Manifestation of T-Exciton Migration in the Kinetics of Singlet Fission in Organic Semiconductors

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Kinetics of singlet fission in organic semiconductors, in which the excited singlet state ($S_1$) spontaneously splits into a pair of triplet (T) excitons, is known to be strongly influenced by back geminate annihilation of TT-pairs. We show that this influence can be properly described only by taking into account the diffusive exciton migration. The migration effect is treated in the model of two kinetically coupled states: the intermediate state of interacting TT-pairs and the state of migrating excitons. Within this model the singlet fission (including magnetic field effects) is studied as applied to the fluorescence decay kinetics (FDK) $I_{S_1}(t)$ for $S_1$-state. The analysis shows that migration strongly affects the FDK resulting, in particular, in the universal long-time dependence $I_{S_1}(t) \sim t^{-3/2}$. The model accurately describes the FDK, recently observed for a number of systems. Possible applications of the considered model to the analysis of mechanisms of migration, using experimentally measured FDK, are briefly discussed.

I. INTRODUCTION

Singlet fission, i.e. spontaneous splitting of the optically excited singlet state $S_0$ into a pair of triplet (T) excitons (TT-pair), is the important photophysical process, playing the key role in many phenomena, which significantly control photovoltaic and spintronic properties of organic semiconductors, important for applications [1–3]. Intensive experimental investigations of fission kinetics inspired considerable theoretical studies of this process [1, 2, 4–11].

Specific features of singlet fission are usually analyzed within the model represented by the kinetic scheme

$$S_0 + S_0 \xrightarrow{k_r} (S_0 + S_1) \xrightarrow{k_{\text{TT}}} [\text{TT}] \xrightarrow{k_e} [\text{T+T}],$$

(1)

in which all stages are conventionally treated as first order reactions. The primary stage of the fission process is the transition (with the rate $k_r$) from the initially excited states (S0 + S1) into the intermediate [TT]-state of coupled T-excitons (called also as e-state). Evolution of [TT]-state is determined by geminate T-exciton annihilation, dissociation into a pair of separate T-excitons, denoted as [T+T]-state (or e-state), and back (geminate) capture into [TT]-state with rates $K_s$, $k_e$ and $k_{\text{TT}}$, respectively. Note, that TT-annihilation is a spin-selective process (with the rate $K_s$), depends on the total TT-spin $S = S_o + S_0$ [eq. (4)], which leads to the dependence of singlet fission kinetics on the magnetic field $B$ (see below).

The fission process is accompanied by deactivation of $S_1$-state with the total rate $k_r$, resulting from radiative and non-radiative transitions with rates $k_r$ and $k'_{r}$, respectively, (i.e. $k_r = k_r + k'_{r}$). The observable under study is usually the normalized fluorescence decay kinetics (FDK) $I_{S_1}(t)/I_{S_1}(0)$ from $S_1$-state, determined by the $S_1$-state population $p_S(t)$ [for which $p_S(0) = 1$]: $I_{S_1}(t) = \kappa_r p_s(t)$, so that $I_{S_1}(t) = I_{S_1}(t)/I_{S_1}(0) = p_s(t)$. In accordance with this formula the characteristic features of singlet fission kinetics are analyzed by comparison of the experimental FDK $I_{S_1}(t)$ with the theoretically calculated dependence $p_s(t)$.

Detailed theoretical investigation of fission kinetics is performed in a large number of papers [1, 2, 4–11]. Note, however, that significant part of theoretical works concern the analysis of the first stage of the process and, in particular, the accurate evaluation of the rate of singlet splitting $(S_0 + S_1) \xrightarrow{k_r} [\text{TT}]$. As for later stages (essentially controlled by geminate/spin/space evolution of TT-pair) they are studied thoroughly as well, though results of the studies are typically represented in fairly complicated mathematical form not quite suitable for describing experiments. For this reason the majority of experimental results are treated within the above-discussed simplified model [1, 2, 5, 12].

Recent investigations [13–16] show, however, that the simplified model (of first order processes) is not able to properly describe important specific features of the FDK $I_{S_1}(t)$, observed in some organic semiconductors, in particular, the long time behavior of the FDK, which is found to be close to the inverse-power type one.

In this work the generalized model is proposed, which allows for accurate description of the effect of three-dimensional diffusive migration of T-excitons (in [T+T]-state) on the FDK. The model is shown to significantly improve the agreement between theoretical and experimental FDK, especially at long times. Good accuracy and potentials of this model are demonstrated by analyzing the above-mentioned FDK $I_{S_1}(t)$, measured for a number of organic semiconductors [13–16].

II. MODEL OF SINGLET FISSION

To describe the important specific features of the FDK we propose the generalized model of singlet fission [1]. In the model the first stage $S_0 + S_1 \xrightarrow{\text{TT}} [\text{TT}]$ is treated as a
conventional first order process. As to the second stage \([TT] \rightarrow [T+T]\), it is described within the two-state approach \([17-19]\), developed earlier to analyze the diffusive escape of a particle from a potential well (intermediate state). In this approach the spatial evolution of geminate TT-pairs is treated as transitions between two states: (intermediate) \([TT]\)-state of coupled T-excitons and \([T+T]\)-state of separated T-excitons, undergoing isotropic three-dimensional diffusive migration.

The population \(p_j(t)\) of \(S_j\)-state is controlled by the spin/space evolution of TT-pairs in \([TT]\)- and \([T+T]\)-states, described by the spin matrix \(\sigma(t)\) and spin density matrix \(\rho(r,t)\), respectively (here \(r\) is the interexciton distance). These matrices satisfy the stochastic Liouville equation \([20]\), which in the two-state approach is written in the form of three coupled equations

\[
\dot{\rho}_s = -(k_s + k_r)\rho_s + \text{Tr}[\mathcal{P}_s(\tilde{\mathcal{K}}_s\sigma)] \quad (2a)
\]

\[
\dot{\sigma} = S_l^{-1}K_s\rho_l - (\tilde{\mathcal{L}}_c + \tilde{\mathcal{K}}_s + \mathcal{K}_s)\sigma + k_s\mathcal{P}_s\rho_s \quad (2b)
\]

\[
\dot{\rho} = (D\nabla^2 - \tilde{\mathcal{L}}_c\rho) + (S_l\mathcal{K}_s - \mathcal{K}_s\rho_l)\delta(r-l) \quad (2c)
\]

where \(S_l = (4\pi^2)^{-1}\), \(D\) is the coefficient of relative diffusion of excitons, \(\nabla^2 = r^{-2}\partial_r(r^2\partial_r)\) is the radial part of the Laplace operator, and \(\rho_l(t) = \rho(l,t)\).

The terms proportional to rates \(K_s\) represent the above-mentioned transitions between the intermediate \([TT]\)-state (c-state) and \([T+T]\)-state (e-state) of freely diffusing T-excitons. Values of \(K_s\) satisfy the detail balance relation \([14]\). In our work we will consider the realistic limit of fast spatial relaxation of TT-pairs in \([TT]\)-state, in which this relation is represented as \([19]\).

\[
\mathcal{K}_s \rightarrow \infty \quad \text{and} \quad \mathcal{K}_e/\mathcal{K}_s = \lambda_e = Z_w/\lambda_s, \quad (3)
\]

where \(Z_w = \int_{r=0}^{\infty} dr r^2 e^{-U(r)/(k_BT)}\) is the partition function for \([TT]\)-state in the well \(U(r)\) and \(l\) is the radius of the state. The parameter \(\lambda_e\) controls effects of \([TT]\)- and \([T+T]\)-states on the FDK: for significant TT-coupling in \([TT]\)-state, when \(\lambda_e = \sqrt{l}\lambda_s < 1 \quad \text{[eq. \(13\)]}\), strong \([TT]\)-effect and weak \([T+T]\)-effect (T-migration effect) is predicted. In the case of weak coupling (\(\lambda_e > 1\)), on the contrary, small \([TT]\)- and marked \([T+T]\)-effects are expected (see Sec. 4.1).

In eqs \((2a)-(2c)\) the terms

\[
k_s\mathcal{P}_s\rho_s \quad \text{and} \quad \tilde{\mathcal{K}}_s\sigma = (1/2)k_s(\mathcal{P}_s\sigma + \sigma\mathcal{P}_s), \quad (4)
\]

with the projection operator \(\mathcal{P}_s = |S\rangle\langle S|\) onto the singlet \((S)\)-state of TT-pair, describe the spin-selective TT-pair generation (resulting from the decay of \(S_j\)-state with the rate \(k_s\)) and annihilation (with the rate \(k_r\)) \([4, 20]\), respectively. Operators \(\tilde{\mathcal{L}}_c\) and \(\tilde{\mathcal{K}}_s\), defined as \((\hbar = 1)\)

\[
\tilde{\mathcal{L}}_c = \mathcal{W}_c + i(H_c\rho - \rho H_c), \quad (\nu = c, e), \quad (5)
\]

for any spin matrix \(\rho\), control the spin evolution in \([TT]\)- and \([T+T]\)-states, respectively. In formula \((5)\) \(\mathcal{W}_c\) is the operator of spin relaxation in \(\nu\)-state of TT-pair (its explicit form is specified below), and

\[
H_\nu = g\beta B(S^2_\nu + S^2_\nu) + H^a_{Tr} + H^b_{Tr}, \quad (6)
\]

is the spin Hamiltonian of the TT-pair in the magnetic field \(B\) (directed along the axis z), in which the first term describes the Zeeman interaction of spins with the field \(B\) and \(H^2_{Tr}\) is the zero-field-splitting interaction (ZFSI) in exciton \(\mu, (\mu = a, b)\), in the state \(\nu, (\nu = c, e)\).

For example, in \(c\)-state \(H^a_{Tr} \equiv H^a_{Tr}((\mu = a, b), with)

\[
H^a_{Tr} = D_\mu[(S^2_\mu)^2 - S^2_\mu/3] + E_\mu[(S^2_\mu)^2 - (S^\nu_\mu)^2]. \quad (7)
\]

Here \(S^\nu_\mu\) is the projection of the spin of the exciton \(\mu\) along the eigenaxis \(j_\mu\), \((j_\mu = x_\mu, y_\mu, z_\mu)\), of the ZFSI-tensor of T-exciton in c-state \([4, 20]\).

As for the ZFSI \(H^a_{Tr}\) in e-state, its precise form depends on the process under study. In our work we will consider two most interesting and experimentally investigated \([13, 16]\) types of them, for which the form of \(H^a_{Tr}\) can easily be obtained:

(1) Singlet fission in amorphous solids, in which in e-state T-excitons undergo fast hopping over chaotically oriented molecules, resulting in the average of the ZFSI (i.e. \(H^a_{Tr} = 0\)), and in fast spin relaxation (see below);

(2) Singlet fission in (molecular) crystals, for which \(H^a_{Tr} = H_{Tr} = H_T\).

The TT-spin evolution, governed by spin-Hamiltonians \(H_{Tr}\), is described with the complete basis of 9 spin states, represented as products \(|j_\mu j_\nu\rangle = |j_\mu\rangle|j_\nu\rangle\) of those \(|j_\mu\rangle\), \((j_\mu = 1 - 3)\), for T-excitons. Hereafter it is convenient to use the eigenstates of the Zeeman Hamiltonian \(|j_\mu = 0, \pm\rangle\) (defined as \(S_{j_\mu} = j_{x_\mu}, y_{x_\mu}, z_{x_\mu}\)) or those of the ZFSI \([7]\) \(|j_\mu = x_\mu, y_\mu, z_\mu\rangle\) (defined by \(S_{j_\mu} = j_{x_\mu}\)) \([4]\). In particular, within these two bases \(|S\rangle\)-state of TT-pair is represented as \([4]\)

\[
|S\rangle = \frac{1}{\sqrt{3}}|00\rangle - |+-\rangle - |-+\rangle = \frac{1}{\sqrt{3}} \sum_{j=x,y,z} |jj\rangle. \quad (8)
\]

The kinetic scheme \([11]\) implies the initial condition for eqs \((2a)-(2c)\)

\[
p_s(t = 0) = 1 \quad \text{and} \quad \sigma(t = 0) = \rho(t = 0) = 0. \quad (9)
\]

These equations should be solved with the reflective boundary condition for \(\rho(r,t)\) at \(r = l: \partial_r\rho|_{r=l} = 0\).

The solution can be obtained by the Laplace transformation in time, defined for any function \(\varphi(t)\) as \(\tilde{\varphi}(\epsilon) = \int_0^\infty dt \varphi(t) e^{-\epsilon t}\) and \(\varphi(t) = (2\pi i)^{-1} \int_{c-i\infty}^{c+i\infty} d\tilde{\epsilon} e^{\tilde{\epsilon} t} \tilde{\varphi}(\tilde{\epsilon})\) \([13, 19]\). In particular, for \(\tilde{p}_s(\epsilon)\) we get the expression

\[
\tilde{p}_s(\epsilon) = \left\{\epsilon + k_{rs} - k_{rs} \text{Tr}[\mathcal{P}_s\tilde{\mathcal{K}}_s \tilde{\mathcal{G}}(\epsilon)\mathcal{P}_s]\right\}^{-1}. \quad (10)
\]

Here \(\mathcal{P}_s\) is the projection operator, \(k_{rs} = k_r + k_s\), with \(k_r = \kappa_c + \kappa_c\), and

\[
\tilde{\mathcal{G}}(\epsilon) = [\epsilon + \tilde{\mathcal{L}}_c + \tilde{\mathcal{K}}_s + \tilde{\mathcal{K}}_s(\epsilon)]^{-1}. \quad (11)
\]
is the Laplace transform of the evolution function of \([\text{TT}]-\) state, decaying with the effective escape rate

\[
\tilde{K}\epsilon(\epsilon) = k_e + \tilde{k}_e \quad \text{with} \quad \tilde{k}_e = \xi [k_e (\epsilon + \tilde{\epsilon}_e)]^{1/2},
\]  
(12)

in which

\[
k_e = D_t / Z_w \quad \text{and} \quad \xi_e = \sqrt{2 k_e / D}.
\]  
(13)

It is worth noting that the rate \(\tilde{K}\epsilon(\epsilon)\) essentially determines the kinetics of diffusion assisted TT-annihilation \([17,19]\) and, thus, the FDK. Of special importance is the second \(\epsilon\)-dependent (non-analytic) term \(\tilde{k}_e\), which is responsible for the non-exponential behavior of the annihilation kinetics at intermediate and long times. Of course, specific features of this behavior are affected by spin evolution of TT-pair, though mainly at times smaller than spin relaxation times. Below we will analyze spin effects in two important limits of fast and slow spin relaxation (Sects. IV.A. and IV.B.). Here we only note that \(\tilde{k}_e\) increases with the increase of \(\xi_e\) \([\text{eq. (12)}]\), and for \(\xi_e > 1\) the T-migration effect on the FDK is expected to be very strong (see below).

Calculation of \(\tilde{p}_s(\epsilon)\) with eq. \([19]\) is a fairly complicated problem which, however, can be simplified in the Johnson-Merrifield approximation (JMA) \([2,2]\).

## III. JOHNSON-MERRIFIELD APPROXIMATION

The JMA allows one to reduce cumbersome operations with elements of TT-spin density matrices to those with state populations only, i.e. diagonal matrix elements in the basis of eigenstates of the Hamiltonian \(H_e\) \([20]\) (as discussed above). The weak effect of non-diagonal elements \([\text{for } ||H_e||/k_{a,e} \gg 1 \quad [21]\) results from their fast oscillations.

To present JMA-results conveniently we introduce the additional notation. Recall, that for any spin system with \(N\) states \(\langle j a b \rangle = |j a\rangle |j b\rangle\) eqs \([21b, 23]\) and \(24\) are systems of \(N^2\) coupled equations for elements of density matrices \(\sigma\) and \(\rho\), i.e. components of vectors in the basis of ”states” \(|j a b\rangle\) in the Liouville space \([22]\). In the JMA these systems reduce to those of \(N\) equations for components ”along” population eigenvectors

\[
\|j a b\rangle \equiv |j a b\rangle |j a b|, \quad (14)
\]
corresponding to diagonal elements of density matrices.

With this notation, the JMA-formula for \(\tilde{p}_s(\epsilon)\) is given by

\[
\tilde{p}_s(\epsilon) = \left[ \epsilon + k_{rs} - N k_e (\langle e \| \tilde{K}\epsilon \tilde{G}(\epsilon) \tilde{P}_e \| \epsilon \rangle) \right]^{-1}.
\]  
(15)

Here \(k_{rs} = k_r + k_s\), \(N\) is the number of spin states of TT-pair \((N = 9)\), and

\[
\|e\rangle = N^{-1} \sum_{j ab} \|j a b\rangle \quad \text{and} \quad \langle e \| = \sum_{j ab} \langle j a b \|
\]  
(16)

are the normalized equilibrium state vector and the corresponding adjoined one \(\langle \langle e \| \rangle \rangle = 1\), and

\[
\tilde{K}_e = k_e \tilde{P}_e, \quad \text{with} \quad \tilde{P}_e = \sum_{j a b} C_{j a b}^S \|j a b\rangle \langle j a b \|
\]  
(17)

is the annihilation rate matrix, proportional to the matrix \(\tilde{P}_s\) of \((B\)-dependent\) weights \(C_{j a b}^S = |\langle S |j a b\rangle|^2\) of \(S\)-state in states \(|j a b\rangle\) of the TT-pair (satisfying the normalization condition \(\sum_{j a b} C_{j a b}^S = 1\)),

\[
\tilde{G}(\epsilon) = \left\{ \epsilon + k_e + \tilde{K}_e + \tilde{W}_c + \xi_e [k_e (\epsilon + \tilde{\epsilon}_e)]^{1/2} \right\}^{-1}
\]  
(18)

is the evolution function for combined \((\epsilon,\tilde{\epsilon})\)-state, in which \(\tilde{W}_c\) are matrices of spin-lattice relaxation for TT-pairs in states \(\nu = c, \tilde{c}\). In our further analysis we will use matrices \(\tilde{W}_c\) in a simplified analytical form:

\[
\tilde{W}_c = w_c (B) \tilde{Q} \quad \text{with} \quad \tilde{Q} = \tilde{E} - \| e \| \langle e \|
\]  
(19)

In this expression \(\tilde{Q}\) is the projection operator \(\tilde{Q}^2 = \tilde{Q}\) with \(\tilde{E} = \sum_{j ab} \|j a b\rangle \langle j a b \|\). The form \([19]\) is sufficient for semi-quantitative treatment of the FDK (see below). Noteworthy is that for small \(\epsilon < w_c\) describing the FDK at long times \(t < w_c^{-1}\), the effect of the relaxation \([19]\) is described by the effective relaxation operator \(\tilde{W}_e = \tilde{W}_c + \xi_e (k_e \tilde{W}_e)^{1/2}\); also represented in the form \([19]\)

\[
\tilde{W}_e = w_c \tilde{Q}, \quad \text{where} \quad w_c = w_c + \xi_e \sqrt{k_e w_c}.
\]  
(20)

In the model \([19]\) formula for \(\tilde{p}_s(\epsilon)\) is very complicated in general. In some systems, however, the FDK at \(B = 0\) and \(B \gg B_s = ||H^2_T||/(g^3)\) can conveniently be analyzed within the simple model of \(n_r\) reactive states, denoted as \(|j_r\rangle\), which turn out to be equivalent and equally contributing to \(p_s(t)\). Similarly equivalent are also \(n_n = N - n_r\) nonreactive states \(|j_n\rangle\). These equivalences enable one to reduce the problem of \(N\) coupled states to that of the pair of states

\[
\| e_\alpha \rangle = n_{a_1}^{n_{a_2}} \langle j_{a_1} \| j_{a_2} \rangle, \quad \| e_\alpha \| = \sum_{j_{a_1} j_{a_2}} \langle j_{a_1} \| j_{a_2} \rangle, \quad (21)
\]

where \(a = r, n\).

In the basis \([21]\) matrices \(\tilde{W}_\nu\) and \(\tilde{K}_s\) are written as

\[
\tilde{W}_\nu = w_\nu \left( \tilde{P}_r - \tilde{P}_n \right) + \xi_n (\tilde{P}_n - \tilde{P}_r) = \sum_{\alpha \alpha'} C_{\alpha \alpha'} \langle e_\alpha \| e_{\alpha'} \rangle, \quad (22)
\]

and \(\xi_n = 1 - n_\alpha / N\) \((a = r, n)\). Within this approach of two effective states general formula \([17]\) reduces to a fairly simple analytical one:

\[
\tilde{p}_s(\epsilon) = \left[ \epsilon + k_{rs} - \frac{(k_{r_\alpha} \kappa_n) \gamma_\alpha(\epsilon)}{1 - \kappa_n \gamma_\alpha(\epsilon)} \right]^{-1},
\]  
(24)

where \(k_{rs} = k_r + k_s\). \(\kappa_n = k_s / n_s\), and

\[
\gamma_\alpha(\epsilon) = \frac{w_c + \xi_n (\sqrt{k_e (\epsilon + w_c)} - \sqrt{k_e \epsilon})}{\sqrt{k_e (\epsilon + w_c)}},
\]  
(25)

\[
g_\alpha(\epsilon) = \left[ \epsilon + k_{rs} + k_e + \kappa_n \gamma_\alpha + \kappa_n \xi_n \sqrt{k_e \epsilon} \right]^{-1},
\]  
(26)
with \( \alpha = r, n \); and \( \kappa_r = \kappa_n = \kappa_s = 0 \).

Noteworthy is that any additional relaxation within sets of reactive \( \langle |j_{rb}\rangle \rangle \) and/or non-reactive \( \langle |j_{sb}\rangle \rangle \) states, separately, does not affect \( p_s(t) \) because of equi-population of states in these sets. This means that the FDK \( p_s(t) \) is essentially determined by relaxation transitions between states of different sets, rates of which can be different for small and large \( B (w_{r}^0 \text{ and } \bar{w}_r) \) (Sec. IV.A).

Formulas \( 14-20 \) are suitable for analyzing the T-exciton migration effect on the FDK. The analysis requires specification of parameters of the model \( 21-20 \), which are essentially determined by the magnetic field \( B \). In our further analysis, for brevity, we will discuss the FDK for \( B = 0 \) and \( B \gg B_s = \|H^s_{2}/(g\beta) \) only.

IV. RESULTS AND DISCUSSION

A. FDK in amorphous organic semiconductors

In the proposed model \( 15 \) specific features of the FDK in amorphous semiconductors result, essentially, from strong disorder of molecule orientations, i.e. orientations of ZFSI eigenaxes.

1. FDK in the absence of magnetic field \( (B = 0) \). In the JMA the orientational distribution of excitons manifests itself in the spread of TT-annihilation rates \( K_{s/jab} = \langle j_{ab}|\bar{K}_s|j_{ab}\rangle \) in c-state \( (\{TT\}) \) with the same distribution function for all states \( \langle |j_{ab}\rangle \rangle, (j = x, y, z) \), i.e. the same mean value \( \langle K_s \rangle = \langle K_{s/jab} \rangle = k_s \langle C^2_{jab} \rangle \) (where \( \langle C^2_{jab} \rangle = (1/3)\langle \cos^2 \theta_{jab}\rangle \theta_{jab} = 1/9 \) is the average over the angle \( \theta_{jab} \) between axes \( j_a \) and \( j_b \)) and dispersion \( \Delta K_s = \sqrt{\langle K_s^2 \rangle - \langle K_s \rangle^2} \approx 0.1 k_s \).

In general, the spread of rates \( K_{s/jab} \) significantly complicates the evaluation of the FDK. Fortunately, in many amorphous semiconductors spin relaxation rates \( w_r (B = 0) = w^0_r, (\nu = c, e) \), are expected to be fairly large (Sec. IV.A.2), resulting in large \( w_r \) [see eq. \( 21 \)]:

\[
w_r (B = 0) = w^0_r \gg \Delta K_s. \quad (27)
\]

So fast relaxation leads to efficient averaging the rates \( K_{s/jab} \), i.e. high accuracy of the approximation \( \bar{K}_s \approx k^2 E \), where \( k^0_s = \langle e || \bar{K}_s || e \rangle = \langle K_s \rangle = k_s/9 \). In such a case \( \nu = r, s, e \), \( \eta_B = N = 9, \xi_r = 0, \eta_n = 1, \) and \( \kappa_s = k^0_s \) in eq. \( 21 \) \( \bar{p}_s(\epsilon) \) is given by

\[
\bar{p}_s(\epsilon) = \left( \epsilon + k^0_s - \frac{k_s k^0_s}{\epsilon + k^0_s + k_e + \xi_\epsilon \sqrt{k_e \epsilon}} \right)^{-1} \quad (28)
\]

with \( k_s = k_r + k_n \) and \( k^0_s = k_s/9 \).

The inverse Laplace transformation of \( \bar{p}_s(\epsilon) \) yields the FDK \( p_s(t) \), predicting the T-exciton migration effect, which shows itself, in particular, in the slow long time dependence: \( p_s(t) \sim \xi_\epsilon t^{-3/2} \), resulted from the nonanalytic behavior of \( \bar{p}_s(\epsilon) \) at small \( \epsilon: \bar{p}_s(0) - \bar{p}_s(\epsilon) \sim \xi_\epsilon \sqrt{\epsilon} \) \( 13,19 \). The amplitude of the migration effect is essentially determined by the value of the parameter \( \xi_\epsilon \), as stated in Sec. II, so that for large \( \xi_\epsilon \geq 1 \) the effect is fairly strong and clearly distinguishable even at relatively short times \( 18,19 \).

![FIG. 1](image)

(a) Comparison of the experimental FDK for amorphous rubrene films \( 13 \) at \( B = 0 \) (circles) and \( B = 8 \) kG (triangles) with the FDK \( p_s(t) \), calculated by eq. \( 21 \) for \( B = 0 \) (line 1) and eq. \( 21 \) for \( B \gg B_s \) (line 2), using the rate value \( k_s = 0.37 \) ns \(^{-1} \), the vector of other parameters \( z = (0.2; 1.44; 0.14; 1.7) \) [eq. \( 21 \)], and relaxation rates \( \bar{w}_r/k_s = 0.04; \bar{w}_r/k_s = 0.5 \). The dependence \( p_s(t) \sim T^{-3/2} \), with arbitrary constant \( A \), is also displayed (dashed line).

(b) Comparison of the FDK \( p_s(t) \) for \( B = 0 \) (line 1 as in Fig. 1a) with the conventional variant of the FDK (determined by first order processes), evaluated with eq. \( 28 \) for the same parameters, except \( \xi_\epsilon = 0 \), i.e. excluding migration effect (line 2).

High accuracy of formula \( 28 \) in the limit \( 27 \) is demonstrated in Fig. 1a by comparison of the theoretical dependence \( p_s(t) \) with the normalized FDK \( \bar{I}_s(t) = I_s(t)/I_s(0) \) (Sec. I), measured for amorphous rubrene \( 13 \), in which the spin-lattice relaxation is expected to be very fast (see Sec. IV.A.2). The function \( p_s(t) \) is calculated with eq. \( 28 \) by adjusting the rate \( k_s \) and other rates, represented as a set of dimensionless parameters

\[
z = (z_r, z_s, z_e, \xi_\epsilon), \quad \text{where} \quad z_q = k_q/k_s. \quad (29)
\]

with \( q = r, s, e \). Good agreement is found at all studied times, including long times when \( p_s(t) \sim t^{-3/2} \). The FDK is also calculated in the conventional model of first order processes \( 28 \), i.e. a particular variant of the general one with \( \xi_\epsilon = 0 \), for the same values of parameters \( z_q \). This model is seen to predict too sharp decrease of \( p_s(t) \) at long times (Fig. 1b), which is, clearly, valid for any values of parameters of the model.

2. FDK for strong magnetic fields. In the limit of strong field \( B \gg B_s = \|H^s_{2}/(g\beta) \) there are 3 spin states with singlet character: \( |1\rangle \approx |0, 0, 0\rangle, |2\rangle \approx |+a−b\rangle, \) and \( |3\rangle \approx |−a^+b\rangle \). Note that for two independently oriented T-excitons at large, but finite, \( B \) the states \( |2\rangle \) and \( |3\rangle \) are, in general, non-degenerate with small splitting \( \omega_{23} \sim \)
\[ D[D/(g\beta B)] \ll D, \text{ where } D = D_a = D_b \text{ is the ZFSI-parameter of T-excitons.} \] In this estimation it is taken into account that for separated aromatic molecules (typically existing in amorphous solids) \( D \gg E \). In the presence of this nearly degenerate pair of states the TTE-spin evolution is, nevertheless, described by the JMA, if \( \omega_{23}/k_c \approx \omega_{23}/k_s > 1 \) [22], where \( k_s = k_s/3 \). For studied amorphous rubrene films, in which \( k_s \approx 3k_c \approx 0.15 \text{ ns}^{-1} \) (see Fig. 1a) and \( D \approx 0.6 \text{ kG} \) [8], this criterion predicts the validity of the JMA at \( B < 40 \text{ kG} \). Hence in the experimentally studied case \([13]\) \( B = B = 8.1 \text{ kG} \) the JMA is valid, and the FDK is described by the model \([23]\) of T-excitons undergoing stochastic migration [23].

Figure 1a displays \( p_s(t) \), calculated for \( B \gg B \) by Eqs. \([20]\) with the same values of parameters \([20]\) as those applied above for \( B = 0 \). The FDK \( p_s(t) \) agrees fairly well with the experimental one at \( B = B = 8.1 \text{ kG} \) [13].

For so large rates \( w_{c,e} \) the effective spin relaxation rate \([20]\) \( w_e = w_e(B = B) \) is also fairly large: \( w_e \approx 3.4 \Delta k \).

This relation is the important argument in favor of good accuracy of the averaging approximation \( K_{\text{av},B} \approx \langle K_{\text{av},B} \rangle = k_s \) (applied above for \( B = 0 \)), especially taking into account that \( w_{c,e} \gg w_r \) because of expected inequalities \( w_{c,e} > 1 \) \((\nu = c,e)\) and therefore \( w_{c,e} > 3.4 \Delta k \). As to the estimation \( w_{c,e} \gg w_r \), it is also described by the JMA, if \( \tau_e > \tau_e^{\text{cor}} \). The dependence \( p_s(t) = A t^{-3/2} \) (with arbitrary amplitude \( A \)) is also displayed in Fig. 2a for comparison (dashed line).

Formula [28] allows for fairly accurate description of the FDK, measured for tetracene: single crystal (circles), annealed PCF (triangles), and (b) PCF film (squares) at \( B = 0 \) with the FDK \( p_s(t) \) (full lines 1, 2, and 3, respectively), calculated using eq (25) for parameters: (1) \( k_s = 6.5 \text{ ns}^{-1} \) and \( k_s = (0.032; 0.039; 0.97; 1.7) \); (2) \( k_s = 8.5 \text{ ns}^{-1} \) and \( k_s = (0.082; 2.9; 0.56; 2.2) \); and (3) \( k_s = 10.0 \text{ ns}^{-1} \) and \( k_s = (0.003; 0.4; 0.08; 0.65) \). The dependence \( p_s(t) = A t^{-3/2} \) (with arbitrary amplitude \( A \)) is also displayed in Fig. 2a for comparison (dashed line).

Formula [28] allows for fairly accurate description of the FDK, measured for tetracene: single crystal, poly-crystalline film (PCF), and annealed PCF at \( B = 0 \) and times \( t < 20 \text{ ns} \) (Figs 2a and 2b) [16]. In our work we will restrict ourselves to pointing out most important features of the T-exciton migration manifestation, concentrating on the behavior of the FDK at relatively long times \( (t > 1 \text{ ns}) \) influenced by migration most strongly.

a) Shapes of the FDK \( \tilde{I}_{s_1}(t) = I_{s_1}(t)/I_{s_1}(0) \) for single crystal and annealed PCF are similar with close values of corresponding kinetic parameters \([28]\) for both systems (Fig. 2a).

b) For the PCF the FDK-shape markedly differs from those for other systems (Fig. 2b). The difference results from fast decay of \( S_1 \)-state \((k_{s,e} - k_s, k_s)\) and weaker effect of T-exciton migration in the PCF, showing itself in the value \( \xi_s \approx 0.65 \) smaller than those for other studied systems (\( \xi_s \approx 1.5 - 2.0 \)).

c) In all three systems the long time tail of the FDK (at \( t > k_{s,e}^{-1} \)) is fairly strongly affected by stochastic migration of T-excitons. This effect manifests itself in the inverse-time behavior of \( p_s(t) \): \( p_s(t) \approx t^{-3/2} \).

d) Fitting of the experimental FDKs \( \tilde{I}_{s_1}(t) \) yields values
\( k_{+} \approx k_{-} \approx 6 - 10 \text{ ns}^{-1} \) for all three systems, close to those, measured at short times \( t < 0.8 \text{ ns} \) [16].

2. FDK for strong magnetic fields. At strong magnetic fields \( B \gg B_{e} \), the FDK is described by formula [15] in a simplified form, obtained in the case of only two TT spin singlet states with singlet character (reactive states), \( |X_{0}\rangle = |00\rangle \) and \( |X_{+}\rangle = \frac{1}{\sqrt{2}}(|++\rangle + |+-\rangle) \) [4, 13], corresponding to identical T-excitons (for some additional discussion see also refs [14] and [15]). This simplified formula can be found, taking into account that for two reactive spin states (for \( N = 2 \)) the matrix of weights [17] is represented as
\[ p_{s}(\epsilon) = \frac{1}{4}\langle |X_{0}\rangle \langle X_{0}| + 2|X_{+}\rangle \langle X_{+}| \rangle, \]
and thus in eq. (15)
\[ \langle e|P_{3}G(\epsilon)P_{1}|e\rangle = \frac{1}{4}[g_{0}(\epsilon) + 4g_{+}(\epsilon)], \]
where functions \( g_{0}(\epsilon) \) and \( g_{+}(\epsilon) \) are defined by eq. (26) with \( \zeta_{\alpha} = 0, \kappa_{0} = k_{s}/3 \) and \( \kappa_{s+} = 2k_{s}/3 \).

The inverse Laplace transformation of thus obtained \( \tilde{p}_{s}(\epsilon) \) predicts \( p_{s}(t) \) similar to those found for above-mentioned systems with the same long time dependence \( p_{s}(t) \sim t^{-3/2} \). We are not going to thoroughly analyze it, noting only two points which concern characteristic properties of the FDK, recently measured in tetracene singlet crystal for \( B = 0 \) and \( B = 8 \text{ kG} \) at times \( t \lesssim 10^{2} \text{ ns} \) [15]:

a) In general, the behavior of the FDK is reproduced by the proposed model qualitatively correctly. At intermediate times \( t < 20 \text{ ns} \) the agreement between experimental and theoretical FDK is fairly good, as has already been shown above for \( B = 0 \) (Figs 2a, 2b).

b) At longer times, however, some disagreement is observed: the experimental FDK [15] decreases certainly slower than the predicted one: \( p_{s}(t) \sim t^{-3/2} \). The description of the slower decrease requires some extension of the model, which is a subject of further investigations (as pointed out below).

V. CONCLUSIONS

In this work we have proposed the simple and universal model for studying the kinetics of singlet fission in organic semiconductors (1). The model enables one to analyze in detail the effect of three-dimensional diffusive T-exciton migration (in \([T+T]\)-state of separated T-excitons) on genuine TT-annihilation and thus on fission process. This model treats the space/time evolution of TT-pair as transitions between two states: \([T\pm T]\)-state of coupled T-excitons and \([T+T]\)-state of separated T-excitons, undergoing three-dimensional relative diffusion [see eqs (23)-(25)]. The model quite accurately describes exponential-type population/depopulation processes in \([T\pm T]\)-state at relatively short times and small TT-distances, and the long-time diffusion-like spatial evolution of T-excitons in \([T+T]\)-state at large TT-distances.

Kinetics of singlet fission is traditionally studied by analyzing the decay of \( S_{1}\)-fluorescence intensity \( \bar{I}_{S_{1}}(t) \) [2-4]. The proposed model is shown to be able to describe fairly accurately the normalized FDK \( \bar{I}_{S_{1}}(t) = I_{S_{1}}(t)/I_{S_{1}}(0) \), observed in the range of times \( 10^{-1} \text{ ns} \lesssim t \lesssim 10^{6} \text{ ns} \) for a number of systems at magnetic fields \( B = 0 \) and \( B = 8 \text{ kG} \) [13, 10]. Of special interest is the observed inverse-time dependence \( (\sim \xi_{t}t^{-3/2}) \) of the FDK at long times \( 10^{2} \text{ ns} \lesssim t \lesssim 10^{6} \text{ ns} \), resulted from T-exciton migration. The amplitude of this dependence is essentially controlled by the parameter \( \xi_{t} \) [13], whose value is determined by characteristic properties of TT-dissociation and annihilation processes [18, 19].

Concluding our discussion it is worth noting that fairly accurate description of experimental results demonstrates great potentialities of the proposed model, which can further be generalized by taking into consideration characteristic features of T-exciton spin relaxation and migration in \([T+T]\) state: anisotropy of migration [18, 19], hopping nature of migration, etc. The proposed model is expected to be sensitive to details of the mechanism of T-exciton migration and TT-interaction, and therefore can be suitable for studying specific structural properties of organic solids and singlet fission processes in them by analyzing the FDK in a wide region of times \( t \lesssim 10^{2} \text{ ns} \) [13, 27, 28].

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[1] Smith, M. B.; Michl, J. Recent Advances in Singlet Fission. Annu. Rev. Phys. Chem. 2013, 64, 361-386.
[2] Pope, M.; Swenberg, C. E. Electronic Processes in Organic Crystals and Polymers; Oxford University Press: New York, 1999.
[3] Žutić, I.; Fabian, J.; Das Sarma, S. Spintronics: Fundamentals and Applications. Rev. Mod. Phys. 2004, 76, 323-410.
[4] Swenberg, C. E.; Geacintov, N. E. In Organic Molecular PhotoPhysics; Birks, J. B., Ed.; Wiley & Sons: Bristol, 1973; Vol. 1, pp 489-564.
[5] Merrifield, R. E. Theory of Magnetic Field Effects on the Mutual Annihilation of Triplet Excitons. J. Chem. Phys. 1968, 48, 4318-4319.
[6] Suna, A. Kinematics of Exciton-Exciton Annihilation in Molecular Crystals. Phys. Rev. B 1970, 1, 1716-1739.
[7] Konyaev, S. N.; Shushin, A. I.; Kolesnikova, L. I.; Tribel, M. M.; Frankevich, E. L. Fluorescence-Detected Low Field Resonances in TT Annihilation in the A-TCNB Single Crystal Lineshape and Dynamic Parameters Phys. Status Solidi B 1987, 142, 461-471.
[8] Tarasov, V. V.; Zorinants, G. E.; Shushin, A. I.; Tribel, M. M. The role of spin-lattice relaxation in magnetic field effects on the luminescence of amorphous and polycrystalline rubrene films. Chem. Phys. Lett. 1997, 267, 58-64.
[9] Berkelbach, T. C.; Hybertsen, M. S.; Reichman, D. R.
Microscopic Theory of Singlet Exciton Fission. I. General Formulation. J. Chem. Phys. 2013, 138, 114102/1-114102/16.

[10] Irkhin, P.; Biaggio, I. Direct Imaging of Anisotropic Exciton Diffusion and Triplet Diffusion Length in Rubrene Single Crystals. Phys. Rev. Lett. 2011, 107, 017402/1-017402/4.

[11] Ryansyanskiy, A.; Biaggio, I. Triplet Exciton Dynamics in Rubrene Single Crystals. Phys. Rev. B 2011, 84, 193203/1-193203/4.

[12] Barhoumi, T.; Monge, J. L.; Mejatty, M.; Bouchriha, H. Short and Long Consecutive Pairs Model in the Interpretation of MFE and F-ODMR Experiments in Molecular Crystals. Eur. Phys. J. B 2007, 59, 167-172.

[13] Pilland, G. B.; Burdett, J. J.; Kurunthu, D.; Bardeen, C. J. Magnetic Field Effects on Singlet Fission and Fluorescence Decay Dynamics in Amorphous Rubrene. J. Phys. Chem. C 2013, 117, 1224-1236.

[14] Burdett, J. J.; Pilland, G. B.; Bardeen, C. J. Magnetic Field Effects and the Role of Spin States in Singlet Fission. Chem. Phys. Lett. 2013, 585, 1-10.

[15] Pilland, G. B.; Burdett, J. J.; Dillon, R. J.; Bardeen, C. J. Singlet Fission: From Coherences to Kinetics. J. Phys. Chem. Lett. 2014, 5, 2312-2319.

[16] Pilland, G. B.; Bardeen, C. J. How Morphology Affects Singlet Fission in Crystalline Tetracene J. Phys. Chem. Lett. 2015, 6, 1841-1846.

[17] Shushin A. I. Diffusive Transient Recombination Kinetics of Interacting Molecules. Chem. Phys. Lett. 1985, 118, 197.

[18] Shushin A. I. The Time Dependent Solution of the Smoluchowski Equation: Kinetics of Escaping From the Well for Different Dimensionalities. J. Chem. Phys. 1991, 95, 3657.

[19] Shushin A. I. Diffusional Escaping from the Well. Simple Model and Qualitative Results. J. Chem. Phys. 1992, 97, 1954.

[20] Steiner, U. E.; Ulrich, T. Magnetic Field Effects in Chemical Kinetics and related Phenomena. Chem. Rev. 1989, 89, 51-147.

[21] Pedersen, J. B.; Shushin, A. I.; Jorgensen, J. S. Magnetic Field Dependent Yield of Geminate Radical Pair Recombination in Micelles. Test of the Johnson-Merrifield approximation. Chem. Phys. 1994, 189, 479-487.

[22] K. Blum, Density Matrix Theory and Applications (Plenum Press, New York, 1981).

[23] Shushin, A. I. Generation of Electron Spin Polarization in Disordered Organic Semiconductors. Phys. Rev. B 2012, 86, 035206/1-035206/10.

[24] Lesin, V. I.; Sakun, V. P. Effect of Spin-Lattice Relaxation on the Dependence of the Triplet Exciton Annihilation Rate on the Strength of Magnetic Field. Phys. Status Solidi B 1980, 98, 411-417.

[25] Schmidberger, R.; Wolf H.C. Spin-Lattice Relaxation of Linear Triplet Excitons in 1,4 Dibromonaphthalene. Chem. Phys. Lett. 1975, 32, 18-20.

[26] Ponte Concalves, A. M. Electron Paramagnetic Resonance of Triplet Excitons in Anthracene-Tetracyanobenzene Crystals. Chem. Phys. 1977, 19, 397-405.

[27] Eaton, S. W.; Shoer, L. E.; Karlen, S. D.; Dyar, S. M.; Margulies, E. A.; Veldkamp, B. S.; Ramanan, C.; Hartzler, D. A.; Savikhin, S.; Marks, T. J.; Wasielewski, M. R. Singlet Exciton Fission in Polycrystalline Thin Films of a Slip-Stacked Perylenediimide. J. Am. Chem. Soc. 2013, 135, 14701-14712.

[28] Eaton, S. W.; Miller, S. A.; Margulies, E. A.; Shoer, L. E.; Schaller, R. D.; Wasielewski, M. R. Singlet Exciton Fission in Thin Films of tert-Butyl-Substituted Terpylenes. J. Phys. Chem. A 2015, 119, 41514161.