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Short and long consecutive pairs model in the interpretation of MFE and F-ODMR experiments in molecular crystals

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Abstract. We have presented a model of two consecutive pairs of triplet excitons, which consists of a succession of two pairs known as short pair and long pair with reference to their respective lifetimes. We have applied this model to the modulation of prompt fluorescence (PF) in crystalline tetracene by a static magnetic field (MFE) and a microwave field (F-ODMR). The two types of experiments have been enough perfectly reproduced by using the same set of kinetics constants. Thus, we have arrived to rise the inconsistencies which one reproached the Seventies kinetic model.

PACS. 71.35.-y Excitons and related phenomena – 32.30.Dx Magnetic resonance spectra – 76.70.Hb Optically detected magnetic resonance (ODMR) – 33.50.Dq Fluorescence and phosphorescence spectra

1 Introduction

The interaction between triplet excitons in molecular crystals (tetracene, anthracene, naphthalene...) was studied in the Seventies [1–12]. The two-triplet excitons (else triplet-triplet) interaction was highlighted by the variation of fluorescence coming from the singlet-excited state of a two triplets pair as a function of the intensity and the direction of a magnetic field (MFE experiments). This variation of fluorescence is the signing of the mixing between singlet state and other exciton pairs spin states.

Tetracene crystals present a well-known case [12–15]: the energy of singlet exciton being twice higher more than that of triplet exciton, what makes difficult the observation of delayed fluorescence, which had with the fusion of two triplet excitons leading to a fluorescent singlet exciton, as in the case of the majority of molecular crystals [2–7,12,16–18]. On the other hand, the process of fission of the singlet exciton in two triplets becomes energetically possible [1]. This fluorescence is called prompt fluorescence (PF), because it is controlled by the decline of singlet that is done in a very short time $\left(\tau \propto 1/k_{fiss} \approx 0,2\ ns\right)$ [1] with the difference of delayed fluorescence that is controlled by the triplet lifetime generally rather long.

The kinetics constants obtained by the analysis of MFE experiments [1–8] allows to expect an easy interpretation of the fluorescence optically detected magnetic resonance (F-ODMR) experiments results [9–11,19–22], where fluorescence is modulated in addition to the magnetic field by a resonant microwave. However, it proved that it is not possible to interpret these two types of experiments with the same constants [19–22]. It is thus necessary to re-examine the model used until now which takes account of the modulation of singlet weight of the pair spin nine states by magnetic field (intensity and direction).

The principal difficulty comes from the lines width that is ten times weaker than envisages it the kinetics constants obtained from MFE experiments [19–22]. This has to lead us to replace the model of the Seventies by a model of two consecutive pairs of triplet excitons.

2 Theory

While referring to studies on photosynthesis mechanisms we have considered a succession of two pairs of triplet excitons whose densities operators kinetics is represented in the Liouville space. Given the operators ρ_1 for the pair (1) and ρ_2 for the pair (2) and the sources terms σ_0 and σ_1, the general diagram of the two consecutive kinetics is represented in Figure 1.

Where σ_0 and σ_1 are densities operators per unit of volume and time, ρ_1 and ρ_2 are densities operators per unit of volume. $\mathcal{L}_1$, $\mathcal{L}'$ and $\mathcal{L}_2$ are super–operators per unit of time.

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Fig. 1. Kinetic scheme for triplet consecutive pairs densities operators.

Being given that the observations are done in stationary regime, we have:

$$\begin{cases} \frac{d\rho_1}{dt} = -\mathcal{L}_1\,\rho_1 + \sigma_0 = 0, \\ \frac{d\rho_2}{dt} = -\mathcal{L}_2\,\rho_2 + \sigma_1 = 0, \end{cases}$$

from where:

$$\begin{cases} \rho_1 = \mathcal{L}_1^{-1}\;\sigma_0, \\ \rho_2 = \mathcal{L}_2^{-1}\;\sigma_1, \end{cases}$$

and like $\mathcal{L}'$ represents the flow of ρ_1 and ρ_2 we have:

$$\sigma_1 = \mathcal{L}'\;\rho_1,$$

from where:

$$\rho_2 = \mathcal{L}_2^{-1}\;\mathcal{L}'\;\mathcal{L}_1^{-1}\;\sigma_0.$$

One can choose any base to represent super–operators $\mathcal{L}$, operators ρ and σ, but as two triplets give nine spin states we will take the base which makes diagonal S^2 and S_z. Given five quintuplet states (Q), three triplet states (T) and one singlet state (S).

By supposing that the triplets pairs disappear according to an independent channel of the spin or following channels with conservation of eigenvalues of S^2, we have:

$$\mathcal{L}_{u=1,\,2} = \mathcal{C}\left(\mathcal{H}_u\right) + \frac{1}{2}\sum_{j=I,S,T,Q} k_{u,\;j}\;\mathcal{A}\left(P_j\right),$$

where P_I, P_S, P_T and P_Q are the identity, the singlet, the triplet and the quintuplet weight operators. $\mathcal{C}$ is a commutator of operator expressed in frequencies and $\mathcal{A}$ is an anti–commutator of operator with no dimension.

The creation of pairs by fission is the fastest kinetics thus by taking into account that the pairs are only created from singlet state we will take $\sigma_0 \propto P_S$ represents by his norm a singlet weight per unit of volume and time while being represented by the operator P_S.

The $\mathcal{L}'$ super–operator represents the flow following the identity (I), the singlet (S), the triplet (T) and the quintuplet (Q) channels of the pair (1). We write then:

$$\mathcal{L}' = \frac{1}{2}\sum_{j=I,S,T,Q} k_j^{'}\;\mathcal{A}\left(P_j\right).$$

We have considered that the pairs spin static Hamiltonians $\mathcal{H}_{0,u}$ $(u = 1,\;2)$ are identical, we will note $\mathcal{H}_{0,1} = \mathcal{H}_{0,2} = \mathcal{H}_0$. By calling t_1 and t_2 the two triplet excitons of the u–pair, we write:

$$\mathcal{H}_{0,1} = \mathcal{H}_{0,2} = \mathcal{H}_{t_1} + \mathcal{H}_{t_2} + \mathcal{H}_{(t_1,\,t_2)}.$$

The contribution of the interaction term $\mathcal{H}_{(t_1,\,t_2)}$ to the spin part of the wave function is negligible [23], we consider then that the u–pair Hamiltonian is sum of spin Hamiltonians of the two triplet excitons. The two-triplet excitons spin Hamiltonians of the u–pair are such as:

$$\mathcal{H}_{t_1} = \mathcal{H}_{t_2} = \mathcal{H}_{ss} + \mathcal{H}_Z,$$

where $\mathcal{H}_{ss}$ is the dipole–dipole interaction Hamiltonian and $\mathcal{H}_Z = g\;\mu_B\;\overrightarrow{H}\cdot\overrightarrow{S}$ is the Zeeman Hamiltonian formally identical for the two triplets excitons of the u–pair by supposing that g is isotropic and independent of movement. In Sternlicht-McConnell model [24], $\mathcal{H}_{ss}$ can be considered as the arithmetic average of the spin Hamiltonians of the nonequivalent molecules of the crystal elementary lattice. For a crystal with two molecules (a) and (b) in the elementary lattice, one has [3,12]:

$$\mathcal{H}_{ss} = \frac{1}{2}\;\left[\vec{S}\;\left(\tilde{D}_a + \tilde{D}_b\right)\;\vec{S}\right] \equiv \vec{S}\;\tilde{D}^*\;\vec{S},$$

where $\tilde{D}^*$ is called zero-field splitting tensor (ZFS) of u– pair triplet exciton, $\tilde{D}_a$ and $\tilde{D}_b$ are the (a) and (b) nonequivalent molecules ZFS tensor and $\vec{S} = \vec{S}_{t_1} + \vec{S}_{t_2}$ the total spin of the u–pair two triplet excitons.

The spin Hamiltonian of the u–pair triplet exciton is written definitively in the form [12]:

$$\mathcal{H}_{t_1} = D^*\;\left(S_z^2 - \frac{1}{3}\;S^2\right) + E^*\;\left(S_x^2 - S_y^2\right) + g\;u_B\;\overrightarrow{H}\cdot\vec{S},$$

where D^* and E^* are the u–pair triplet ZFS constants in the crystal and $\left(\vec{X},\;\vec{Y},\;\vec{Z}\right)$ are the principal axes of the ZFS tensor $\tilde{D}^*$, i.e. the axes of a referential where $\mathcal{H}_{ss}$ is diagonal. The u–pair spin static Hamiltonian is then:

$$\mathcal{H}_0 = 2\mathcal{H}_{t_1} = 2D^*\;\left(S_z^2 - \frac{1}{3}\;S^2\right) + 2E^*\;\left(S_x^2 - S_y^2\right) + 2g\;u_B\;\overrightarrow{H}\cdot\vec{S}.$$

Based on this Hamiltonian we can obtain the eigenvalues and eigenvectors of the u–pair for a given magnetic field.

3 Matrix density formalism

The u–pair two triplets evolution can be described by a matrix density formalism obeying to the following equation:

$$\frac{\partial\rho_u}{\partial t} = -i\;\left[\mathcal{H},\rho_u\right] - k_{u,\;I}\;\rho_u - \frac{1}{2}\;k_{u,\;S}\;\left[P_S,\rho_u\right] + \Phi_u \qquad u = 1,2, \quad \text{(E 1)}$$

with $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}'$ where $\mathcal{H}_0$ is the u–pair spin static Hamiltonian and $\mathcal{H}' = g\;\mu_B\;H_1\;S_x\cos\left(\omega t\right)$ is the Hamiltonian associated to the microwave field with strength H_1 and frequency ω. $k_{u,\;I}$ and $k_{u,\;S}$ are the dissociation and the annihilation u–pair constants, $P_S = \left|S\right\rangle\left\langle S\right|$ is the singlet-states projection operator. The pairs sources terms are $\Phi_1 = \sigma_0$ for the pair (1) and $\Phi_2 = \sigma_1$ for the pair (2).

To solve the equation (E 1) we use the concept of super-operators defined by:

$$\begin{cases} \mathcal{C}\left(\mathcal{H}_0\right) = [\mathcal{H}_0,\ \rho_u] = \hat{\mathcal{H}}_0 \rho_u, \\ \mathcal{C}\left(S_x\right) = [S_x,\ \rho_u] = \hat{S}_x\ \rho_u, \\ \mathcal{A}\left(P_S\right) = [P_S,\ \rho_u]^+ = \hat{P}_S\ \rho_u, \end{cases}$$

with:

$$\begin{cases} \hat{\mathcal{H}}_0 = \mathcal{H}_0 \otimes \tilde{I} - I \otimes \tilde{\mathcal{H}}_0, \\ \hat{S}_x = S_x \otimes \tilde{I} - I \otimes \tilde{S}_x, \\ \hat{P}_S = P_S \otimes \tilde{I} + I \otimes \tilde{P}_S, \end{cases}$$

where $\hat{\mathcal{H}}_0$, $\hat{S}_x$ and $\hat{P}_S$ are the super-operators related to the commutators and anti–commutators that contain the operators $\mathcal{H}_0$, S_x and P_S in the equation (E 1) and $\tilde{\mathcal{H}}$, $\tilde{S}_x$ and $\tilde{P}_S$ are the transposed of the corresponding operators.

By using the preceding notations, equation (E 1) is then written in the form:

$$\frac{d\hat{\rho}_u}{dt} = -i\ \hat{\mathcal{H}}_0\ \hat{\rho}_u - k_{u,\ I}\ \hat{I}\ \hat{\rho}_u - \frac{1}{2}\ k_{u,\ S}\ \hat{P}_S\ \hat{\rho}_u + \alpha\, H_1\, \hat{S}_x\ \hat{\rho}_u\ \left(e^{i\omega\, t} + e^{-i\omega\, t}\right) + \hat{\Phi}_u; \quad u = 1, 2,$$

with $\alpha = -\frac{i}{2}\, g\, \mu_B$ and $\hat{I}$ is the super-operator associated to the identity operator. $\hat{\rho}_u$ and $\hat{S}_u$ designate the super-vectors corresponding to the vectors ρ_u and S_u.

In the continuation, we will omit the symbol "^" on the super-operators to simplify the expressions.

$\mathcal{L}_1$, $\mathcal{L}_2$ and $\mathcal{L}^{'}$ super-operators are written:

$$\begin{cases} \mathcal{L}_1 = i\mathcal{H}_0 + k_{1,\,I}\ I + \frac{1}{2}\ k_{1,\,S}\ P_S, \\ \mathcal{L}_2 = i\mathcal{H}_0 + k_{2,\ I}\ I + \frac{1}{2}\ k_{2,\ S}\ P_S, \\ \mathcal{L}^{'} = k_I^{'}\ I + \frac{1}{2}\ k_S^{'}\ P_S. \end{cases}$$

we obtain then:

$$\frac{d\rho_u}{dt} = -\mathcal{L}_u\ \rho_u - \alpha H_1 S_x\, \rho_u\ \left(e^{i\omega\, t} + e^{-i\omega\, t}\right) + \Phi_u \qquad u = 1, 2. \quad \text{(E 2)}$$

The resolution of this equation is done by considering that the solution is forced with the pulsation ω of the microwave field i.e. of the form:

$$\rho_u = \rho_u^{(0)} + \sum_{\ell=1} \left[\rho_u^{\prime(\ell)} \cos\left(\ell\omega t\right) + \rho_u{}^{"(\ell)} \sin\left(\ell\omega t\right)\right],$$

that we can write it too in the form:

$$\rho_u = \rho_u^{(0)} + \sum_{\ell=1} \left(Z_u^{(\ell)}\ e^{-i\ell\omega t} + \overline{Z}_u^{(\ell)}\ e^{i\ell\omega t}\right)$$

with:

$$Z_u^{\ \ell} = \frac{\rho_u^{\prime\,(\ell)} + i\rho''^{(\ell)}_u}{2}, \qquad \overline{Z}_u^{\ \ell} = \frac{\rho_u^{\prime\,(\ell)} - i\rho''^{(\ell)}_u}{2}.$$

The resolution details of equation (E 2) are presented in [22,25]. We obtain the following system:

$$\begin{cases} \mathcal{L}_u\ \rho_u^{(0,0)} = \Phi_u, \\ \tilde{\mathcal{L}}_u\ Z_u^{(1,1)} = \alpha\, S_x\, \rho_u^{(0,0)}, \\ \mathcal{L}_u\ \rho_u^{(0,2)} = \alpha\, S_x\ \left(Z_u^{(1,1)} + \bar{Z}_u^{(1,1)}\right), \end{cases} \qquad \text{(E 3)}$$

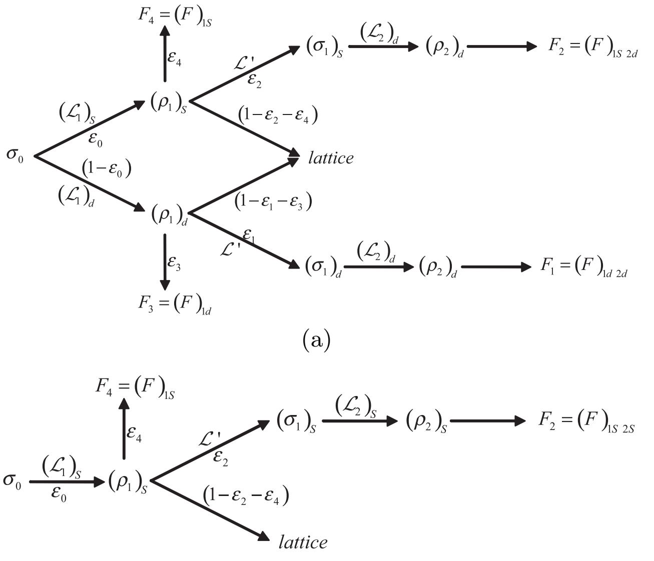


Fig. 2. (a): General Fluorescence diagram used to interpret the F-ODMR spectra. (b) Fluorescence diagram used to interpret the MFE spectrum

with $\tilde{\mathcal{L}}_u = \mathcal{L}_u - i\,\omega\, I$ and $u = 1, 2$. We solve this system for each $u-$pair by taking into account the fact that $\Phi_1 = \sigma_0 = P_S$ and $\Phi_2 = \sigma_1 = \mathcal{L}^{'}\rho_1$.

4 General diagram of fluorescence

The calculus of the relative variation of the fluorescence under the microwave field effect is obtained from the general diagram of Figure 2a where $(\mathcal{L}_1)_S$ characterizes the channel where the pair (1) does not undergo the action of the microwave field and $(\mathcal{L}_1)_d$ the channel where the pair (1) undergoes the action of the microwave field. The radiative proportions ε_i are positive numbers with no dimensions inferior or equal to the unit, they characterize the various contributions to the measured total fluorescence F so that:

$$F = \varepsilon_0 \varepsilon_2\, (F)_{1S\ 2d} + (1-\varepsilon_0)\, \varepsilon_1\ (F)_{1d\, 2d} + (1-\varepsilon_0)\, \varepsilon_3\ (F)_{1d} + \varepsilon_0 \varepsilon_4\ (F)_{1S}$$

In the F-ODMR experiments, we observe the quantity:

$$\left(\frac{\Delta F}{F}\right)_{F-ODMR} = \frac{\left[F\left(\overrightarrow{H} + \overrightarrow{H_1}\right) - F\left(\overrightarrow{H}\right)\right]}{F\left(\overrightarrow{H}\right)},$$

where $\overrightarrow{H}$ is the static field and $\overrightarrow{H_1}$ is the microwave field.

The relative variation of the total fluorescence under the microwave field effect for the fission process is obtained from [12,25]:

$$\left(\frac{\Delta F}{F}\right)_{F-ODMR} = \frac{tr\left(P_S\ \rho_{F-ODMR}^{(0,2)}\right)}{tr\left(P_S\ \rho_{F-ODMR}^{(0,0)}\right)}\, H_1^2$$

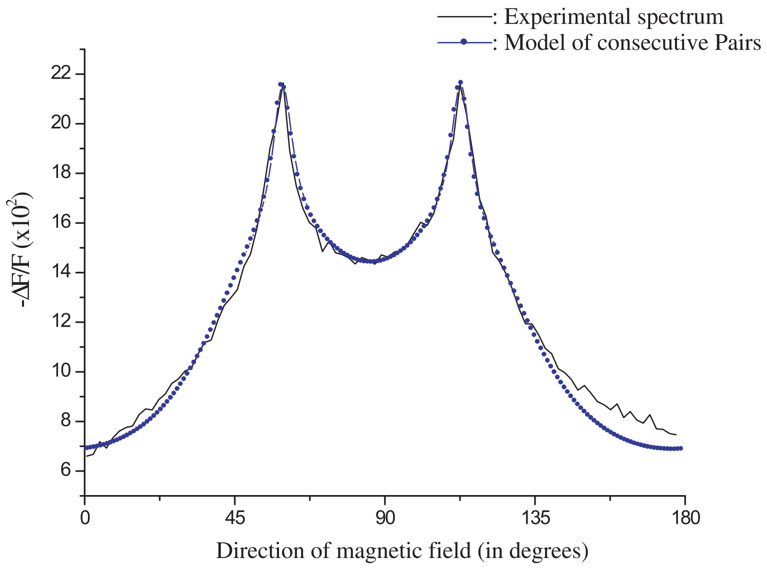


Fig. 3. The best fit obtained with the two consecutive pairs model and the MFE experimental spectrum of the prompt fluorescence variation as a function of the direction of a high magnetic field ($H = 6 \times 10^3$ Gauss) in the a-b plan of crystalline tetracene.

where:

$$\rho^{(0,2)}_{F-ODMR} = \varepsilon_0\varepsilon_2\rho^{(0,2)}_{1S\;2d} + (1-\varepsilon_0)\,\varepsilon_1\,\rho^{(0,2)}_{1d\,2d} + (1-\varepsilon_0)\,\varepsilon_3\,\rho^{(0,2)}_{1d} + \varepsilon_0\varepsilon_4\rho^{(0,2)}_{1S}$$

and:

$$\rho^{(0,0)}_{F-ODMR} = \varepsilon_0\varepsilon_2\rho^{(0,0)}_{1S\;2d} + (1-\varepsilon_0)\,\varepsilon_1\,\rho^{(0,0)}_{1d\,2d} + (1-\varepsilon_0)\,\varepsilon_3\,\rho^{(0,0)}_{1d} + +\varepsilon_0\varepsilon_4\rho^{(0,0)}_{1S}.$$

For MFE experiments, the preceding diagram is reduced to the diagram of Figure 2b.

In the case of experiments MFE we observe the quantity:

$$\left(\frac{\Delta F}{F}\right)_{MFE} = \frac{\left[F\left(\overrightarrow{H}\right) - F\left(\overrightarrow{H} = \overrightarrow{0}\right)\right]}{F\left(\overrightarrow{H} = \overrightarrow{0}\right)},$$

so that the measured static effect is:

$$F = \varepsilon_0\varepsilon_2\,(F)_{1S\;2S} + \varepsilon_0\varepsilon_4\,(F)_{1S}\;,$$

and its relative variation is obtained from [12,25]:

$$\left(\frac{\Delta F}{F}\right)_{MFE} = \frac{tr\left(P_S\,\rho^{(0,0)}_{MFE}\left(\overrightarrow{H}\right)\right)}{tr\left(P_S\,\rho^{(0,0)}_{MFE}\left(\overrightarrow{0}\right)\right)} - 1.$$

where:

$$\rho^{(0,0)}_{MFE}\left(\overrightarrow{H}\right) = \varepsilon_0\varepsilon_2\rho^{(0,0)}_{1S\;2S}\left(\overrightarrow{H}\right) + \varepsilon_0\varepsilon_4\,\rho^{(0,0)}_{1S}\left(\overrightarrow{H}\right)$$

and:

$$\rho^{(0,0)}_{MFE}\left(\overrightarrow{H} = \overrightarrow{0}\right) = \varepsilon_0\,\varepsilon_2.\rho^{(0,0)}_{1S\;2S}\left(\overrightarrow{H} = \overrightarrow{0}\right) + \varepsilon_0\,\varepsilon_4\,\rho^{(0,0)}_{1S}\left(\overrightarrow{H} = \overrightarrow{0}\right)$$

Table 1a. Zero-field splitting (ZFS) constants of the $u-$pair triplet exciton in tetracene ($u = 1$, 2).

D^* (cm^{-1})	E^* (cm^{-1})
−0.00703	0.0241

Table 1b. Director cosines of the $u-$pair triplet exciton ZFS axes ($u = 1$, 2).

	a	b	c
X	0.9636	0.0291	0.2657
Y	0.2645	0.2475	0.9320
Z	0.0386	0.9684	0.2462

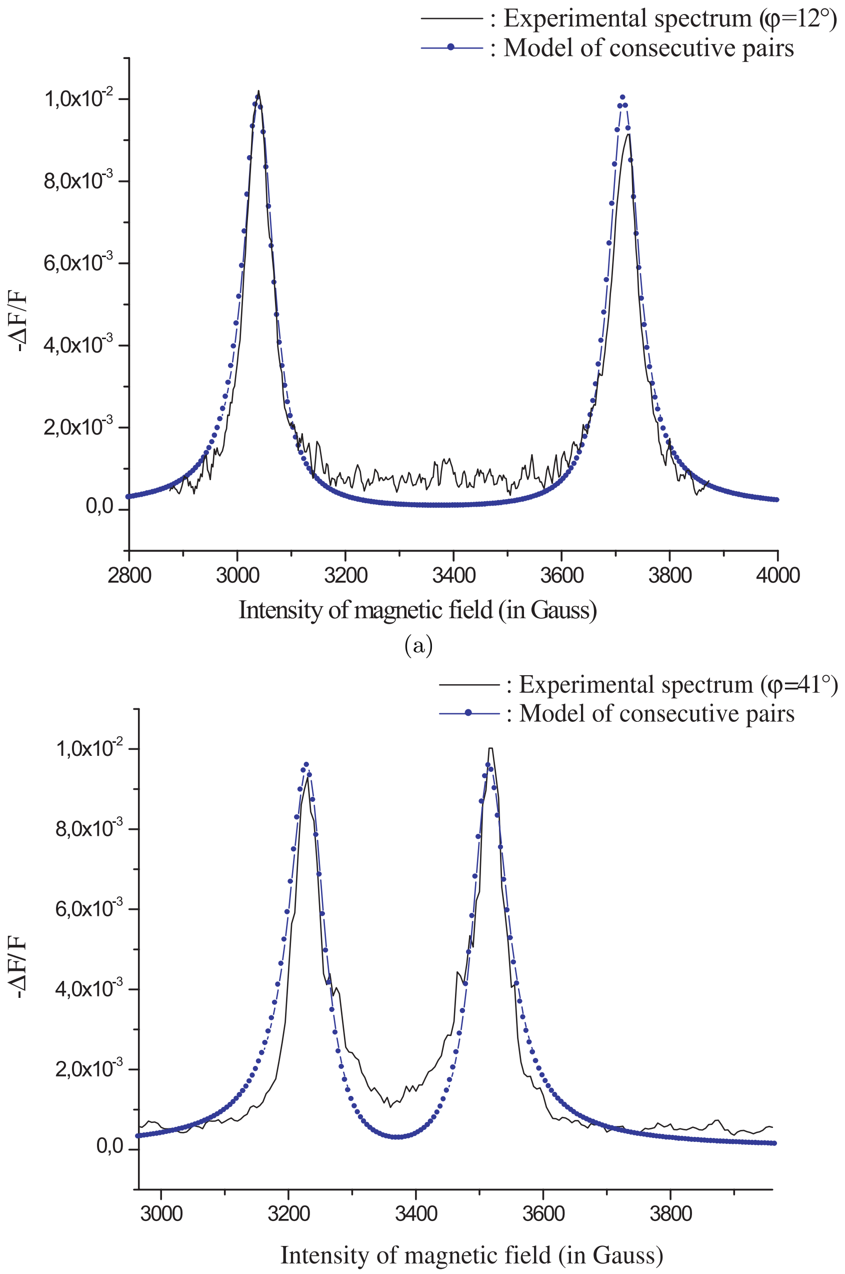
The elements $\rho^{(0,0)}$ and $\rho^{(0,2)}$ corresponding to the various channels that contribute to the total fluorescence F, $(F)_{MFE}$ or $(F)_{F-ODMR}$, are calculated by using the system equations (E 3).

5 Results and discussion

We have applied this model to account for the experimental results related to the fluorescence modulation by a static magnetic field called MFE, and those by a microwave field called F-ODMR in the crystalline tetracene.

We have used, to carry out calculations, the crystallographic data relating to tetracene [26–29] as well as the triplet excitons ZFS parameters and tensor [19] (Tabs. 1a and 1b). $k_I^{'}$ and $k_S^{'}$ constants were selected of the same order of magnitude as the sources terms of the reference [12].

In Figures 3 and 4, we have represented the best fit obtained with this consecutive pairs model and our experimental results presented in [22]. MFE experiments (Fig. 3) represent the variation of fluorescence as a function of the



(b)

Fig. 4. The best fit obtained with the two consecutive pairs model and the F-ODMR spectra obtained for two directions of the magnetic field in *a*-*b* plan of crystalline tetracene. (a) for $\varphi = 12°$. (b) for $\varphi = 41°$.

direction of a high magnetic field ($H = 6000$ Gauss) in the tetracene crystal a-b plan. Figures 4a and 4b represent the F-ODMR lines for two directions of the magnetic field in the crystal *a*-*b* plan far from the static "resonances" directions [12].

On Table 2, we have presented various values of the kinetics constants that give the best fit between the experimental observations and the used model.

Table 2. The kinetics constants, relating to the two consecutive pairs (1) and (2), used to obtain the best fit with MFE and F-ODMR experiments.

$k_{1,\ I}$ (s^{-1})	$k_{1,\ S}$ (s^{-1})	$k_{2,\ I}$ (s^{-1})	$k_{2,\ S}$ (s^{-1})
10^9	0.68×10^9	0.9×10^8	0.6×10^8

We have been able to give suitably an account for the spectra giving the fluorescence variation as a function of the magnetic field direction (MFE) as well as the F-ODMR spectra by using the same set of kinetics constants $k_{u,\ I}$ and $k_{u,\ S}$ while exploiting the radiative proportions ε_i (the various contributions) presented on Table 3.

Table 3. Radiative proportions, relating to the various contributions, used to obtain the best fit with MFE and F-ODMR experiments.

ε_0	ε_1	ε_2	ε_3	ε_4
0.5	0.2	0.2	0.8	0.8

The $u-$pair lifetime is proportional to $1/k_{u,\ I}$ [21]. The pair (1) lifetime is about 10^{-9} s, the pair (2) has a lifetime about $1,1 \times 10^{-8}$ s. We call the "short pair" pair (1) and the "long pair" pair (2) by references to their respective lifetimes.

From these results, we have noted that the MFE spectrum corresponding to the prompt fluorescence modulation of the tetracene comes mainly ($\approx 80\%$) from singlet excitons fission, who are present in the crystal excited volume ($\propto \sigma_0$), in triplet exciton pairs known as short pairs. However, we know that prompt fluorescence is proportional to the number of singlet excitons present in the crystal excited volume $F \propto N_S$ [12], and that its modulation comes only from the modulation, by a magnetic field, of the triplet-triplet pairs spin states which we called in this work short pairs. Therefore, we can consider that $\sim 80\%$ of the singlets will give, by fission, short pairs who are responsible for the partial fluorescence F_4 and that the 20% will serve as sources to generate other triplet exciton pairs known as long pairs according to the diagram of Figure 2b.

In the case of F-ODMR experiments, we have noticed that partial fluorescence F_1 and F_2 coming from ($1d$ $2d$) and ($1S$ $2d$) channels (Fig. 2a) are equivalent and that those coming from ($1d$) and ($1S$) channels, i.e. F_3 and F_4, are 10^{-2} weaker than F_1 and F_2. This is explained by the fact that the pair (1) has a rather short lifetime and consequently the microwave field cannot induce transitions between the short pair sub-levels, consequently the microwave does not have practically an effect on the short pair. This result explains also the equivalence between ($1d$ $2d$) and ($1S$ $2d$) channels.

By applying the consecutive pairs concept to the Seventies kinetic model we have arrived to rise the inconsistencies which one reproached to this model which will remain always very effective with regard to its simple formulation and the results provided by this model.

6 Conclusion

Finally, we can note the effectiveness of this consecutive pairs model since it enables us to reproduce rather perfectly at the same time the MFE lines shape as well as the F-ODMR lines shape with the same set of kinetics constants. However, with the Seventies kinetic model, we cannot reproduce the two kind of experiments with the same set of kinetics constants and we always obtain Lorentzian lines form for MFE experiments what does not make it possible to reproduce rather perfectly the shape of these lines.

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