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# Microwave-perturbed static-magnetic-field delayed-fluorescence modulation experiments in anthracene

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The fusion of free triplet excitons in anthracene crystals at room temperature has been investigated by detection of the changes induced in the delayed fluorescence by a microwave field perturbing a static magnetic field applied to the crystal. This allowed detection of resonances at pair energy levels other than the degenerate one at which the static high-field resonances can be seen. A detailed study in the *ab* plane gave good agreement with the currently accepted energy-level diagram for the pair states. Possible approaches to account for the observed resonance intensities and linewidths are discussed.

Microwave modulation of delayed fluorescence (DF) at zero and at high magnetic fields has been extensively studied in charge-transfer (CT) crystals.[1-6] Notably, the family of CT crystals anthracene (A/TCBN), naphtalene (N/TCBN), and biphenyl-tetracyanobenzene (B/TCBN) has been studied[2-6] both at room temperature by high-field quasistatic DF microwave modulation (DF-ESR)[2] and at zero field at low temperature by delayed-fluorescence (DF-ODMR)[3] and phosphorescence (P-ODMR)[3] optical detection of magnetic resonance. The DF experiments on these materials are typically performed by excitation in the CT band of the singlet state $S_1$ and a subsequent population of the triplet band by the $S_1 \rightarrow T_1$ intersystem crossing. Experimentally, this requires the use of phosphoroscope or of synchronized choppers[3] to eliminate the prompt fluorescence which is several orders of magnitude stronger than the DF signal of which only the decaying part can be thus studied. The theory of the observed effects is complicated by the fact that in general one should consider the spin-selective generation of the unpaired triplet-exciton system which leads to a density-matrix formalism[6] consisting of two coupled equations whose solution can only be obtained in some limiting cases.[6]

Theoretically, more attractive systems are the molecular crystals in which the elementary excitations are the hopping neutral Frenkel excitons. The unpaired triplet-exciton population can be generated by a direct excitation in the triplet band and at room temperature the unpaired triplet system can be considered to be in thermal equilibrium with the bath and feeding with equal probability the nine pair states. One notable exception is that of tetracene crystals in which a thermally activated singlet fission can take place and the prompt fluorescene signal can be used to detect microwave modulation with a continuous irradiation in the singlet band at room temperature.[7] It is also well known that the DF signal in molecular crystals can be simply modulated by a static magnetic field[1,8-12] so that weakly-microwave perturbed and unperturbed static-field experiments may be used as complementary techniques[12] to test the consistency of any density-matrix theory for the triplet exciton-pair state formation, dissociation, and the mutual annihilation in a molecular material. The currently accepted density-matrix theories of triplet-triplet annihilation leading to delayed fluorescence in molecular crystals are that of Johnson and Merrifield (JM)[8] which introduces three phenomenological rate constants[8-10] to describe pair formation, dissociation, and annihilation, and the more elaborate theory of Suna[11] which specifically takes into account the triplet motion, notably its dimensionality, to describe the triplet pair formation and dissociation processes.

Although the JM[8] theory can give reasonably good agreement with the static-field experiments by adjustment of the pair-dissociation rate constant $k_{-1}$ which essentially determines the predicted (Lorentzian) linewidths of the resonances,[8-10] Suna's theory[11] was found to give a better non-Lorentzian fit to experimental line shapes in some crystals.[11,13,14] In anthracene, the nearly-two-dimensional, *ab*-plane–confined, free triplet motion has been thoroughly studied independently.[15] This allowed to fit Suna's theory with a minimum of disposable parameters for one sample,[11] but in most of the studied samples the JM approach was found to be reasonably sufficient to account for the observed static-field dependence of the DF signal. More recently, extensive experiments on the effects of a microwave field on the DF in anthracene crystals were reported.[16] However, the experiments were performed at zero field and low temperatures at which most of the emission and the microwave-induced resonances are due to heterofusion with trapped excitons and only at high rf powers could effects which can be attributed to the free-exciton fusing pairs also be observed.[16] Under these conditions either the extension of JM's[8] or Suna's[11] density-matrix approaches or the elaboration of any other reliable theory for the resonances is doubtful and none has been proposed to analyze the observations.

These considerations encouraged us to extend the room-temperature static-magnetic-field studies[8-11] on free-triplet fusion in anthracene crystals by using as an additional probe a resonant microwave field perturbing the static magnetic field applied to the crystal. Otherwise, experimental conditions identical to those for the static-field studies were used, namely, a direct optical steady-state excitation in the triplet band as well as crystals in which the absence of exciton trapping at room temperature was previously checked from the single-exponential-type buildup and decay of the delayed-fluorescence signal.[1,15] The effect of the perturbing microwaves can be thus considered as essentially due to changes in the single and paired populations of the neutral, hopping triplet excitons. The experimental results as well as possible applications of Merrifield's kinetic scheme[8] are briefly reported here.

The experiments were performed using a cylindrical microwave cavity, adapted to resonate in the $\mathrm{TE}_{011}$ mode, which was vertically suspended in the gap of an electromagnet whose base could be rotated in the horizontal plane with an angle resolution of $\pm 0.5°$. The cavity was driven by a standard microwave source amplifier (5 W, 9.4 GHz) whose power was square-wave modulated at 2.0 KHz by a pin diode. The electromagnet's power supply was digitally controlled by a Tektronix 4051 computer. For a chosen direction of the static magnetic field, this allowed us to scan its strength in the $(3.0\text{–}4.0)\times 10^3$ Oe region with a resolution which was typically 0.6 Oe per point. The samples were high-quality *ab*-surface-plane platelets ($\sim$2 mm thick) cleaved from Bridgman melt-grown crystals of highly purified anthracene. Triplet lifetimes were in the range 8–12 msec with exponential-type buildup and decay of delayed fluorescence as expected for free triplet-triplet annihilation.[15] The platelets were mounted in the cavity so that the electromagnet's field was lying in the *ab* crystal plane at a known, variable by magnet's rotation, angle $\phi$ with respect to the *a* axis. The delayed fluorescence was collected with a flexible light guide and conveyed to a photomultiplier through a stack of 2BG-12 and CS-5.58 filters. The samples were excited in the triplet exciton band from the bottom of the setup with the filtered 5145-Å line of an argon laser through sample-supporting light guide.

The delayed-fluorescence signal $F \propto \gamma n^2$, which is proportional to the square of the triplet concentration,[1,8] was fed to a lock-in amplifier tuned to the 2.0-KHz microwave-power-modulating frequency. The output of the lock-in amplifier was on-line digitized and data fed to the 4051 computer for processing and plotting of the relative microwave effect $\Delta F/F$ ($\Delta F = F' - F$, $F'$ and $F$ being the delayed fluorescence signals in the presence and absence of the microwave field, respectively) as a function of the static magnetic field strength **H**. For a given angle $\phi$ of the field's direction with respect to the crystal *a* axis, the data were averaged over 20 scans in order to achieve reasonable signal-to-noise ratios. It should be stressed that an efficient delayed-fluorescence collection, high triplet lifetimes, and good sample surface quality (to avoid excessive scattering) are required in order to keep data-collection times within reasonable limits.

Several runs were performed at angles $\phi$ which were changed in steps of $\Delta\phi = 10°$ in going from the crystal *a* ($\phi = 0$) to *b* ($\phi = 90°$) axes. The region about $\phi = 60°$ was explored in more detail with steps $\Delta\phi = \pm 5°$. In this region one would expect a disappearance of the resonances because of the crossing of the two triplet pair levels having a singlet $|S\rangle$ and a quintet $|Q_0\rangle$ character, states labeled in the high-field limit as $|1\rangle$ and $|2\rangle$.[17] These two eigenstates have squared amplitudes of, $|S\rangle$, $\frac{1}{3}$,$\frac{2}{3}$ and, for $|Q_0\rangle$, $\frac{2}{3}$,$\frac{1}{3}$, respectively.[8,9] For static field directions at which $|1\rangle$ and $|2\rangle$ cross one gets one pure singlet state and the $\Delta m_s = \pm 1$ microwave-induced transitions to the $|Q_{\pm 1}\rangle$ pair states would be no longer possible. Figure 1 shows a representative example of such runs on a sample having a triplet lifetime of $\tau = 12$ msec. Microwave source power was 4 W. In the restricted microwave power range of 2 to 5 W that could be investigated with the present setup the relative effects $\Delta F/F$ were found to be positive (increase of delayed fluorescence under microwave field) for all directions of the static field and, within the available signal-to-noise ratio, no saturation could be observed. One sees that, in going from the *a* towards the crystal *b* axis, the two resonance lines approach each other, merge in the 60°–75° region, the effect becoming undetectable at $\phi \simeq 67°$, as expected from the consideration given above.

This evolution of the resonance positions is readily predictable in the high-field approximation for which the energies of the $|1\rangle, |2\rangle$ and $|Q_{\pm 1}\rangle$ pair states can be approximated by the values $2\varepsilon_0$, $-\varepsilon_0$, and $\pm g\beta H + \frac{1}{2}\varepsilon_0$, respectively, where $\varepsilon_0 = D^*(\frac{1}{3} - n^{*2}) + E^*[m^{*2} - l^{*2}]$, $D^*$, $E^*$ being the triplet-exciton zero-field-splitting

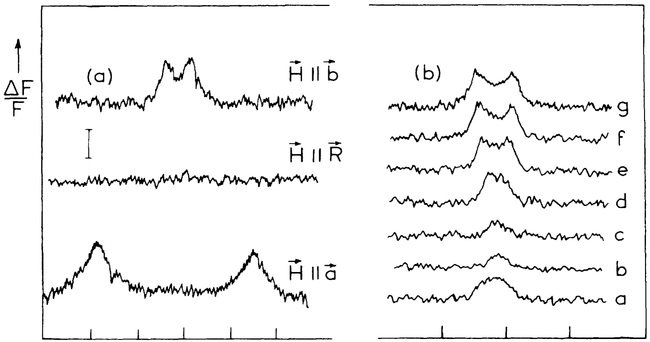

FIG. 1. Microwave modulation of delayed fluorescence as a function of a static magnetic field lying in the *ab* plane of an anthracene crystal at room temperature. For each curve, the scale is $5\times 10^{-4}$ for the vertical bar shown on the left. (a) From bottom to top: effect for the field oriented along the *a* axis corresponding to the far-off static field resonance direction, along the resonance (level crossing) direction **R** at $\phi = 67°$ from *a*, and along the crystal symmetry axis *b*. (b) Detailed evolution (in $\Delta\phi = 5°$ steps, curve *a* $\phi = 60°$) of the effect in the neighborhood of the level crossing direction, the microwave induced resonance becoming undetectable (within the signal-to-noise ratio) at $\phi = 67° \pm 0.5°$. Microwave source power 4 W. The triplet exciton population lifetime of the sample is $\tau = 12$ msec.

(ZFS) parameters, and where $l^*$, $m^*$, $n^*$ are the cosine directors of the direction of **H** with respect to the principal ZFS tensor axes $x^*$, $y^*$, $z^*$, respectively. The separation $\Delta H$ between the two resonances will be then given by $\Delta H = 3\varepsilon_0$ which for the *ab* plane, for the usual axis-orientation convention,[18] can be written as a function of $\phi$ as

$$\Delta H = D^*(1-3\sin^2\phi) - 3E^*\cos^2\phi\cos(2\alpha) \ , \tag{1}$$

where $\alpha$ is the angle that the $x^*$ principal tensor axis makes with the crystal *a* axis. A best fit of the data to the above expression yields the values $D^* = -54$ Oe, $E^* = 330$ Oe, $\alpha = 27°$ with an uncertainty estimated to be $\pm 10\%$, in satisfactory agreement with the conventional ESR reported values.[18,19] The pair $|1\rangle$ and $|2\rangle$ level crossing lies at $\phi = 67° \pm 0.5°$, in good agreement also with the value obtained from the static-field experiments.[8] Figure 2 illustrates the overall fit of the data with the predictions for the above values of the triplet-exciton ZFS parameters.

This angular dependence of the resonance separations is nearly the same[19] as that observed by conventional ESR.[18] Resonance positions cannot thus be used to determine whether the DF-detected microwave effect is predominantly due to changes in the populations of the individual triplet or of the paired triplet sublevels. Spectral features like linewidths and intensities of the resonances must be, in principle, obtained from a numerical solution of a system of two coupled density-matrix equations[6] which takes into account both transitions, as well as the coupling between the two manifolds via the pair formation and dissociation mechanisms,[8,11] In practice,[2-4,6] solutions of such a problem have been obtained using simplifying assumptions whose validity must be justified by the crystal properties as well as by the particular experimental conditions used to detect the microwave-induced changes in the DF signal. For anthracene crystals at room temperature one already knows several of the relevant parameters obtained by independent work, like conventional ESR linewidths[18,20,21] and saturation-field studies,[18] triplet-exciton hopping-rate measurements,[15] and, in the framework of Merrifield's kinetic scheme,[9,22] measurements of the pair state formation, dissociation, and fusing rates, $k_1$, $k_{-1}$, and $k_2$, respectively, in the static-field DF-modulation experiments.[8,9,23] As a first step toward future, more elaborate computations, we shall assess here the relative importance of the two effects in the present experimental conditions by neglecting the coupling between the two manifolds[24] and separately evaluating the $\Delta F/F$ signals due to either the microwave-induced changes in the populations of the isolated triplet levels or those of the paired triplet states.

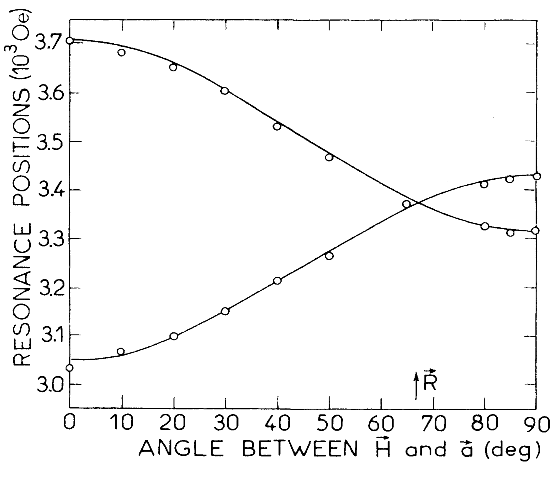

FIG. 2. Evolution of static magnetic field positions of the observed (open circles), microwave-induced, peaks of delayed fluorescence plotted as a function of the angle $\phi$ that the field makes in the *ab* plane with the crystal *a* axis. The curves shown are the best fit prediction, with triplet exciton ZFS parameters $D^* = -54$ Oe, $E^* = 330$ Oe, and $\alpha = 27°$ (see text), obtained by computer diagonalization of the triplet pair states $6\times 6$ matrix for any static field strength and direction. They coincide, within the experimental error ($\pm 20$ Oe), with the high-field approximation prediction given in text.

For static fields $H \approx 3.5\times 10^3$ Oe used here, the high-field approximation can be considered as sufficiently adequate for anthracene.[8] The contribution of the two effects, considered separately, can be most readily obtained by considering the $\Delta F/F$ signal observed for $\phi = 0°$, **H**$\|$**a** in Fig. 1. At this angle the two (singlet-amplitude-containing) pair state levels $|1\rangle$ and $|2\rangle$, with populations labeled as $P_1$ and $P_2$, respectively, are sufficiently far from the degeneracy direction.[25] The microwave-induced change in the DF signal $F = \gamma n^2$, $n$ being the triplet-exciton concentration, can be then written as[8,9]

$$\Delta F = F' - F = k_2[\tfrac{1}{3}(P_1' - P_1) + \tfrac{2}{3}(P_2' - P_2)] \ , \tag{2}$$

where the prime indicates the microwave-modified quantities.

If one considers first that $\Delta F$ is entirely due to microwave transitions between individual triplet levels, with populations $n_0, n_\pm$, expression (2) can be simply written as[8,9]

$$\Delta F = \frac{1}{3}\frac{k_1 k}{AB}\{B[(n_0')^2 - n_0^2] + 2A(n_+' n_-' - n_+ n_-)\} \ , \tag{3}$$

where $k = k_2/k_{-1}$, and $A = 1 + k/3$, $B = 1 + 2k/3$. In the absence of microwaves the populations of the three triplet sublevels are in thermal equilibrium and as for fields of $\sim 3.5\times 10^3$ Oe the exponents of the Boltzmann factors at room temperature are of the order of $1.5\times 10^{-3}$, one can write $n_0 \simeq n(1-\alpha_0)/3$, $n_\pm \simeq n(1-\alpha_\pm)/3$,[26] with $\alpha_0 = \varepsilon_0/k_b T$, $\alpha_\pm = (-\varepsilon_0/2 \pm g\beta H)/k_b T$, $\alpha_0 + \alpha_+ + \alpha_- = 0$. ESR triplet-exciton work[18] on anthracene indicates that saturation effects are apparent for microwave field strengths $H_1 > 2$ Oe. In present experiments microwave fields of $H_1 = 6.5$ Oe (Ref. 27) were used so that the two $\Delta F/F$ peaks for **H**$\|$**a** in Fig. 1 will correspond to nearly equal populations $n_0' \simeq n_+'$, and $n_0' \simeq n_-'$, respectively. As in anthracene $\varepsilon_0 < 0$, the lower-field ($H_l = 3.05$ kOe) peak corresponds to the $|0\rangle \rightarrow |+1\rangle$, and the higher-field ($H_h = 3.72$ kOe) peak to the $|-1\rangle \rightarrow |0\rangle$ transition, the populations being $n_0' \simeq n_\pm' \simeq n(2+\alpha_\mp)/6$, and $n_\mp' \simeq n(1-\alpha_\mp)/3$, respectively. Expression (3) together with the far-from-degeneracy DF expression $F = \gamma n^2 = k_1 k n^2 (1$

$+4k/9-2k\alpha_0/9)/9AB \simeq k_1 kn^2(1+4k/9)/9AB$ [see (12) in Ref. 8] gives for the lower- and higher-field peaks,

$$\left[\frac{\Delta F}{F}\right]_{l,h} \simeq \frac{k(2\alpha_0+\alpha_{\mp})}{9+4k} = \mp \frac{k}{9+4k}\frac{\hbar\omega}{k_b T} , \tag{4}$$

respectively, which for $k=0.4$ (Ref. 8) and 9.5 Ghz at room temperature yields $\Delta F/F \simeq \mp 6\times 10^{-5}$. Expression (4) predicts thus one order of magnitude smaller peak intensities and a *decrease* of the DF signal under the microwave field for the low-field resonance which is inconsistent with the experimental result $\Delta F/F \simeq 9\times 10^{-4} > 0$ for both peaks in Fig. 1.

We shall analyze next the approximation that $\Delta F$, given by (2), is nearly entirely due to transitions between the pair states. In this case, one can consider the system to be far from saturation as $(g\beta H_1 \hbar^{-1})^2 \tau_p^2 \ll (g\beta H_1 \hbar^{-1})^2 T_1 T_2 \sim 2$,[18] the correlated triplet pair lifetime $\tau_p$ for anthracene being $\tau_p \simeq 3\times 10^{-10}$ sec,[28] and for present purposes an analysis to first order in microwave power can be considered to be a sufficiently good approximation. Resolution of the corresponding system of ten coupled algebraic equations,[12] yielding the pair populations $P_1'$ and $P_2'$ needed in (2), can be readily obtained, to first order in microwave power and sufficiently low exciting intensities, in a closed form [see Eqs. (A1), (A12), and (6) in Ref. 12]. Assuming the microwave-induced resonances to have Lorentzian line shapes of half widths at half maximum $\Delta H$, one gets in present notation,

$$\left[\frac{\Delta F}{F}\right]_{l,h} \simeq \frac{k}{9+4k}\frac{B^2+2A^2}{AB}\frac{g\beta H_1^2}{2\hbar\Delta H k_{-1}} . \tag{5}$$

For $k=0.4$ and $k_{-1}=3\times 10^9$ sec$^{-1}$ given in Ref. 8, $H_1=6.5$ Oe, and the *experimentally* observed width at half maximum of $2\Delta H \simeq 70$ Oe for **H**||**a**, expression (5) yields for *both* peaks a relative *increase* of DF of $\Delta F/F \approx 3\times 10^{-4}$ which is more consistent with the experimental observation than the previous result.[29]

One can proceed one step further within this approximation and seek $\Delta F/F$ spectra for any angle $\phi$, without resorting to the high-field limit. If one considers the kinetic equation for the pair-density matrix of Ref. (8) in which the source term is kept constant, proportional to the unity matrix, and if one introduces the microwave field just as a perturbation to the pair spin Hamiltonian, one has

$$\frac{\partial\rho}{\partial t} = -\frac{i}{\hbar}[\mathcal{H}_0+\mathcal{H}',\rho] - \tfrac{1}{2}k_2(\sigma\rho+\rho\sigma) - k_{-1}\rho + \tfrac{1}{9}k_1 n^2 I , \tag{6}$$

where, $\mathcal{H}' = g\beta H_1 S_x \cos\omega t$ is the microwave perturbation Hamiltonian, the matrix $\sigma$ is $\sigma = |S\rangle\langle S|$, having as diagonal elements the squares of the singlet amplitudes of the pair states,[8,9] $I$ is the unity matrix all other notation being the same as in (2) of Ref. 8. Considering the microwave field as a perturbation to second order in $H_1$, solution of (6) can be written as

$$\rho(t) = \rho_{00} + \rho_{11}' H_1 \cos\omega t + \rho_{11}'' H_1 \sin\omega t + \rho_{02} H_1^2 , \tag{7}$$

where in the four density matrices $\rho_{00}$, $\rho_{11}'$, $\rho_{11}''$, and $\rho_{02}$, the first index labels the temporal harmonic and the second the power of the microwave field. The problem reduces then to a system of the three coupled equations given in the Appendix, and whose resolution by iteration on a computer yields the matrix elements $(\rho_{00})_{mn}$ and $(\rho_{02})_{mn}$ needed to compute the relative microwave effect

$$\Delta F/F = \mathrm{Tr}(\sigma\rho_{02})H_1^2/\mathrm{Tr}(\sigma\rho_{00}) , \tag{8}$$

for a given orientation and strength of the applied static magnetic field. Figure 3 shows a computation of (8) for the static field lying in the *ab* plane at angles $\phi$ similar to those of the data presented in Fig. 1. Although the approach reproduces qualitative features like the disappearance of the effect at the level-crossing direction and a $\Delta F/F > 0$ effect for both peaks, the best fit to the data shown has been obtained for kinetic parameters $k=0.4$ and $k_{-1}=6\times 10^8$ sec.$^{-1}$. This last value which is essential for obtaining the observed half width at half maximum of 35 Oe for the resonances for **H**||**a** (peak maxima of $\simeq 10^{-3}$), is by a factor of $\sim 5$ smaller than the value $k_{-1}=3\times 10^9$ sec$^{-1}$ obtained from the static field DF modulation experiments.[8,9] If this last value were to be used in the computation one will get completely unresolved peaks for **H**||**b**, and for **H**||**a** half-widths of $\sim 200$ Oe (peak maxima of $\simeq 7\times 10^{-5}$) in disagreement with the observations.[30]

From the brief analysis given above we conclude that the simplified description by just one, uncoupled, density-matrix equation is not sufficient to describe the observed effects on the delayed fluorescence. The observed resonance half-width is intermediate between the single-exciton ESR half width of $\sim 5$ Oe,[18,20] and the

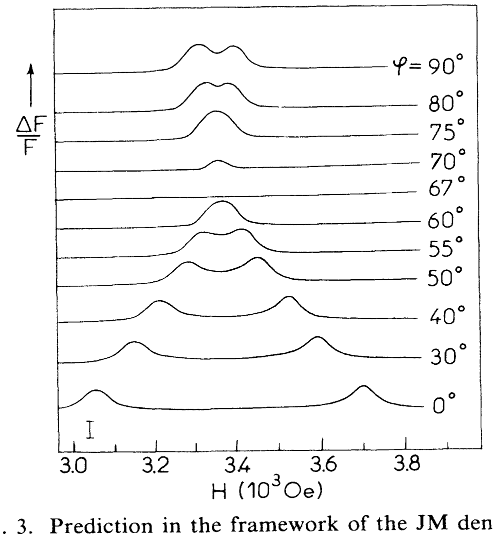

FIG. 3. Prediction in the framework of the JM density matrix kinetics for the microwave effect $\Delta F/F$ on delayed fluorescence in anthracene as a function of the strength of a static field lying in the crystal *ab* plane for several angles between **H** and **a**. For all curves the scale is $0.4\times 10^{-4}$ for the vertical bar, shown on the left as in Fig. 1. The curves shown are computed with equation (8) given in text, for the triplet pair kinetic parameters $k=0.4$, $k_{-1}=6\times 10^8$ sec$^{-1}$, microwave field $H_1=1$ Oe, and triplet exciton ZFS parameters as given in text.

~200 Oe half-width predicted here by the static-field modulation effect. The simple pair-density-matrix kinetic equation (6) should be generalized by its coupling, within the assumed kinetic scheme, to the single-exciton manifold in which microwave resonant transitions are also allowed to take place.[6] This generalization[6] consists in substituting, proportional to the unity matrix, source term on the right-hand side of (6) by the matrix $k_1(\eta \times \eta)$, that is, proportional to the direct (also called outer) product of the matrixes $\eta$, where $\eta$ describes the evolution of single-exciton states via the equation of motion (4a) of Ref. 6.[31] The trace of $\eta$, $\mathrm{Tr}\eta = n$, obeys the macroscopic triplet-exciton concentration kinetic equation (see Ref. 24).

The numerical resolution of such system of two coupled density matrix equations is complicated by the fact that proper knowledge or assumptions about crystal properties like the spin-lattice relaxation, the spin selectivity of the optical excitation and of the decay rates for the single-exciton states are required. For instance, in anthracene at room temperature the triplet decay rate ($\beta \simeq 10^2$ sec$^{-1}$) could be, in principle, considered as negligible with respect to the spin relaxation rates of $\simeq 6$ Oe,[21] however, one cannot completely exclude that the proper decay rate to be used in the context of annihilation in a two-dimensional system as anthracene is an effective rate determined by the out-of-plane hopping rate,[11] which for anthracene was estimated to be $\beta_{\mathrm{eff}} \simeq 20$ Oe.[11] Additional complication to be examined is the possibility that the introduction of a microwave field (and spin lattice relaxation) in the pair hamiltonian may lead to mixing of the triplet states with the singlet or any one of the quintet states[23,28] and the separation into six even and three odd states[8] will be no longer possible for present purposes. Exploratory computer work along these lines is now underway for both anthracene and tetracene[30] and will be published in the future.

We are grateful to Dr. M. Schott for encouragement and stimulating discussions throughout this work.

## APPENDIX

For convenience it is useful to eliminate the matrix $\rho''_{11}$ by defining the non-Hermitian matrix

$$Z = \rho'_{11} + i\rho''_{11} \ . \tag{A1}$$

Substitution of the perturbation solution (7) in (6) yields then immediately the following system of coupled equations:

$$(\rho_{00})_{mn} = \frac{2\alpha\delta_{mn} - k(\sigma\rho_{00} + \rho_{00}\sigma)_{mn}}{2(1+i\Omega_{mn})} \ , \tag{A2}$$

which is just the static-field equation[8] [Eq. (10) in Ref. (8)], with $\Omega_{mn} = (E_m - E_n)/\hbar k_{-1}$, $k = k_2/k_{-1}$, and $\alpha = k_1 n^2/9k_{-1}$, the delayed fluorescence signal under a static field being proportional to $k_2\mathrm{Tr}(\sigma\rho_{00})$;

$$Z_{mn} = -\frac{2\Gamma H_1[S_x, \rho_{00}]_{mn} + k(\sigma Z + Z\sigma)_{mn}}{2[1+i(\Omega_{mn} - \Omega)]} \tag{A3}$$

where $\Gamma = g\beta/\hbar k_{-1}$ and $\Omega = \omega/k_{-1}$ is the microwave frequency scaled to the pair-dissociation rate constant $k_{-1}$ and finally

$$(\rho_{02})_{mn} = -\frac{i\Gamma[S_x, \rho'_{11}]_{mn} + k(\sigma\rho_{02} + \rho_{02}\sigma)_{mn}}{2(1+i\Omega_{mn})} \ . \tag{A4}$$

As by (A1) $\rho'_{11}$ in (A4) can be substituted by $\rho'_{11} = (Z + \tilde{Z}^*)/2$, where $\tilde{Z}^*$ stands for the complex conjugate of the transposed $Z$, system (A2)–(A4) can be solved by iteration on a computer. The delayed fluorescence signal under microwave field perturbation is proportional to $k_2\mathrm{Tr}(\sigma\rho_{00} + \sigma\rho_{02}H_1^2)$ and the relative effect of microwave on the delayed fluorescence is given by

$$\frac{\Delta F}{F} = \frac{\mathrm{Tr}(\sigma\rho_{02})}{\mathrm{Tr}(\sigma\rho_{00})} H_1^2 \ , \tag{A5}$$

which can be computed for a given direction and strength of the static magnetic field **H** which determine the adimensional energy differences $\Omega_{mn}$ for the pair states.

For a field orientation far from the degeneracy direction in the high-field limit, (A5) yields $\Delta F/F$ as given by expression (19) in Ref. 12, and which, to a good approximation, is equivalent, for both peaks for **H**$\|$**a** in Fig. 1, to a single Lorentzian line shape whose half width at half maximum is given by

$$\Delta H \simeq (1 + k/6)\hbar k_{-1}/g\beta \ , \tag{A6}$$

and its maximum by

$$\frac{\Delta F}{F} \simeq \frac{k}{9+4k} \, \frac{B^2 + A(A+1)}{AB} \, \frac{g\beta}{2\hbar(1+k/6)} \, \frac{g\beta H_1^2}{\hbar k_{-1}^2} \ , \tag{A7}$$

which for the usual case of $k \leq 1$, yields essentially the same result as that given by (5) in text.

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[21] For theoretical work on triplet exciton spin relaxation and ESR linewidth see, for instance, (a) Appendices C and D in Ref. 11; (b) P. Reineker, in *Exciton Dynamics in Molecular Crystals and Aggregates,* edited by G. Höhler (Springer, Berlin, 1982), and references therein; (c) N. F. Berk, J. Rosenthal, and L. Yarmus, Phys. Rev. B **28**, 4963 (1983), and references therein.

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[24] The kinetic equation for the triplet concentration $n$ is usually written as $dn/dt=\alpha i-\beta n-\gamma n^2$, where $\alpha$, $\beta$, and $\gamma$ are the absorption coefficient for the exciting light of intensity $i$, the monomolecular decay rate, and the overall mutual annihilation rate constant, respectively. For the steady state, $\alpha i=\beta n+\gamma n^2$. The coupling with pair states manifold is most easily seen in the high field, far from pair levels crossing case, discussed in text. One can write, $\alpha i=\beta n+k_1 n^2-k_{-1}\sum_l P_l$, where, in general, the sum is over the populations $P_l$ of the nine pair states (see Refs. 9 and 12). At sufficiently low intensities of excitation ($\alpha i \ll \beta^2/\gamma$) the overall contribution of the last two terms can be considered sufficiently small so that $n=\alpha i/\beta$. For additional details, see also Refs. 8, 15 and 23.

[25] The condition is that $g\beta\Delta H_a \gg \hbar k_{-1}$, which is satisfied here as the resonance separation for the field parallel to crystal $a$ axis is $\Delta H_a \simeq 700$ Oe, and $k_{-1}=3\times10^9$ sec$^{-1}$ (see also Ref. 8).

[26] Contrary to the case of naphthalene, spin-polarization effects have not been observed in anthracene at room temperature (see Ref. 18 and references therein).

[27] The microwave field strength in the cavity was estimated as $H_1 \simeq 0.45\times10^{-1}\sqrt{QP}$ [C. P. Poole, *Electron Spin Resonance,* (Wiley, New York, 1967)]. With a measured quality factor of $Q\simeq5\times10^3$ and for a microwave power of $P=4$ W, $H_1\simeq6.5$ Oe.

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[29] If one introduces in this analysis the near saturation of single-exciton levels as discussed above by just substituting in the nine pair states rate equations the uniform source terms $k_1 n^2/9$ by the corresonding $k_1 n_i n_j$, $i,j=0,\pm1$, then, for $H_1 \geq \hbar/g\beta T_1 T_2$, once can write, $(\Delta F/F)_{l,h} \simeq k(9+4k)^{-1}\{[B^2+2A^2+(B^2-A^2)\alpha\mp\ ]g\beta H_1^2/2AB\hbar\Delta H k_{-1} \mp \hbar\omega/k_b T\}$, which predicts two positive, slightly asymmetric, peaks.

[30] A similar discrepancy has been pointed out also in Ref. 12 for the sole microwave resonance peak (at an unspecified field direction) published up to now for tetracene (Ref. 7). A detailed experimental study of this material is being carried out now in our laboratory. For tetracene much better, by a factor of 10, than for anthracene signal-to-noise ratios can be obtained. This will permit exploration of a wider microwave power range than it was feasible for anthracene.

[31] In the used notation $\rho$ is the pair density matrix, the single-exciton density matrix being labeled by $\eta$. In Ref. 6, these matrices are labeled as $\sigma$ and $\rho$, while in Ref. 11 as $\rho_2$ and $\rho_1$, respectively.