectra that could arise from the microwave field modulation of phosphorescence.

Discussion

After the excitation by visible light in the CT band of DPA-TCNB and subsequent generation of triplet excitons three distinct processes take place giving rise to delayed fluorescence.

1) Annihilation of two identical triplet excitons (homofusion) with delayed fluorescence emitted from the lower-lying excited singlet state of DPA-TCNB (maximum at 19 160 cm	extsuperscript{-1}) according to the scheme

\[ E + E \rightarrow [E \ldots E] \rightarrow S_{E}^{1} \rightarrow S_{E}^{0} + S_{E}^{1} \text{.} \quad (i) \]

2) Annihilation of two different triplets: an exciton and a triplet trap with production of the DPA-TCNB singlet state that relaxes radiatively into the ground state (maximum at 19 160 cm	extsuperscript{-1}) following the reaction

\[ T + E \rightarrow [T \ldots E] \rightarrow S_{E}^{1} \rightarrow S_{E}^{0} + S_{E}^{1} \text{.} \quad (ii) \]

3) Annihilation of two different triplets as in the case 2 but with production of an excited singlet trap, followed by fluorescence at longer wavelength (maximum at 16 780 cm	extsuperscript{-1}) as indicated by the reaction

\[ T + E \rightarrow [T \ldots E] \rightarrow S_{E}^{1} \rightarrow S_{E}^{0} \text{.} \quad (iii) \]

The DF emission at \( v_{E} \) can be caused by the annihilating process of homofusion together with that of heterofusion. – When the exciton populations are perturbed by microwaves, the DF-ODMR signal monitored at \( v_{E} \) contains a contribution resulting from the scheme (i) and another from the scheme (ii). Instead, when the spin levels of the trap are connected by the microwave field and the light at \( v_{E} \) is again collected, the DF-ODMR signal arises solely from the heterogeneous process (ii).

When light is detected at \( v_{T} \), the DF-ODMR signal obtained by perturbing the spin levels of the trap monitors the neat effect of the heterofusion. However, it contains not only the contribution arising from the scheme (iii) but also one from the scheme (ii) if the tail of the emission spectrum of the exciton at longer wavelengths overlaps substantially with the fluorescence from the trap. This is the case with the emission spectra of the DPA-TCNB and tS-(TCNB)	extsubscript{2} complexes. Due to that overlap, when the populations of the exciton spin levels are modified by the microwaves the DF-ODMR signal detected at \( v_{T} \) is fed by the contributions arising from all the three processes represented above.

The intensity of the DF-ODMR signal for a purely heterogeneous process of annihilation can be calculated by employing the expressions for \( \Delta \gamma_{1} \) and \( \Delta \gamma_{2} \) given by (3) and (6). They account for the effect that microwave transitions produce between the spin levels of the free species and between those of the heterogeneous triplet pair, respectively. The quantities \( n_{i} \) which enter the \( R^{A,B} \) definitions are obtained as steady-state solutions of (9). These depend on the rate constants of decay \( k \) and of spin-lattice relaxation \( w \). The latter could not be measured because of the long response time (~ 100 \( \mu \)s) of our EPR spectrometer. However, a rough estimate of \( k/w \) can be obtained from a comparison of the amount of spin polarization carried by the DPA-TCNB and tS-(TCNB)	extsubscript{2} triplets with that of the triplet exciton in A-TCNB crystal having a value \( k/w = 0.1 \) [6]. As judged from the EPR signals intensity, the A-TCNB exciton and our triplet species display a comparable amount of spin polarization, and hence a value of \( k/w = 0.1 \) seems reasonable. As already done for similar systems [6, 10], the calculations were carried out by employing the set of populating rate constants \( P_{x} : P_{y} : P_{z} = 1:0.32:0.16 \) measured by the MIDP method for the TCNB triplet [11]. This fact stems for the observation that in TCNB complexes with hydrocarbons the most
important contribution to the ISC process arises from the mixing of the electronic states involving the TCNB molecule in the complex wave functions.

In the crystal of DPA-TCNB both the exciton and the trap exhibit spin polarized EPR spectra, the spectral lines appearing with opposite phases, one in emission and the other in absorption. Moreover, as mentioned above, at any orientation of the magnetic field the EPR lines of the exciton and of the trap corresponding to one microwave transition (i.e. \( |0\rangle \rightarrow |+\rangle \)) have the same phase. This fact indicates that the original alignment of the exciton spin states is preserved during the trapping process.

If we assume the high field approximation \((g \beta B \gg D, E)\), certainly valid for this system in our experimental conditions, we can take \(n_+ \approx n_-\) and then the two factors \((R_{+}^{A}B - 1)\) and \((R_{-}^{A}B - 1)\) of (3) take on the same sign and \(\Delta \gamma_1\) is negative (or zero) for each orientation of the magnetic field. Therefore, the negative sign of the DF-ODMR signal observed experimentally is fully reproduced by the model in which only the spin levels of the free species are efficiently perturbed by microwave transitions. Our calculations show that \(\Delta \gamma_1^{(E)}\) and \(\Delta \gamma_1^{(T)}\) as well as \(\Delta \gamma_2^{(E)}\) and \(\Delta \gamma_2^{(T)}\) maintain throughout the same sign. In Fig. 4 the calculated curves of \(\Delta \gamma_1^{(T)}\) and \(\Delta \gamma_2^{(T)}\) are reported.

The DF-ODMR spectra recorded at \(v_E\) and reported in Fig. 2 for two orientations of \(B\) result from the contributions due to the homofusion and the heterofusion. The orientation dependence of the \(\Delta \gamma_1\) and \(\Delta \gamma_2\) values can not account for the change of the signal sign on passing from \(B \parallel a\) to \(B \parallel b\). This suggests that the homofusion contribution must prevail on that of heterofusion in determining the spectral features.

As already found in the A-TCNB crystal [6], the annihilation between two identical species can give rise to a DF-ODMR signal that changes its sign at those orientations of the magnetic field where an inversion in the phase of the EPR signal is observed. This occurs when the variations of DF are produced by resonant transitions affecting the free exciton sublevels. In our EPR measurements on the DPA-TCNB crystal we have observed a change in the phase of the spectral lines by rotating the magnetic field from \(B \parallel a\) to \(B \parallel b\) [7]. We have verified that the signs of the DF-ODMR signals were those expected for the annihilation between excitons, in the case that the spin levels of the triplet species outside the triplet pair are efficiently perturbed by the microwave field (see (8) of [4]).

In conclusion, we have shown that the presence of the mobile and the localized triplet states in the crystal of DPA-TCNB makes it possible to observe the delayed fluorescence resulting from the annihilation in which two excitons or an exciton and a trap are involved. In the latter heterogeneous process, the DF-ODMR signal has a negative sign for each orientation of the magnetic field because the exciton and trap display the same orientation dependence of spin polarization, and moreover only the free triplet species are efficiently perturbed by the microwave field.