

## Applicability of the kinematic pair-density-matrix theory to optically detected magnetic-resonance spectra of two-dimensional molecular crystals

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(Received 23 July 1990)*

The kinematic pair-density-matrix theory of triplet-pair annihilation has been applied including the dimensionality of exciton motion to optically detected magnetic-resonance (ODMR) spectra observed optically in two-dimensional molecular crystals under microwave perturbation of a static magnetic field. It is shown that, contrary to previous work with the kinetic scheme, the kinematic approach using the known parameters of motion provides an excellent fit of ODMR spectra for both fusion of triplet pairs in anthracene and for fission of singlets into pairs in tetracene. The nearest-neighbor annihilation and the effective exciton decay rates are found to be similar to those used in the literature to account for the shapes of the orientational static-field effect. The linewidths of the ODMR resonances are found to be nearest-neighbor-annihilation-rate independent and nearly linearly proportional to the single-exciton effective decay rate in the plane of motion.

### I. INTRODUCTION

Modulation by a static magnetic field of delayed fluorescence (DF) due to triplet-triplet exciton annihilation and of prompt fluorescence (PF) due to singlets fissioning into triplet pairs has been known for some time in molecular and in charge-transfer (CT) crystals.<sup>1-8</sup> Two exciton-pair density-matrix approaches have been proposed to account for the static-magnetic-field experiments. Namely, the kinetic scheme by Johnson and Merrifield (JM),<sup>2</sup> who introduce in the evolution equation of the pair states two phenomenological, separate rates  $k_2$  and  $k_{-1}$  for the annihilation and pair-dissociation rates, respectively, and the more elaborate *kinematic* approach by Suna,<sup>3</sup> who explicitly takes into account the *dimensionality* of the free-triplet hopping transport to be determined by independent measurements.<sup>9</sup> The parameters of the kinematic theory are then the nearest-neighbor-pair transition rate toward the singlet manifold  $\lambda_s$  and the effective, for a correlated-pair formation, decay rate  $\beta$  of the unpaired exciton which in one and two dimensions is essentially determined by the out-of-main-dimension hopping rate  $\psi_{\text{out}}$  eventually perturbed by the rate of triplet spin relaxation.<sup>3-8</sup> The correlated pair lifetime  $(2\beta)^{-1}$  should be sufficiently long compared with the exciton residence time on a site  $1/\Psi$ ,  $\Psi$  being the total hopping rate out from the site in the main dimension of motion so that repeated collisions and pair reformation become possible.<sup>1,3</sup>

If the lifetime of the pair states is long compared with

the Larmor precession time in an external magnetic field of strength  $H$ , it is also possible to modulate the total pair-annihilation rate by inducing transitions between the Zeeman pair levels using microwave radiation.<sup>10-16</sup> Such optically detected magnetic resonance (ODMR) has first been observed in CT crystals by populating the triplets via intersystem crossing from the singlet band and detecting the microwave modulation via delayed fluorescence at high static fields (DF-ESR) (Refs. 10-12) and also at zero field (DF-ODMR) at low temperatures, at which phosphorescence ( $P$ ) modulation ( $P$ -ODMR) can also be observed.<sup>13,11</sup> As for the better characterized molecular solids,<sup>1</sup> one PF-ESR resonance peak has been reported for a field direction in tetracene,<sup>10</sup> and DF-ODMR spectra have been observed in anthracene crystals but at low temperatures at which most of the triplet excitons are trapped so that the main component of the signal was due to heterofusion.<sup>14,1</sup>

Recently, detailed microwave-induced, optically detected spectra have been obtained at high (room) temperature for both anthracene<sup>15</sup> and tetracene<sup>16</sup> crystals. At room temperature one deals with free-hopping triplet excitons<sup>9</sup> and the kinematic approach for nearly two-dimensional materials<sup>3</sup> is, in principle, applicable.<sup>4-8</sup> The experiments were performed using microwave fields  $H_1$  in the range of 4-6 Oe perturbing a variable-orientation static magnetic field in the  $3.5 \times 10^3$  Oe range. In anthracene, the unpaired triplet population was obtained by direct optical excitation in the triplet band and the microwave-induced effect was detected via delayed

fluorescence due to triplet-pair-state formation and subsequent annihilation into the excited singlet manifold. At room temperature and for the microwave powers used, the transitions between the unpaired-triplet-exciton Zeeman levels are saturated<sup>17,18</sup> and their contribution to the overall microwave effect on DF involving transitions between pair levels was estimated to be negligible.<sup>15</sup> In tetracene, the triplet-pair population was generated by singlet fission into pairs and the microwave-induced resonances were detected via the prompt fluorescence. The microwave effect was found, as expected, to have a sign opposite to that observed for anthracene via DF; that is, one now has a *decrease* of fluorescence under microwave field application.<sup>16</sup>

For both materials the orientational static-field spectra<sup>1-6</sup> could be reasonably well accounted for using just the kinetic scheme with phenomenological rate constants  $k_{-1} = 3 \times 10^9 \text{ sec}^{-1}$ ,  $k = k_2/k_{-1} = 0.4$  for anthracene,<sup>2</sup> and  $k_{-1} = 2 \times 10^9 \text{ sec}^{-1}$ ,  $k = k_2/k_{-1} = 1.0$  for tetracene,<sup>1,6</sup> respectively. However, the extension of the kinetic scheme to include the microwave-induced transitions was found for both materials<sup>15,16</sup> to qualitatively reproduce the microwave spectra *only* by using, for the pair dissociation rate  $k_{-1}$ , values which were *1 order of magnitude smaller* than those previously obtained for the static-field orientational effect. This contradiction within the kinetic scheme indicated to us that the introduction of two separated rates  $k_2$  and  $k_{-1}$  in the pair-density-matrix evolution equation is indeed physically not warranted<sup>3,12</sup> and that the kinematic approach might be the appropriate tool to handle the problem further. In this paper, we report the extension and application of the kinematic pair-density-matrix theory<sup>3</sup> to the experimental microwave-induced spectra in anthracene and tetracene.<sup>15,16</sup> It is found, for both fusion and fission and at least for the *two-dimensional* materials studied here, that the extended kinematic approach consistently yields microwave-induced resonance peak heights and linewidths in accord with the experiments using similar values for the parameters as for the static case,<sup>3-6</sup> and notably for the effective pair reformation exciton lifetimes<sup>3</sup> which, in practice, determine the linewidth of the microwave-induced resonances.

## II. MICROWAVE PERTURBED KINEMATIC THEORY

### A. Triplet excitons in the smooth approximation

We shall consider, from the start, hopping triplet excitons and adopt the smooth approximation for nearest neighbors with an isotropic diffusion constant in three, two, or one dimensions. The algebraic manipulation can then be greatly simplified from the start by considering the pair-density-matrix evolution equation of the form<sup>3,19</sup>

$$\begin{aligned} \frac{\partial \rho(R)}{\partial t} = & -\frac{i}{\hbar} [\mathcal{H}, \rho(R)] - 2\beta \rho(R) \\ & + 2 \sum_{R'} \psi(R') [\rho(R+R') - \rho(R)] \\ & - \delta(R) \frac{\lambda_s}{2} [\sigma, \rho(0)]^+ + S(R), \end{aligned} \quad (1)$$

where  $[\dots, \dots]$  stands for the commutator and  $[\dots, \dots]^+$  for anticommutator,  $\rho(R)$  being the density matrix for a pair separated by distance  $R$ ,  $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}'$ , in which  $\mathcal{H}_0$  is the static-field spin Hamiltonian and

$$\mathcal{H}' = g\mu_B H_1 S_x \cos(\omega t)$$

is the perturbation by the microwave field of strength  $H_1$  and frequency  $\omega$ .<sup>15</sup> The quantity  $\beta$  in the second term of the right-hand side is the effective single-exciton decay rate<sup>3</sup> in the dimension of motion having an isotropic diffusion constant  $D$ .<sup>3,9</sup> In the third term, the quantities  $\psi(R')$  are the hopping rates between sites separated by distances  $R'$ , the sum being taken over all sites. The rate  $\lambda_s$  is the nearest-neighbor pair-annihilation rate leading to singlets, and  $\sigma = |S\rangle\langle S|$  is the singlet-state projection matrix. Finally,  $S(R)$  is the pair-source term which, for *fusion*, will be considered as  $R$  and spin independent<sup>2,3,15</sup>

$$S_{\text{DF}}(R) = \alpha I, \quad (2)$$

in which  $I$  is the unit matrix and  $\alpha = 2\beta n_t^2/9$ , where  $n_t$  is the *unpaired*-triplet-exciton concentration in the crystal.<sup>3</sup> For *fission*, as in tetracene,<sup>6,8</sup> the pair-source term will be considered to be of the form

$$S_{\text{PF}} = n_s \delta(R) \sigma, \quad (3)$$

where  $n_s$  is proportional to the rate of singlet-exciton density optical excitation. The singlet fission is considered thus to occur locally; that is, to produce only nearest-neighbor geminate pairs. Note that, in (1), the mutual pair-annihilation term is also local and the  $R=0$  site is thus considered here to correspond to the averaged cluster of nearest-neighbor molecules as defined in the smooth approximation of the theory.<sup>3</sup> In crystals where both fusion and fission have similar orders of magnitude, the sum of (2) and (3) must be taken as the source term in (1).

To solve (1), one first considers the Green's function  $G(\beta, R)$ , satisfying the hopping diffusion equation

$$\sum_{R'} \psi(R') [G(\beta, R+R') - G(\beta, R)] - \beta G(\beta, R) = \delta(R) \quad (4)$$

where  $\delta(R)$  is the  $\delta$  function  $\delta(0)=1$ ,  $\delta(R)=0$  for  $R \neq 0$ . Note that  $G(\beta, 0)$  is essentially the function  $G(\beta)$  of Ref. 3 [Eqs. (20) and (38)] for the usual case  $\beta \ll \Psi$ ,  $\Psi$  being the total hopping rate out from the site in the main dimension of motion.<sup>3</sup> Considering now the microwave field  $\mathcal{H}' = \mathcal{H}_1 \cos(\omega t)$ ,  $\mathcal{H}_1 = g\mu_B H_1 S_x$ , as a perturbation to second order in  $H_1$ , the solution of (1) can be written in the form<sup>15</sup>

$$\rho(R, t) = \rho^{00}(R) + Z(R) e^{-i\omega t} + \bar{Z}(R) e^{i\omega t} + \rho^{02}(R) H_1^2, \quad (5)$$

where one has three unknown matrices, namely,  $\rho^{00}(R)$  for the usual static field effect, an auxiliary matrix  $Z(R)$ , which allows one to get matrix  $\rho^{02}(R)$  which, in turn, determines, to second order in microwave field strength  $H_1$ , the relative microwave effect  $\Delta F/F$ ,  $\Delta F = F' - F$  in

which  $F'$  and  $F$  are the fluorescence signals in the presence and absence of the microwave radiation, respectively.<sup>15</sup>

Introducing (5) in (1), one gets the system of three matrix equations, namely,

$$\begin{aligned} 0 = & -\frac{i}{\hbar}[\mathcal{H}_0, \rho^{00}(R)] - 2\beta\rho^{00}(R) \\ & + 2\sum_{R'}\psi(R')[\rho^{00}(R+R') - \rho^{00}(R)] \\ & - \delta(R)\frac{\lambda_s}{2}[\sigma, \rho^{00}(0)]^+ + S(R), \end{aligned} \quad (6)$$

which just describes the static-field effect and the system of two equations coupled to (6),

$$\begin{aligned} -i\omega Z(R) = & -\frac{i}{\hbar}[\mathcal{H}_0, Z(R)] - 2\beta Z(R) \\ & + 2\sum_{R'}\psi(R')[Z(R+R') - Z(R)] \\ & - \delta(R)\frac{\lambda_s}{2}[\sigma, Z(0)]^+ - \frac{i}{2\hbar}[\rho^{00}(R), \mathcal{H}_1], \end{aligned} \quad (7)$$

$$\begin{aligned} 0 = & -\frac{i}{\hbar}[\mathcal{H}_0, \rho^{02}(R)] - 2\beta\rho^{02}(R) \\ & + 2\sum_{R'}\psi(R')[\rho^{02}(R+R') - \rho^{02}(R)] \\ & - \delta(R)\frac{\lambda_s}{2}[\sigma, \rho^{02}(0)]^+ - \frac{i}{2\hbar H_1^2}[Z(R) + \bar{Z}(R), \mathcal{H}_1], \end{aligned} \quad (8)$$

allowing one to obtain the relative microwave effect. Calling  $E_m$  the pair state eigenvalues in the static field  $\mathcal{H}_0|m\rangle = E_m|m\rangle$ , and introducing the notation  $\omega_{mn} = (E_m - E_n)/\hbar$ ,  $\Omega_{mn} = \omega_{mn} - \omega$ ,  $\beta_{mn} = \beta + i\omega_{mn}/2$ ,  $\tilde{\beta}_{mn} = \beta + i\Omega_{mn}/2$ ,  $G(\beta_{mn}, 0) = G(\beta_{mn})$ , with the aid of (4), one gets the formal solution of (6) in the form

$$\begin{aligned} \rho_{mn}^{00}(R) = & \frac{\alpha}{2\beta}\delta_{mn} \\ & + G(\beta_{mn}, R)\left\{\frac{1}{2}n_s\sigma_{mn} + \frac{1}{4}\lambda_s[\sigma, \rho^{00}(0)]^+\right\}, \end{aligned} \quad (9)$$

where, for generality, the pair source has been taken as the sum

$$S(R) = S_{\text{DF}}(R) + S_{\text{PF}}(R)$$

as given by (2) and (3). Setting first in this equation  $R=0$  and solving for  $\rho^{00}(0)$ , one then obtains  $\rho_{mn}^{00}(R)$  for any  $R$ . Note that, if  $n_s=0$ , that is, just for fission with excitation of unpaired triplets, as in anthracene static field experiments,<sup>3</sup> (9) is formally equivalent to Eqs. (37)–(43) of Ref. 3 in the smooth approximation. Equation (7) for  $Z(R)$  can now be solved as

$$\begin{aligned} Z_{mn}(R) = & \frac{1}{4}\lambda_s G(\tilde{\beta}_{mn}, R)[\sigma, Z(0)]^+ \\ & + \frac{i}{2\hbar}\sum_{R'}G(\tilde{\beta}_{mn}, R-R')[\rho^{00}(R'), \mathcal{H}_1]_{mn} \end{aligned} \quad (10)$$

and the  $\rho^{02}(R)$  matrix obtained from

$$\begin{aligned} \rho_{mn}^{02}(R) = & \frac{1}{4}G(\tilde{\beta}_{mn}, R)[\sigma, \rho^{02}(0)]^+ \\ & + \frac{i}{2\hbar H_1^2}\sum_{R'}G(\tilde{\beta}_{mn}, R-R') \\ & \times [Z(R') + \bar{Z}(R'), \mathcal{H}_1]_{mn}. \end{aligned} \quad (11)$$

As will be seen below, the algebra can be simplified by eliminating the sums over  $R'$  using the following property of the Green's functions. If  $G(\beta_2, R)$  and  $G(\beta_1, R)$  are two Green's functions where  $G(\beta_1, R)$  satisfies (4), then the equation for  $G(\beta_2, R)$  can be written as

$$\begin{aligned} \sum_{R'}\psi(R')[G(\beta_2, R+R') - G(\beta_2, R)] - \beta_1 G(\beta_2, R) \\ = \delta(R) + (\beta_2 - \beta_1)G(\beta_2, R), \end{aligned}$$

which may be solved as

$$\begin{aligned} G(\beta_2, R) = & G(\beta_1, R) \\ & + (\beta_2 - \beta_1)\sum_{R'}G(\beta_1, R-R')G(\beta_2, R') \end{aligned}$$

so that

$$\sum_{R'}G(\beta_1, R-R')G(\beta_2, R') = \frac{G(\beta_2, R) - G(\beta_1, R)}{\beta_2 - \beta_1}. \quad (12)$$

The task is then to substitute for each element  $\rho^{00}(R')$  appearing in (10) the corresponding expression (9), and then use (12) to obtain the sum over  $R'$ . The resulting equation (10) for  $R=0$ , is then the equation for  $Z_{mn}(0)$ ; its solution yields  $Z_{mn}(R)$  for all  $R$ , via (10), a result which must be used in (11) for  $\rho^{02}(R)$  where a similar procedure is to be applied. The relative microwave effect<sup>15</sup> on the delayed fluorescence signal  $(\Delta F/F)_{\text{DF}}$  ( $\Delta F = F' - F$ ,  $F'$  and  $F$  being the DF signals in the presence and absence of microwave field), is then obtained for fission from<sup>15</sup>

$$\left[\frac{\Delta F}{F}\right]_{\text{DF}} = \frac{\text{Tr}[\sigma\rho^{02}(R)]}{\text{Tr}[\sigma\rho^{00}(R)]}H_1^2. \quad (13)$$

Similarly, if  $F'$  and  $F$  are now the prompt fluorescence signals, the relative microwave effect for fission into triplet pairs is given by<sup>16</sup>

$$\left[\frac{\Delta F}{F}\right]_{\text{PF}} = \frac{\text{Tr}[\rho^{02}(R)]}{\text{Tr}[\rho^{00}(R)]}H_1^2. \quad (14)$$

For the typical crystals studied here, (13) will be obtained for anthracene<sup>15</sup> setting  $n_s=0$  in (9), while  $\alpha$  will be considered as negligible in getting (14) for fission in tetra-<sup>16</sup>

## B. The far-off degeneracy high-field limit

For arbitrary static magnetic field orientation and strength, numerical resolution of the system of equations (9)–(11) with  $6\times 6$  matrices is a tedious task. However,

analytical solutions giving a good insight of the applicability of the kinematic theory to the observed ODMR spectra for typical crystals<sup>15,16</sup> can be obtained for field orientations for which the pair energy levels are far from degeneracy, namely, when the  $E_m - E_n$  are sufficiently large so that  $G(\beta_{mn}, R) \ll G(\beta, R)$ . For this, in one- and two-dimensional systems, the condition  $E_m - E_n \gg \hbar\beta$  is, in practice, sufficient.<sup>3,20</sup> Moreover, if the static field (here of the order of  $3.5 \times 10^3$  Oe) is sufficiently large with respect to the typical values ( $2 \times 10^2$  Oe) of the exciton zero-field-splitting (ZFS) parameters  $D^*, E^*$ , only two pair levels,<sup>2</sup> henceforth labeled  $|1\rangle$  and  $|2\rangle$ , have a singlet  $|S\rangle$  and quintet  $|Q_0\rangle$  character, their squared singlet amplitudes being  $\sigma_{11} = \frac{1}{3}$  and  $\sigma_{22} = \frac{2}{3}$  (hence, for  $|Q_0\rangle$ ,  $\frac{2}{3}$  and  $\frac{1}{3}$ ), respectively. The  $\Delta_{ms} = \pm 1$  microwave-induced transitions to the pure quintet states  $|Q_{\pm 1}\rangle$ , labeled as before<sup>15</sup>  $|4\rangle$  and  $|5\rangle$ , involve the energies  $E_1 = 2\varepsilon_0$ ,  $E_2 = -\varepsilon_0$ ,  $E_4 = \varepsilon_0/2 + g\mu_B H$ ,  $E_5 = \varepsilon_0/2 - g\mu_B H$ , in which

$$\varepsilon_0 = D^*(1/3 - n^{*2}) + E^*(m^{*2} - l^{*2}),$$

where  $l^*$ ,  $m^*$ , and  $n^*$  are the cosine directors of the direction of  $H$  with respect to the principal ZFS exciton axes  $x^*$ ,  $y^*$ , and  $z^*$ , respectively. If  $H_0 = \omega/g\mu_B$  is the central field corresponding to the microwave frequency for  $\varepsilon_0 < 0$ , one will have the lower-field resonances occurring when

$$\hbar\Omega_{14} = \hbar\Omega_{52} = -\frac{3}{2}\varepsilon_0 + g\mu_B H - \hbar\omega \quad (15)$$

vanishes for fields  $H_l < H_0$ , and similarly for fields  $H_h > H_0$  for which the energy difference

$$\hbar\Omega_{24} = \hbar\Omega_{51} = +\frac{3}{2}\varepsilon_0 + g\mu_B H - \hbar\omega \quad (16)$$

vanishes.<sup>15</sup> The notation will be further simplified by introducing the definitions

$$k = -\frac{1}{2}\lambda_s G(\beta), \quad \gamma = \frac{g\mu_B}{\hbar}, \quad G_r = \frac{G(\beta, R)}{G(\beta)}, \quad (17)$$

$$A_1 = 1 + \frac{k}{3}, \quad A_2 = 1 + \frac{2k}{3}$$

in which<sup>21</sup>  $G(\beta) = G(\beta, R) - 1/\Psi$ , and  $\lambda_s$  is the nearest-neighbor annihilation rate.<sup>3</sup>

For *fusion* with  $n_s = 0$ , Eq. (9) becomes

$$\rho_{mn}^{00}(R) = \frac{\alpha}{2\beta} - \frac{1}{2}k \frac{G(\beta_{mn}, R)}{G(\beta)} [\sigma, \rho^{00}(0)]_{mn}^+, \quad (18)$$

from which, solving first for  $R = 0$ , one gets, for the two states,

$$\rho_{nn}^{00}(R) = \frac{\alpha}{2\beta} \left[ 1 - G_r \frac{A_n - 1}{A_n} \right], \quad n = 1, 2 \quad (19)$$

and  $\rho_{nn}^{00}(R) = \alpha/2\beta$  for  $n > 2$ . For the transitions (15) and (16) one then gets, from (10) and with the aid of (12),

$$Z_{14}(R) = \frac{1}{6}\lambda_s \gamma H_1 \rho_{11}^{00}(0) [G(\beta, R) - G(\tilde{\beta}_{14}, R)] / \Omega_{14}, \quad (20)$$

$$Z_{52}(R) = \frac{\sqrt{2}}{6}\lambda_s H_1 \rho_{22}^{00}(0) [G(\beta, R) - G(\tilde{\beta}_{52}, R)] / \Omega_{52}.$$

This result is now used in (11) which, using (12) again, allows one to obtain the diagonal elements of the matrix  $\rho^{02}(R)$  needed to get the relative microwave effect (13) on *delayed* fluorescence. One finally gets

$$\left[ \frac{\Delta F}{F} \right]_{\text{DF}} = \frac{2}{9} \frac{k\gamma^2 H_1^2}{(1 - G_r) A_1 A_2 + (1 + \frac{4}{9}k) G_r} \times \left[ \frac{A_2}{A_1} [A_1(1 - G_r) + G_r] F(\tilde{\beta}_{14}) + \frac{2A_1}{A_2} [A_2(1 - G_r) + G_r] F(\tilde{\beta}_{52}) \right] \quad (21)$$

in which

$$F(\tilde{\beta}_{mn}) = \frac{1 - \text{Re}[G(\tilde{\beta}_{mn}, R)/G(\beta)]}{\Omega_{mn}^2}. \quad (22)$$

For *fission* in tetracene<sup>16</sup> one considers  $\alpha = 0$ , so that, by (9), the diagonal static-field matrix elements are

$$\rho_{nn}^{00}(R) = G(\beta, R) \left\{ -\frac{1}{2}n_s \sigma_{nn} + \frac{1}{4}\lambda_s [\sigma, \rho^{00}(0)]_{nn}^+ \right\}. \quad (23)$$

Using, then, a similar procedure and the same notation as above, one gets, for the relative microwave effect (14) on the *prompt* fluorescence,

$$\left[ \frac{\Delta F}{F} \right]_{\text{PF}} = -\frac{2}{3} \frac{\gamma^2 H_1^2}{(1 - G_r) A_1 A_2 + (1 + \frac{4}{9}k) G_r} \times \left[ \frac{A_2}{A_1} [A_1(1 - G_r) + G_r] F(\tilde{\beta}_{14}) + \frac{2A_1}{A_2} [A_2(1 - G_r) + G_r] F(\tilde{\beta}_{52}) \right], \quad (24)$$

where  $F(\tilde{\beta}_{mn})$  is given by (22). As expected, the effect now has a negative sign as the *prompt* fluorescence diminishes upon application of the microwave resonant field.<sup>15,16</sup>

### III. APPLICATION TO ODMR SPECTRA OF TWO-DIMENSIONAL CRYSTALS: RESULTS AND DISCUSSIONS

The theory as given by (21) and (24) in the high-field limit was numerically applied to the experimental ODMR spectra for anthracene<sup>15</sup> and tetracene<sup>16</sup> reported elsewhere. Both materials were taken to be two dimensional with an isotropic diffusion constant  $D$  in the  $a$ - $b$  plane. This assumption has been verified by independent measurements of motion ( $D = 1.5 \times 10^{-4}$  cm<sup>2</sup> sec<sup>-1</sup>) in anthracene crystals.<sup>9,3</sup> For tetracene, the components of the triplet diffusion tensor are experimentally not known; however, similarity of the molecular packing to that of anthracene, the calculation of the transfer integrals,<sup>22</sup> the analysis of the measurements<sup>23</sup> of one component via ESR spectra,<sup>24</sup> and of the static-field effect on prompt fluorescence<sup>6</sup> suggest a nearly two-dimensional motion also in the  $a'$ - $b$  plane with a diffusion constant of a simi-

lar order of magnitude ( $D = 3.5 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$ ) as for anthracene.<sup>24,6</sup> Function (22) is then obtained in the smooth approximation using the Green's function of the form<sup>3</sup>

$$G(\tilde{\beta}_{mn}, R) = -\frac{v_{ab}}{2\pi D} K_0 \left[ \frac{R}{(D\tilde{\beta}_{mn}^{-1})^{1/2}} \right], \quad (25)$$

where  $v_{ab}$  is the volume (area) per molecule in the plane of motion,  $R$  is the averaged cluster length,<sup>21</sup> and  $K_0$  is the modified Bessel (Hankel) function in which  $\tilde{\beta}_{mn} = \beta + i\Omega_{mn}/2$ . The two microwave-induced resonance peaks occur for static fields  $H$  such that the  $\Omega_{mn}$  given by (15) and (16) vanish. Using well-known properties of the Hankel function (25), one then gets for (22) the limiting form

$$\begin{aligned} F(\beta, R) &= \lim_{\Omega_{mn} \rightarrow 0} F \left[ \beta + \frac{i}{2} \Omega_{mn}, R \right] \\ &= \frac{P}{8K_0(P)} [PK_0(P) + 2K_1(P)], \end{aligned} \quad (26)$$

in which the parameter

$$P = \frac{R}{(D\beta^{-1})^{1/2}} \quad (27)$$

scales the nearest-neighbor cluster length<sup>21</sup>  $R$ , in which annihilation is assumed to take place, to the pair healing (re-formation) length  $(D\beta^{-1})^{1/2}$  for the motion in the plane.<sup>3</sup> Function (26) when inserted in (21) or (24) yields the maxima of the resonance.

Figure 1 illustrates the behavior predicted by (21) for the typical DF-ODMR spectra for a two-dimensional crystal using (25) and (26) for function (22). The three spectra are drawn for the static field lying in the  $a$ - $b$  plane of motion and making angles with the crystal  $a$  axis such that the far-off-degeneracy approximation (21) can be considered to be valid. The crystal structure, the triplet-exciton ZFS and motion parameters are taken as those for an anthracene crystal,<sup>13,9,17</sup> and the experimental conditions are those of Ref. 15. The spectra are calculated for the pair parameters  $\beta = 2.8 \times 10^8 \text{ sec}^{-1}$  (16 Oe),  $k = 1.0$ , which provide a satisfactory fit of the orientational static-field effect<sup>3</sup> ( $6 \text{ Oe} < \beta/\gamma < 25 \text{ Oe}$ ,  $0.8 < k < 1.2$ ) for DF in anthracene. Figure 2 shows examples of the fit judged as best (open circles) obtained via (21) and (24) for the reported experimental ODMR spectra (solid curves): (a) for DF (fusion) in anthracene<sup>15</sup> and (b) for PF (fission) in tetracene,<sup>16</sup> respectively. In Fig. 2(a) the fit is obtained via (21), (25), and (26) using the anthracene exciton structure and motion parameters<sup>3,15,17</sup>  $D^* = -54 \text{ Oe}$ ,  $E^* = 330 \text{ Oe}$ ,  $v_{ab} = 25.8 \times 10^{-16} \text{ cm}^2$ ,  $R = 5.5 \times 10^{-8} \text{ cm}$ ,  $D = 1.5 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$ , and  $\Psi = 2.4 \times 10^{11} \text{ sec}^{-1}$ , the microwave-radiation parameters  $H_1 = 4.5 \text{ Oe}$ ,  $\omega/2\pi = 9.45 \text{ GHz}$ ,<sup>15</sup> and, as disposable parameters, the effective, for correlated pair re-formation, decay rate  $\beta$  and the nearest-neighbor annihilation rate  $\lambda_s$ . The fit shown (open circles) is for  $\beta = 14 \pm 1 \text{ Oe}$  [ $(2.5 \pm 0.2) \times 10^8 \text{ sec}^{-1}$ ] and  $\lambda_s = (2.5 \pm 0.5) \times 10^{11} \text{ sec}^{-1}$  ( $k = 1.0$ ), in the range of values which also yield correct line shapes for the static-field effect in anthracene.<sup>3</sup> Simi-

larly, in Fig. 2(b), the open circles are for fits obtained via (24), (25), and (26) for the prompt fluorescence in tetracene<sup>16</sup> using  $D^* = -70.2 \text{ Oe}$ ,  $E^* = 258 \text{ Oe}$ ,  $R = 5.3 \times 10^{-8} \text{ cm}$ ,  $v_{ab} = 28.1 \times 10^{-16} \text{ cm}^2$ ,  $D = 4 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$ ,  $\Psi = 7 \times 10^{11} \text{ sec}^{-1}$ , and  $H_1 = 4.5 \text{ Oe}$ ,  $\omega/2\pi = 9.4 \text{ GHz}$  from Ref. 16. From the fit, one gets  $\beta = 6.8 \pm 0.4 \text{ Oe}$  [ $(1.1 \pm 0.1) \times 10^8 \text{ sec}^{-1}$ ] and  $\lambda_s = 1.8 \times 10^{12} \text{ sec}^{-1}$  ( $k = 4.3$ ) which are analogous to the set of parameters labeled (B) (see Table III in Ref. 6) also giving the correct line shapes for the orientational static-field effect.<sup>6,4</sup> Figure 3 shows a more refined fit (open circles) for the lower-side static-field resonance peak for PF in tetracene<sup>16</sup> drawn on an expanded scale with a resolution of 1 Oe/point. The fit shown is obtained with  $\beta = 6.9 \pm 0.2 \text{ Oe}$  [ $(1.20 \pm 0.05) \times 10^8 \text{ sec}^{-1}$ ] and  $k = 4.3 \pm 0.1$ , which also consistently fits the static effect.<sup>6</sup> The small peak seen on the higher-static-field side is believed to be due to a slight orientational disorder in the samples.<sup>16</sup> For comparison, the inadequacy<sup>15,16</sup> of the kinetic parameters  $k_{-1}$  and  $k = k_2/k_{-1}$ , as obtained from the static-field experiments,<sup>2,6</sup> is illustrated by the dashed curves for  $\mathbf{H} \parallel \mathbf{a}$  shown in Fig. 2(b) for tetracene ( $\varphi = 0^\circ$ ) and in Fig. 1 for fusion in anthracene (dashed curve  $a'$ ).

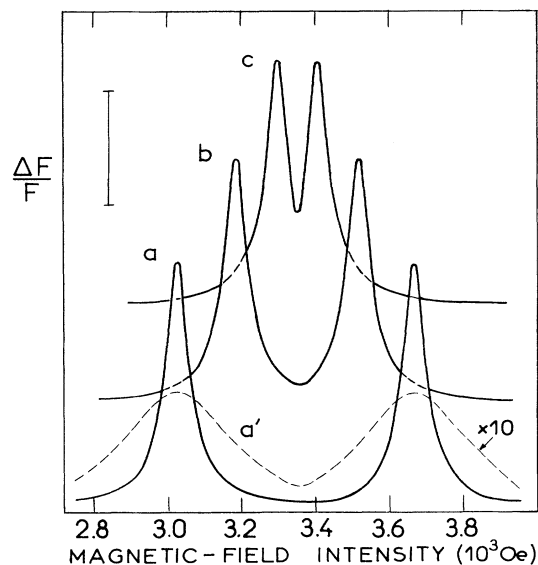


FIG. 1. Examples of DF-ODMR spectra for fusion in a two-dimensional crystal as calculated via expressions (21), (25), and (26) in text (solid curves). The static field  $H$  lies in the  $a$ - $b$  plane and makes, with the crystal  $a$  axis, the angles curve  $a$ ,  $\varphi = 0^\circ$ ,  $b$ ,  $\varphi = 30^\circ$ , and curve  $c$ ,  $\varphi = 90^\circ$  for which the far-off-level-degeneracy approximation is valid. The magnetic and motion parameters are those of anthracene as given in text. The spectra are calculated for the pair parameters  $\beta = 16 \text{ Oe}$  and  $k = 1.0$  as obtained from the static-field effect in Ref. 3. For each curve, the scale is  $+2 \times 10^{-4}$  for the vertical bar shown on the left. For comparison, the dashed curve, labeled  $a'$ , illustrates the prediction of the kinetic theory (Ref. 15) for the  $\varphi = 0^\circ$  spectrum using the kinetic parameters  $k = 0.4$  and  $k_{-1} = 3 \times 10^9 \text{ sec}^{-1}$  as obtained from the directional static-field effect in Ref. 2. Note that the vertical scale for curve  $a'$  is expanded by an order of magnitude.

Note that, in both cases, the vertical scale for the relative microwave effect is expanded by an order of magnitude. Clearly, the simpler kinetic approach,<sup>15,16</sup> although capable of yielding nearly satisfactory fits of the static experiments,<sup>2,6,10</sup> yields too small and too broad Lorentzian ODMR spectra.

The ODMR half-width  $\Delta H$  at half maximum is, for both fusion and fission, essentially a function of the effective, for pair re-formation, decay rate  $\beta$  of the triplet diffusing isotropically in the plane. If the parameter (27)

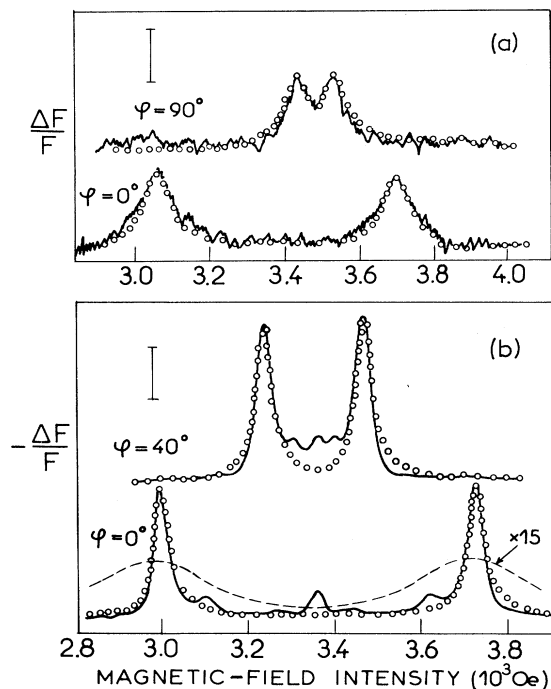


FIG. 2. The fit, judged best, of typical experimental ODMR spectra (from Refs. 15 and 16) using the extended kinematic theory in the high-field far-off-degeneracy approximation for two-dimensional crystals given in text. (a) solid curves are the DF-ODMR spectra for anthracene crystals at room temperature with the field lying in the  $a$ - $b$  plane and making the angles  $\varphi=0^\circ$  and  $90^\circ$  with the crystal  $a$  axis (from Ref. 15). Open circles correspond to the fit obtained with expressions (21), (25), and (26) for the anthracene parameters given in the text. The fit shown is for the adjustable pair parameters  $\lambda_s=(2.5\pm 0.5)\times 10^{11}\text{ sec}^{-1}$  and  $\beta=(2.5\pm 0.2)\times 10^8\text{ sec}^{-1}$  ( $14\pm 1$  Oe) for the effective, for pair re-formation, decay rate. For each curve, the vertical bar on the left is  $\Delta F/F=+5\times 10^{-4}$ . (b) The solid curves are two far-off-degeneracy PF-ODMR spectra for fission in a tetracene crystal at room temperature (from Ref. 16). Open circles correspond to a fit obtained with expressions (24), (25), and (26) using the set of parameters for tetracene as indicated in text (see also Table III of Ref. 6). The pair parameters are  $\beta=(1.2\pm 0.1)\times 10^8\text{ sec}^{-1}$  ( $6.8\pm 0.4$  Oe) and  $k=4.3$ , consistent with the static effect. For comparison, the dashed curve (expanded by a factor 15) shows the prediction for the PF-ODMR spectrum (for  $\varphi=0^\circ$ ) now using the kinetic approach with the parameters  $k=0.68$  and  $k_{-1}=2.2\times 10^9\text{ sec}^{-1}$ , which provide reasonable fits for the static-field effect (Ref. 6). The vertical bar on the left-hand side is  $\Delta F/F=-1.0\times 10^{-3}$ .

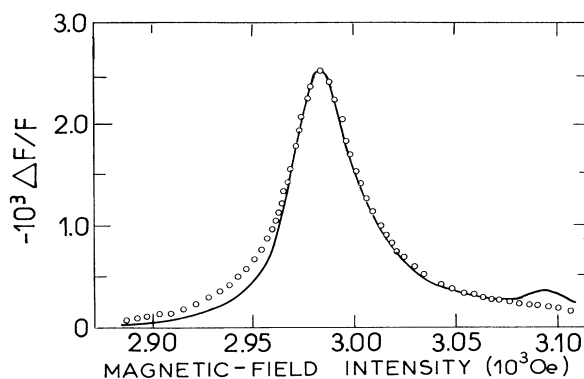


FIG. 3. Refined fit of the PF-ODMR lower-field resonance line shape for the tetracene crystal shown in Fig. 2(b) for the  $\varphi=0^\circ$  direction of the static field. The solid curve is from Ref. 16. The resolution is now 1 Oe/point. The best fit shown (open circles) is for the adjustable pair parameters  $\lambda_s=(1.20\pm 0.05)\times 10^{12}\text{ sec}^{-1}$  ( $k=4.3\pm 0.1$ ) and  $\beta=(1.20\pm 0.05)\times 10^8\text{ sec}^{-1}$  ( $6.9\pm 0.2$  Oe).

$P$ , scaling the nearest-neighbor cluster radius to the pair healing length,<sup>3</sup> is  $P\ll 1$ , as is the case for the materials studied here,<sup>25</sup> the simple expansion of the Hankel function (25) for small arguments predicts, with the aid of (26), a nearly linear dependence on  $\beta$  for the half-width at half maximum of (22),  $\Delta H=2r\beta$ , in which  $r$  is determined by the transcendental relation  $\ln(1+r^2)=r^2/2$ , whose solution is  $r=1.585\dots$  Figure 4 shows such nearly linear dependence of the half-width  $\Delta H$  for two-dimensional crystals in which  $P\leq 5\times 10^{-2}$ . The values observed when  $\mathbf{H}\parallel\mathbf{a}$  for anthracene<sup>15</sup> ( $\Delta H=38$  Oe) and tetracene<sup>16</sup> ( $\Delta H=20$  Oe), indicated by the arrows labeled  $A$  and  $T$ , correspond graphically to the values  $\beta=2.2\times 10^8\text{ sec}^{-1}$  (12.0 Oe) and  $\beta=1.1\times 10^8\text{ sec}^{-1}$  (6.5 Oe), respectively. The correlated pair lifetimes<sup>3</sup> are

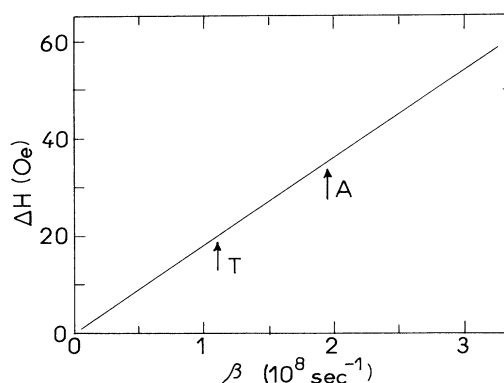


FIG. 4. Calculated dependence of the ODMR half-width at half maximum  $\Delta H$  as a function of the effective, for pair re-formation, decay rate  $\beta$  for a two-dimensional crystal with isotropic diffusion in the plane of motion. The nearly linear dependence shown (see text) has been calculated via (22), (25), and (26) in text and is valid whenever  $P<5\times 10^{-2}$ . The arrows labeled  $A$  and  $T$  indicate the experimental half-widths when  $\mathbf{H}\parallel\mathbf{a}$  as found for anthracene ( $\Delta H=38$  Oe) and tetracene ( $\Delta H=20$  Oe), respectively.

$$\tau_c = (2\beta)^{-1} \cong 2.3 \times 10^{-9} \text{ sec}$$

for anthracene and  $\tau_c \cong 4.5 \times 10^{-9}$  sec for tetracene, so multiple recollisions and pair reformation can take place in both materials.<sup>3,1</sup> This functional dependence for the half-width can be considered as valid for any two-dimensional material as long as  $P \ll 1$ , so that the graph of Fig. 4 can provide, from ODMR experiments, an immediate determination of the effective decay rate.

As  $3\beta = \psi_{c^*} + \zeta$ , where  $\psi_{c^*}$  is the out-of-plane hopping rate along the  $c^*$ , direction perpendicular to the crystal  $a$ - $b$  plane, and  $\zeta$  is the single-triplet spin relaxation, the knowledge of  $\beta$  provides an upper limit for both  $\psi_{c^*}$  and  $\zeta$ . In anthracene,<sup>17,18,3</sup> the spin-lattice relaxation is, in the  $a$ - $b$  plane, of the order of  $\zeta \approx 6 \times 10^7 \text{ sec}^{-1}$  (3.5 Oe) so that the effective decay rate is essentially determined by the out-of-plane hopping rate  $\psi_{c^*} \approx 1.5 \times 10^8 \text{ sec}^{-1}$  ( $D_{c^*c^*} \approx 1.3 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ ). For tetracene, on the other hand, the PF-ODMR half-width is only  $\Delta H = 20$  Oe and  $\beta = 6.5$  Oe, so that the spin-lattice relaxation in this material<sup>24</sup> can account, by more than 50%, for the effective decay rate. This could explain the slight anisotropy of the ODMR half-widths when the static field is rotated in the  $a'$ - $b$  plane of tetracene.<sup>16</sup> This assumption may be tested by performing the PF-ODMR experiments using higher microwave-frequency bands (e.g., the 35.5-GHz band) and hence of higher static fields so that the

influence of the spin relaxation becomes smaller.<sup>8,24</sup>

In conclusion, the kinematic approach was found, at least for the materials studied here, to provide correct half-widths and intensities for the experimental ODMR spectra of *two-dimensional* materials using, consistently, pair parameters which also yield correct fits for the orientational static-field effect.<sup>3,6</sup> Experimental and theoretical studies of other two-dimensional materials like naphthalene and phenanthrene,<sup>7,8,1</sup> where spin-lattice relaxation is more important, should be helpful to corroborate this point further. Meanwhile, further refinement of the theory by considering the temperature and microwave dependence of the source term (2), notably is proposed in Ref. 12 within the kinetic scheme, seems not to be warranted. Presently, DF-ODMR experiments are being performed in our laboratory on 1,4-dibromonaphthalene to test the applicability of the present approach on one-dimensional systems also.

#### ACKNOWLEDGMENTS

We are indebted to Dr. Andris Suna, Central Research and Development Department, E. I. Dupont de Nemours Co., for essential advice and to Dr. Michel Schott, Groupe de Physique de Solides de l'ENS et Université Paris 7, for constant encouragement. The IPCMS is the Unité Mixte UM38046-CNRS-ULP-EHICS.

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<sup>19</sup>We are grateful to Dr. A. Suna, Central Research and Development Department, E. I. du Pont de Nemours and Company, for suggesting this form to us (private communication).

<sup>20</sup>If  $\Delta'H$  is the separation of two ODMR resonances [expression (1) in Ref. 15], this condition is then equivalent to  $g\mu_B\Delta'H \gg \hbar\beta$  which is satisfied for spectra which are at least  $\pm 10^\circ$  away from the level-crossing resonance directions indicated in Ref. 15.

<sup>21</sup>See Eqs. (38) and (20) in Ref. 3. Note that the average nearest-neighbor cluster size  $R$  is labeled as  $\bar{R}$  in Ref. 3, and that the effective lifetime rate is  $\beta \ll \Psi$ .

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<sup>25</sup>For the parameters given in text, one has  $P = 0.05$  for anthracene and  $P = 0.03$  for tetracene, respectively.