Photoinduced polarons in polymers. Time-resolved ESR analysis of polaron pairs in polymer:fullerene blends.

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The work concerns the analysis of experimental time-resolved ESR spectra in photoexcited polymer:fullerene blend, consisting of poly(3-hexilthiophene) and fullerene [6,6]-phenyl C_{61}-butyric acid methyl ester (at low temperature $T = 100$ K). The spectra are assumed to be determined by spin-coherent pairs of charged polarons ($P^+$ and $P^-$) generated in the singlet state. The analysis is made within simple model of a set of first order processes, in which $P^+P^-$-pair spin evolution is described by the stochastic Liouville equation, allowing for fairly accurate description of experimental results. Simple analytical interpretation of obtained numerical results demonstrates that trESR spectra can be represented as a superposition of antiphase and CIDEP contributions together with the conventional thermal one. These contributions are shown to change their signs with the increase of time in agreement with experimental observations.

I. INTRODUCTION

Time-resolved ESR (trESR) spectra of pairs of doublet (D) particles and, in particular, spin-correlated pairs have been studied very actively both experimentally\cite{1,14} and theoretically\cite{1,14,15}. The analysis of these spectra is known to give important information on characteristic properties of spin-dependent interactions between particles in pairs (Zeeman, spin-exchange, spin dipole-dipole, and hyperfine, etc.) as well as spin relaxation and spin-dependent recombination rates.

The interference of effects of spin-dependent interactions and relaxation/recombination leads to well known contributions to trESR spectra: antiphase structure (APS), chemically induced dynamic electron polarization (CIDEP) both multiplet and net, and some other contributions. The manifestation of them is found in a large number of photochemical condensed phase D-D reactions, charge separation in photosynthetic systems, etc.\cite{14}

Close attention has, recently, been attracted to the trESR investigation of photoinduced charge transfer processes in solids (organic semiconductors, polymer blends, etc.)\cite{19,22} which determine the efficiency of generation of charged D-particles, i.e. $P^-$-polarons. Great interest in studies of charge transfer processes is inspired by possible practical applications in spintronics\cite{24} and solar cells.\cite{20}

Some recent experiments concern trESR investigation of photoexcited polymer:fullerene blend, consisting of poly(3-hexilthiophene) (P3HT) and fullerene [6,6]-phenyl C_{61}-butyric acid methyl ester (PCMB), at low temperature $T = 100$ K.\cite{24} The observed trESR spectra indicate the generation of geminate spin-correlated doublet-doublet pairs in the initial singlet state, which are suggested to be the pairs of polarons $P^+$ (in P3HT) and $P^-$ (in PCMB).\cite{24} The APS and CIDEP contributions are found to change their sign at long times because of the effect of spin-selective reactivity and spin population relaxation on spin evolution of $P^+$-pairs. Naturally, the amplitudes of obtained APS and CIDEP contributions decrease with the increase of times but remain quite distinguishable against the background of the thermal ESR spectrum even at long times $t \gtrsim 10 \mu$s.

II. GENERAL FORMULATION

The trESR spectra of $P^+P^-$-pairs are determined by the spin evolution of interacting $P^\pm$ polarons. In this work the spin evolution is described by the $P^\pm$ spin density matrix $\rho(t)$, satisfying the SLE. The characteristic features of the evolution essentially depend on the form of the SLE, which, in turn, depends on the model of the process under study. In our work we consider the $P^\pm$ spin evolution in the simple exponential model.\cite{15} In this
model SLE is written as \((h = 1)\)

\[
\dot{\rho} = -\hat{L}\rho \quad \text{with} \quad \hat{L} = i\hat{H} + \hat{W}_e + \hat{W}_c + \hat{W}_d + \hat{K}_s.
\]  

(1)

Here \(\hat{L}\) is the superoperator [operator in the Liouville space (vide infra)], in which \(\hat{H}\) is the superoperator representation of the commutator of the \(P^+P^-\) spin-Hamiltonian \(H\), defined by \(\hat{H}\rho = H\rho - \rho H\). \(\hat{W}_e\) is the superoperator of intraradical spin relaxation, \(\hat{W}_c\) is the superoperator of spin-exchange-induced relaxation rate, \(\hat{W}_d\) is the rate of irreversible PP dissociation, and \(\hat{K}_s\) is the spin-selective-recombination rate superoperator.

Hereafter we will use the term "superoperator" and the notation \(\hat{A}\) (with hat) for any operator \(A\) in the Liouville space (the space, in which the density matrix is represented as the vector), in order to distinguish this operator from those in the Hilbert space.

In our analysis we consider the pairs of \(P^\pm\) polarons, with different electron spin \(g\)-factors, \(g_+\) and \(g_-\), and exchange interaction \(J_e\), in the magnetic field \(B\). The \(P^+P^-\) spin-Hamiltonian is represented in a simple form

\[
H = \omega S_z + Q(S_+ - S_-) - J_e(S^2 - 1).
\]

(2)

In this formula

\[
\omega = \frac{1}{2}(g_+ + g_-)\beta B \quad \text{and} \quad Q = \frac{1}{2}(g_+ - g_-)\beta B;
\]

(3)

\(S_{\nu z}, (\nu = \pm),\) are the \(z\) components (along the magnetic field direction) of the \(P^\pm\)-spin operators with eigenvectors, corresponding to the projections +1/2 and −1/2, denoted as \(|\uparrow\rangle\) and \(|\downarrow\rangle\), respectively; \(S = S_+ + S_-\) is the operator of the total spin and \(S_z\) is its \(z\) component. First two terms in eq. (2) represent the Zeeman interaction of (electron spins) with frequencies \(\omega_\nu = g_\nu\beta B, (\nu = \pm),\) and the third term describes the spin exchange interaction.

The intraradical spin relaxation is modeled within the simple Bloch-type approach with relaxation supermatrix

\[
\hat{W}_r = \hat{W}_+ + \hat{W}_-,
\]

(4)

in which

\[
\hat{W}_\nu = w^\nu\rho_\nu |\uparrow\rangle_\nu \langle\downarrow|_\nu - |\downarrow\rangle_\nu \langle\uparrow|_\nu + w^\nu_\nu (|\uparrow\rangle_\nu \langle\uparrow|_\nu + |\downarrow\rangle_\nu \langle\downarrow|_\nu), (\nu = \pm),
\]

(5)

are the supermatrices of relaxation in \(P^\pm\)-polarons, represented in the Liouville space in the bases \(|\mu\rangle_\nu = |\mu\rangle_\nu^\prime, (\mu, \mu' = \uparrow, \downarrow)\).

The terms in first and second lines of formula (5) describe the population and phase relaxation (\(\sim w^\nu\rho_\nu\) and \(\sim w^\nu_\nu\)), respectively. The parameters \(p_\nu = e^{-\omega_\nu/(k_B T)}\) are the Boltzmann factors, controlling the difference of thermal populations of the Zeeman sublevels. Note that in the considered experimental conditions the parameters \(p_\nu\) is very close to unity because \(\omega_\nu/(k_B T) \sim 10^{-3}\).

So far we have discussed the spin states and corresponding operators for single \(P^\pm\) particles. For the analysis of \(P^+P^-\)-pair spin evolution, however, we need the proper basis of pair spin states. The most convenient are the basis of states \(|j\rangle, (j = 1-4),\) of separate \(P^\pm\) particles and the basis of eigenstates of the total spin \(S\) \((S-T\)-basis) \(|Z\rangle, (Z = S, T_{0,2})\). In terms of \(|\uparrow\rangle, |\downarrow\rangle\) states of \(P^\pm\)-particles both sets of basis states are represented as

\[
|\uparrow\rangle, |\downarrow\rangle = |1\rangle = |T_0\rangle; \quad |\uparrow\rangle, |\downarrow\rangle = |2\rangle = \frac{1}{\sqrt{2}}(|T_0\rangle + |S\rangle); \quad |\uparrow\rangle, |\downarrow\rangle = |3\rangle = \frac{1}{\sqrt{2}}(|T_0\rangle - |S\rangle); \quad |\downarrow\rangle, |\downarrow\rangle = |4\rangle = |T_0\rangle.
\]

(6a)

In particular, the recombination rate superoperator \(\hat{K}_s\) is represented in terms of the operator \(P_s = |S\rangle\langle S|\) of projection on the singlet \(|S\rangle\) state:

\[
\hat{K}_s = \frac{1}{2}k_s\hat{P}_s \quad \text{with} \quad \hat{P}_s\rho = P_s\rho + \rho P_s.
\]

(7)

The superoperator \(\hat{W}_c\) of the rate of spin-exchange-induced relaxation can also be written in terms of this operator:

\[
\hat{W}_c\rho = w_c(P_s\rho + \rho P_s - 2P_s\rho P_s).
\]

(8)

To obtain the spin density matrix \(\rho\) [from the SLE (1)] one needs to specify initial condition \(\rho(t = 0) = \rho_0\). In our work we will mainly consider the case of initial creation of PPs in the singlet \((\rho_s)\) or the thermalized tritplet \((\rho_t)\) state:

\[
\rho_s = |S\rangle\langle S| \quad \text{and} \quad \rho_t = \frac{1}{4} \sum_{\nu = 0, \pm} |T_\nu\rangle\langle T_\nu|,
\]

(9)

respectively.

The specific features of the above-described \(P^+P^-\) spin dynamics essentially manifest themselves in the trESR spectrum, formed during the time of \(P^+P^-\) spin evolution in the presence of the microwave field \(B_1\), assumed to rotate with the frequency \(\omega_0\) around the magnetic field \(B\) (around the axis \(z\)). The spectrum is determined by the \(P^+P^-\) spin evolution, governed by the Liouville superoperator \(\hat{L}_\nu\). In the frame of reference \((x', y', z')\), rotating with \(B_1\), this superoperator is written as

\[
\hat{L}_\nu = i(\hat{H}_\nu + \hat{H}_1) + \hat{W}_e + \hat{W}_c + \hat{W}_d + \hat{K}_s.
\]

(10)

In this formula \(\hat{H}_\nu\) is the superoperator representation of the commutator of the spin-Hamiltonian

\[
\hat{H}_\nu = H - \omega_0 S_z\quad \text{and} \quad H_1 = \omega_1 S_{x'},
\]

(11)

in which \(\omega_1 \approx \frac{1}{4}(g_+ + g_-)B_1\). In terms of the superoperator \(\hat{L}_\nu\) the trESR spectrum \(I_\nu(\omega)\) can be expressed as

\[
I_\nu(\omega) = \int_0^\infty d\tau f(\tau)\text{Tr}[S_{y'}(e^{-\hat{L}_{\nu}\tau}\rho_0)] = \text{Tr}[S_{y'}(\hat{F}_\nu\rho_0)],
\]

(12)

where \(f(\tau) = w_s e^{-w_s\tau}\) is the characteristic window function of the ESR spectrometer, with small time \(w_s^{-1} \ll t, \rho_t \equiv \rho(t)\) is the \(P^+P^-\) spin-density matrix at the moment \(t\) of measurement, and

\[
\hat{F}_\nu = w_y(\hat{W}_c + \hat{L}_\nu)^{-1}
\]

(13)

is the spectrum-shape matrix.
III. NUMERICAL DESCRIPTION

In general, in the considered model trESR spectra can be evaluated only numerically. Here we compare numerically calculated spectra with the experimental ones.

In our numerical treatment of trESR spectra we use the parameters of the spin-Hamiltonian close to those obtained from experiments. Moreover, the considered model [2], taking into account only the isotropic Zeeman and exchange interactions, is actually based on the experimental results and suggestions of the work [24].

The anisotropic Zeeman and the hyperfine interactions are neglected, though the effect of these two types of interactions is taken into consideration, in terms of spin relaxation, which is represented by the matrix $\hat{W}_e$ (resulted from polaron-jump-induced fluctuations of these interactions).

Detailed analysis of experimental spectra shows that anisotropic Zeeman and hyperfine interactions lead also to some inhomogeneous broadening of lines. In reality, however, it is impossible to accurately describe this broadening, because of not very high accuracy of experimental spectra. In such a case it looks quite appropriate to approximate the effect of inhomogeneous broadening with that of homogeneous one, by properly adjusting the values of rates in the relaxation matrix $\hat{W}_e$.

The inhomogeneous broadening can also result in some (small) change of frequencies of lines. Taking into account this effect we will slightly adjust the (effective) Zeeman frequencies $\omega_\nu$, $(\nu = \pm)$ in the spin-Hamiltonian [2] to the average experimental ones (see below).

In this section we show fairly good accuracy of the model, proposed and discussed in Sec. II. Despite evident limitations of this semi-quantitative model, its accuracy turns out to be high enough to demonstrate the most important specific features of the time evolution of experimental trESR spectra of P$^+$-pairs.

The model contains the parameters of two types: (a) specifying the measurement conditions and (b) describing P$^+$-pair under study.

The parameters of the first type (a) are the microwave field $\omega_1$ (in frequency unit) and characteristic inverse time $w_g$ of the window function $f(t)$ [see eq. (12)]. The field $\omega_1$ is considered to be weak $\omega_1 \ll w_0^\nu, k_s$ (corresponding to experimental conditions [24]), for which trESR spectra $I_i(\omega) \sim \omega_1^2$ and the shape of these spectra are independent of $\omega_1$. As for the parameter $w_g$, its value satisfies the relation $w_g^\nu \ll w_w \ll w_0^\nu$, $(\nu = \pm)$, which on the one hand, ensures that measurements do not lead to additional broadening (due to uncertainty principle) and on the other hand, the important kinetic features of the trESR signal generation are well resolved (as was realized in the experimental analysis [24]).

The most important parameter of the second type (b) is $Q = \frac{1}{2}(\omega_+ - \omega_-) = 3.25 \cdot 10^7$ s$^{-1}$. This value is slightly larger ($\approx 12\%$), than that $Q_g \approx \frac{1}{2}(g_+ - g_-)\omega_0$, corresponding to $\Delta g = g_+ - g_- = 1.9 \cdot 10^{-3}$ (obtained in ref. [24] from cwESR spectra of P$^\pm$ polarons).

All other parameters of the model are considered as adjustable in fitting of experimental data. Some relations between relaxation rates are, however, evident without numerical analysis.

In particular, experimental results clearly show that widths of trESR lines of P$^+$-pairs are fairly large, corresponding to dephasing rates $w_0^\nu$ comparable with the difference of Zeeman frequencies $Q$: $w_0^\nu \lesssim Q \sim (2 - 4) \cdot 10^7$ s$^{-1}$, $(\nu = \pm)$. At the same time, the population relaxation rates $w_w^\nu$ are much smaller than the dephasing rates $w_0^\nu$, as well as relaxation rates $w_d^\nu$ for $\nu = \pm$, so as it follows from the characteristic time of changing of the experimental trESR spectrum $\tau_{ESR} \sim 10^{-6}$ s (see Fig. 1). The obtained estimation $w_0^\nu \ll w_0^\nu$ allows for the proper choice of the inverse width of the window function $w_g$ mentioned above.

Special assumption is made on the absolute value of the spin-exchange interaction $J_\nu$. Analysis shows that the best agreement between experimental and theoretical trESR spectra is obtained for small $|J_\nu| \ll |Q|, w_0^\nu$ in accordance with the suggestion of the work [24] in this limit the trESR shape does not strongly depend of $J_\nu$.

In our calculations we neglect the effect of the dissociation of P$^+$-pair by taking $W_d = 0$, because the decay manifests itself in trESR spectrum only at very long times ($t > 10 \mu$s), which, first, are not of special interest for the

![FIG. 1. Comparison of experimental (dashed lines) and theoretical (full lines) ESR spectra of P$^+$-pair $I_i(b)$ (in arbitrary units) [with $b = B - B_0$ defined in eq. (13) for four times $t (\mu$s): (1) 0.8, (2) 1.4, (3) 3.5, (4) 5.8. Other parameters used are $Q = 3.25 \cdot 10^7$ s$^{-1}$, $J_\nu = 7.3 \cdot 10^7$ s$^{-1}$, $k_s = 6.0 \cdot 10^7$ s$^{-1}$, and $w_0 = 3.2 \cdot 10^7$ s$^{-1}$, as well as relaxation rates $w_w^\nu = 4.2 \cdot 10^7$ s$^{-1}$, $w_0^\nu = 2.5 \cdot 10^7$ s$^{-1}$, $w_d^\nu = 2.0 \cdot 10^7$ s$^{-1}$, $w_0^\pm = 6.5 \cdot 10^7$ s$^{-1}$](image-url)
analysis of spin-correlated P'P' pairs and, second, the experimental ESR spectra at these times are not accurate enough for unambiguous interpretation. Though, it is worth noting that some contribution of the dissociation process improves agreement between theoretical and experimental trESR spectra at \( t > 10 \mu s \) (as it follows from the numerical investigation).

The proposed analysis does not allow to clearly distinguish the effect of the spin-exchange induced relaxation \( \tilde{W}_E \) against that of relaxation in free polarons \( \tilde{W}_P \), especially taking into account that \( \tilde{W}_P \)-effect can hardly be distinguished from that of reactivity \( \tilde{K}_a \) in the system under study. For this reason, the spin-exchange induced relaxation is also neglected (\( \tilde{W}_E = 0 \)).

As for the reactivity, according to the analysis, good agreement between experimental and theoretical results is found for not very large values \( k_s \lesssim \omega_s^d \).

Figure 1 displays the comparison of experimental and numerically calculated trESR spectra \( I_t(b) \), in which

\[
b = B - B_0, \quad \text{where } B_0 = \omega_0/(\bar{g} \beta)
\]

with \( \bar{g} = \frac{1}{2}(g_+ + g_-) \), for four values of time delays: 0.8, 1.4, 3.5, and 5.8 (\( \mu s \)).

The spectra (in Fig. 1) are obtained for the singlet \( |S\rangle \) initial state of P'P' pairs, using eq. [12] with \( \omega(B(b)) \) defined in eq. [13].

It is seen that the proposed model allows one to reproduce experimental spectra fairly accurately, particularly taking into consideration that the accuracy of measured spectra is not very high.

The observed bits between lines of experimental spectra at \( t = 3.5 \) and 5.8 (\( \mu s \)) are somewhat deeper than those, obtained in the considered model. This discrepancy can be caused by the approximation of partially inhomogeneous broadening of the trESR spectra by homogeneous one, which results in relatively broad lines of lines. The fact is that the homogeneous mechanism predicts Lorentzian line shape with slowly decreasing wings while the inhomogeneous mechanism usually yields Gaussian one with very rapidly decreasing wings. The slower decrease of Lorentzian lines can certainly lead to less deep bits between Lorentzian lines than those between Gaussian ones.

Concluding discussion we would like to draw attention to the fact that E/A-distortion of trESR spectra, observed at small times 0.8 and 1.4 (\( \mu s \)) is changed by the A/E-one at longer times 3.5 and 5.8 (\( \mu s \)). Of course, at long times relative distortion amplitudes are fairly small, but still quite pronounced and distinguishable. It is seen that the calculation within the proposed model correctly reproduces the distortion behavior.

IV. ANALYTICAL ANALYSIS OF ESR SPECTRA

Detailed analysis shows that the shape of trESR spectra, predicted by the proposed model, can markedly be changed with the change of parameters of the model. There are, however, some important general properties, which essentially determine the shape. Here we discuss them both analytically and numerically.

A. APS contribution

One of the most well known manifestations of the spin-correlation of P'P' population is the APS. To demonstrate important features of the APS contribution we will discuss two simple variants of spin correlation, corresponding to the population of the singlet \(|S\rangle\)-state and isotropic triplet \(|T\rangle\)-state [see eq. (2)].

The most important specific features of the APS can be illustrated with the simplest model, based on the analysis of \( \omega_1 \)-induced transitions between spin states of the Hamiltonian \( H_0 \), using simple approach:

\[
I_A^S(\omega) = \sum_{j,k} P_{jk} \Phi(\omega - \omega_{jk}), \quad (X = S, T),
\]

where \( \Phi(\omega) = 1/(\bar{w}_1^2 + \omega^2) \) is the shape function with the characteristic width \( \bar{w}_1 \sim \omega_0^d \). In eq. [15] the sum is taken over the pairs of states \( (j,k = 1 - 4) \) of the spin-Hamiltonian \( H_0 \), involved in ESR \( (H_1 \)-induced) transitions, and superscript \( X = S, T \) of parameters \( P_{jk}^X \) denotes P'P'-pair spin state, defined in eq. [9]. Amplitudes of lines are determined by transitions intensities \( P_{jk}^X = P_0 (p_1^X - p_2^X) \), \( X = S, T \), in which \( p_1^X, p_2^X \) are the populations of the initial \( (j) \) and final \( (k) \) states, and \( P_0 \) is a constant parameter.

To further simplify the problem we consider the limit of weak exchange interaction \( |J_1| \ll |\omega_1 - \omega|, \bar{w}_1 \). In this limit, i.e. for the small parameter \( \xi = |J_1|/|Q| \ll 1 \), the APS can be interpreted, neglecting the effect of the exchange interaction on eigenstates of the spin-Hamiltonian \( H_0 \), i.e. assuming them to coincide with eigenstates \(|j\rangle\), \( (j = 1 - 4) \). Within this approximation the APS results from the change of corresponding eigenenergies:

\[
\epsilon_1 \approx \Delta \omega - J_1; \quad \epsilon_2 \approx Q; \quad \epsilon_3 \approx -Q; \quad \epsilon_4 \approx -\Delta \omega + J_1,
\]

with \( \Delta \omega = \omega - \omega_0 \) and \( Q = \frac{1}{2}(\omega_+ - \omega_-) \), for which we get the following transition frequences \( \omega_{jk} \): \( \omega_{12} \approx \omega_+ - J_1; \omega_{13} \approx \omega_+ + J_1; \omega_{33} \approx \omega_- - J_1; \omega_{34} \approx \omega_- + J_1 \). As to populations \( p_1^X \), they depend on the spin state \( X \); for the singlet state \( (S = 0) p_{1,4} = 0, p_{2,3}^S = 1/2 \), and for the triplet state \( (S = 1) p_{1,4}^T = 1/3, p_{2,3}^T = 1/6 \). Substitution of these values into eq. [15] yields for \( X = S, T \):

\[
I_A^S(\omega) \sim (-1)^3 J_1 \{ \Phi(\omega_+ - \omega) + \Phi(\omega_- - \omega) \},
\]

where \( \Phi'(\omega) = d\Phi(\omega)/d\omega = -2\omega / (\bar{w}_1^2 + \omega^2)^2 \).

B. ST_0-CIDEP contribution

Another important contribution, which essentially determines the shape of trESR spectra of P'P'-pairs, is the
multiplet CIDEP. Specific features of the kinetics of the multiplet CIDEP generation can be analyzed within the simple, but quite realistic limit of weak spin exchange interaction and dephasing faster than the population relaxation and recombination, i.e., for $w_n^Z \gg w_n^Z, k_s$.

In the natural case of large magnetic field $B$ and for not very long times $t < 1/w_n^Z, 1/k_s$ the multiplet CIDEP generation is described by the $S_{00}$-mechanism neglecting population relaxation and recombination (see Sec. IV.A). The $S_{00}$-CIDEP generation kinetics is described by the SLE for the reduced spin-density matrix $\rho_\gamma(t)$ in the subspace $|S\rangle, |T_0\rangle \equiv (|2\rangle, |3\rangle)$, which in the vector form is represented as $\rho_\gamma = [\rho_{22}, \rho_{23}, \rho_{32}, \rho_{33}]^T$. For $\hat{\rho}_\gamma(t) = \int_0^\infty dt \rho_\gamma(t)e^{-\kappa t}$ this SLE is written as

$$(\epsilon + \hat{L}_c)\hat{\rho}_\gamma = \rho_\gamma^0 \tag{18}$$

with

$$\hat{L}_c = \begin{pmatrix}
0 & iJ_e & -iJ_e & 0 \\
iJ_e & \Omega & 0 & -iJ_e \\
-iJ_e & 0 & \Omega^* & iJ_e \\
0 & -iJ_e & iJ_e & 0
\end{pmatrix} \tilde{\rho}_{22}$$

$$\tilde{\rho}_{32}$$

$$\tilde{\rho}_{33}$$

Here $\Omega = w_n + 2iQ$ with $w_n = w_n^Z + w_n^W$, and $\rho_\gamma^0 = \frac{1}{2}[1, (-1)^{S+1}, (-1)^{S+1}, (-1)^{1+S}, 1]^T$ is the initial spin-density matrix singlet for $(S = 0)$ and triplet $(S = 1)$ initial state.

Equation (18) can be solved analytically in the studied case of fast dephasing and small $|J_e| \ll w_n^Z$. The solution leads to the following expression for the Laplace transform of the multiplet CIDEP $P_\gamma^\nu(\epsilon) = -2\langle S^+ S^- \rangle$:

$$P_\gamma^\nu(\epsilon) = -P_\gamma(\epsilon) = 2[\tilde{\rho}_{33}(\epsilon) - \tilde{\rho}_{22}(\epsilon)]$$

$$\approx 4\sigma_\gamma J_e Q \{ e[(\epsilon + w_n)^2 + 4Q^2] + 4J_e^2(\epsilon + w_n) \}^{-1}, \tag{20}$$

where $\sigma_\gamma = (-1)^S$ with $S = 0$ and $S = 1$ for the singlet and triplet initial condition, $\rho_\gamma^0 = |S\rangle\langle S|$ and $\rho_\gamma^0 = |T_0\rangle\langle T_0|$ respectively. The inverse Laplace transformation of the expression (20) yields for small $|J_e| \ll w_n$

$$P_\gamma^\nu(t) = -P_\gamma^\nu(\epsilon) \approx P_\gamma^\nu \left[ 1 - e^{-w_n t} \phi(t) \right] e^{-w_n t}, \tag{21}$$

where $\phi(t) = \cos(2Qt) + (w_n/2Q)\sin(2Qt)$,

$$P_\gamma^\nu = 4(-1)^S(J_e Q/|\Omega|^2), \quad w_n = 4w_n(J_e^2/|\Omega|^2) \tag{22}$$

with $|\Omega|^2 = w_n^2 + 4Q^2$.

In the case $|J_e| \ll w_n$, formula (21) describes the generation of the CIDEP $P_\gamma^\nu(t)$ for $t \lesssim w_n^{-1}$, the attainment of the maximum amplitude $P_\gamma^\nu$ at $t > w_n^{-1}$, and then slow relaxation with the rate $w_n \ll w_n$. The relaxation (induced by the exchange interaction) is the manifestation of the fact that the observable operators $(S_{zz})$ do not commute with the spin-Hamiltonian $H$.

C. Effect of spin relaxation and reaction

In the above analysis we have considered the $S_{00}$-CIDEP generation kinetics at relatively short times $t \sim 1/w_n^Z \ll 1/w_n^W, 1/k_s$. At longer times the dependence of the $S_{00}$-CIDEP $P_\gamma^\nu(t)$ can be strongly affected by slow population relaxation and recombination. The manifestation of this effect can be described within the extended model, taking into account [apart from recombination (4)] relaxation transitions between all states $|S\rangle, |T_{z=0}\rangle$, in addition to $S_{00}$ transitions, considered above.

In the model the relaxation-affected-CIDEP generation kinetics is described by the extended vector of spin-density matrix elements $\rho_\gamma = [\rho_{22}, \rho_{23}, \rho_{32}, \rho_{33}, \rho_{44}]^T$, satisfying the SLE of type of eq. (18)

$$(\epsilon + \hat{L}_c)\hat{\rho}_\gamma = \rho_\gamma^0, \quad \text{with } \hat{L}_c = \hat{L}_c + \hat{W}_r + \hat{K}_s^c, \tag{23}$$

in which $\hat{W}_r$ is the intraparticle relaxation supermatrix defined by eq. (4), and $\hat{K}_s^c$ is the part of the reaction supermatrix (4), operating in the subspace of matrix elements $\rho_\gamma$. The approximate is quite accurate in the considered strong magnetic field limit, i.e. the limit of large Zeeman frequencies $\omega \gg w_n^Z$.

Solution of the SLE (23) is, in general, fairly cumbersome and not suitable for the analytical analysis. To simplify the problem we consider the case of weak reactivity $k_s \ll w_n^Z$ and weak exchange interaction, where $w_n \ll w_n^Z$ (see eq. (22)).

In this limit we get the following expression for the Laplace transform of the difference $\tilde{\rho}_{33}(\epsilon) - \tilde{\rho}_{22}(\epsilon)$, which determines the relaxation-affected multiplet CIDEP

$$\tilde{\rho}_{33}(\epsilon) - \tilde{\rho}_{22}(\epsilon) \approx (2J_e Q/|\Omega|^2)[\sigma_\gamma - k_s(\epsilon + k_s)^{-1}]D_c^{-1}, \tag{24}$$

where $\sigma_\gamma = (-1)^S$ (with $S = 0, 1$), $|\Omega|^2 = w_n^2 + 4Q^2$, and

$$D_c \approx (\epsilon + 2w_n^W)/(\epsilon + w_n^W), \quad w_n = w_n^W + w_n^W \tag{25}$$

Taking into account the relation $P_\gamma^\nu(\epsilon) = -P_\gamma^\nu(\epsilon) = 2\tilde{\rho}_{33}(\epsilon)$ and making the inverse Laplace transformation we obtain formula

$$P_\gamma^\nu(t) = -P_-^\nu(t) \approx P_\gamma^\nu \left[ (\epsilon - w_n^W) \phi(t) \right] e^{-w_n t}, \tag{26}$$

in which $\tilde{\rho}_{33}(\epsilon) = \frac{1}{2}(e^{-2w_n^W} + e^{-2w_n^W})$, $\tilde{\rho}_{33}(\epsilon) \approx 4w_n^W w_n^W / w_n^W$, $k_s \approx \frac{1}{2}k_s$, and $P_\gamma^\nu$ is defined by eq. (22).

The population relaxation results in marked population of states $|1\rangle$ and $|4\rangle$. It is easily seen that, in general, this population leads to the net CIDEP $P_\gamma^\nu(t)$. The above-discussed solution of the SLE (23) yields simple expression for this (Laplace transformed) net contribution

$$P_\gamma^\nu(\epsilon) = P_-^\nu(\epsilon) = 2\tilde{\rho}_{33}(\epsilon), \tag{27}$$

which appears to be directly related to the multiplet CIDEP, $i.e.$ to $\tilde{\rho}_{33}(\epsilon)$:

$$\tilde{\rho}_{33}(\epsilon) = \tilde{\rho}_{44}(\epsilon) - \tilde{\rho}_{11}(\epsilon) = [(w_n^W - w_n^W)/w_n^W] \tilde{\rho}_{33}(\epsilon). \tag{27}$$

By summing up both multiplet and net contributions we obtain following formula for the total $P^\nu$-CIDEP

$$P_\gamma^\nu(t) = (w_n^W/w_n^W) P(-\nu)(t) \quad \text{with } w_n^W = w_n^W + w_n^W. \tag{28}$$
This formula shows that the difference in population relaxation rates leads to the difference in values of the total relaxation-affected $ST_0$-CIDEP of $P^\pm$ particles (without change of signs).

The expressions (26) and (28) predict another interesting effect of population relaxation and spin-selective reactivity: the change of the CIDEP sign for the singlet initial $P^P$ state (i.e. for $S = 0$) at certain time $\tau_s$, which can be evaluated by $P^{\mu}(\tau_s) = 0$ (recall, we assume that $k_s \ll w_\pm^s$). In the simplest case $w_\mp = w_\pm^s$:

$$
\tau_s \approx w_\mp d \ln(w_\mp/k_s).
$$

(29)

This CIDEP-sign change can easily be understood, taking into account that at long times the population relaxation leads to almost complete equilibration of spin subsystem. In this limit the spin-correlation is generated by recombination in the singlet state. The recombination-induced decay of the singlet component of population manifests itself similarly to the case of overpopulation of the (equilibrated) triplet state [see eq. (9)], i.e. the sign of the initial $ST_0$-CIDEP, corresponding to $\rho_1 = \rho_0$, is changed by the opposite one (for $\rho_1 = \rho_0$).

Note that the proposed mechanism of the change of population-relaxation-affected $ST_0$-CIDEP sign also predicts the change of the APS-sign at times $t > \tau_s$ because the APS-sign depends on the $P^P$ spin coherence as well [see eq. (17)]; in other words, the found change of the singlet spin state by the triplon one at $t > \tau_s$ is accompanied by the change of the APS-sign.

In the consideration of the relaxation/recombination effect we have assumed that the reactivity is small $k_s \ll w_\pm^s$. The numerical analysis shows, however, that this effect persists for $k_s \gtrsim w_\pm^s$ as well.

**V. NUMERICAL ANALYSIS OF CONTRIBUTIONS**

**A. General remarks**

It is worth beginning the numerical analysis of specific features of trESR spectra with some general illustrative calculations of APS and $ST_0$-CIDEP contributions, considered above.

The shape of trESR spectra and, in particular, the amplitudes of these two contributions are essentially determined by spin-evolution during the measurement [apart from the spin density matrix $\rho_t$ at time $t$ of the measurement], i.e. by characteristic properties of the super-operators $\hat{L}_s$ and $\hat{F}_s$ [see eqs. (10) and (13)]. General methods of rigorous, but cumbersome calculation of the contributions have already been discussed in literature.

In the considered limit of weak exchange interaction $J \ll w_\pm, w_\mp, |Q|$, however, the calculation of contributions can be simplified using the linear approximation in $\hat{J} = J_s(S^2 - 1)$, in which

$$
\hat{F}_s \approx \hat{F}_s^0 + \hat{F}_s^1 \quad \text{with} \quad \hat{F}_s^0 = \hat{F}_s^0(i\hat{J}/w_g)\hat{F}_s^0
$$

(30)

and

$$
\hat{F}_s^0 = w_g(w_g + \hat{L}_s^0)^{-1}.
$$

(31)

In formula (31) the superoperator $\hat{L}_s^0$ is defined by eq. (10) with $\hat{H}_s$ replaced by $\hat{H}_s^0 = (\omega - \omega_0)\hat{S}_z + Q(\hat{S}_a - \hat{S}_b)$.

Substitution of the expansion (30) into eq. (12) yields the representation for the trESR spectrum

$$
I_i(\omega) \approx I_i^0(\omega) + I_i^1(\omega) \quad \text{with} \quad I_i^1(\omega) = \text{Tr}[S_y(\hat{F}_s^0 \rho_0)]
$$

(32)

and $j = 1, 2$. This formula is found to be very accurate (with relative error $\delta < 10^{-2}$) for parameters of the model used in the analysis.

Previous investigation and the analysis of Sec. IV.A show that the term $I_i^0(\omega)$, in which the effect of $\hat{J}$ on measurement is neglected, describes the relaxation-affected $ST_0$-CIDEP (multiplet and net). The term $I_i^1(\omega)$, taking into account $\hat{J}$-effect in linear in $\hat{J}$ approximation, represents APS$^{15}$ (see also the analysis in Sec. IV.A).

**a. APS-contribution.** For small dephasing rates $w_\pm < |Q|$ the APS is of the (conventional) shape of two E/A lines, located at ESR frequencies $\omega_s^\pm$ of $P^\pm$ polarons (in accordance with the analysis in Sec. IV.A). For $w_\pm \gtrsim |Q|$, however, the APS shape drastically changes$^{15}$ with the increase of rates $w_\pm$ the two E/A lines collapse into one A/E shape at the center of the spectrum.

**b. CIDEP-contribution.** The shape of the (extended $ST_0$) CIDEP contribution $I_i^1(b) \equiv I_i^1(\omega(b))$ remains nearly the same for any relation between $w_\pm$ and $|Q|$.

**c. Relaxation/recombination effect.** Predicted effect of the relaxation/recombination induced change of signs of APS and $ST_0$-CIDEP contributions is completely confirmed by the exact numerical calculations in the considered symmetric variant of the system. The analysis demonstrates the sign change for $w_\pm \sim Q$. In the calculation we deliberately consider the case $k_s \sim w_\pm^s$ to demonstrate the occurrence of the sign change independently of the relation of between $k_s$ and $w_\pm^s$ (not only for $k_s \ll w_\pm^s$, as it is proved in Sec. IV.A.).

**B. Analysis of experimental spectra**

Formulas (30) - (32) allow for the representation of calculated spectra, reproducing the experimental results, as a sum of APS and $ST_0$-CIDEP contributions. Figure 2 shows this representation for two times. Noteworthy is that both contributions are somewhat distorted by the temperature effect (effect of $p_\pm = e^{-\omega_\pm/(k_BT)} < 1$), resulting in the conventional thermal contribution to trESR spectra. This distortion manifests itself in the $ST_0$-CIDEP contribution at long times $t \gtrsim 1/w_g^s$.

The presented results clearly demonstrate that the observed significant time dependence of the shape of ESR spectra results from the subtle superposition of APS and $ST_0$-CIDEP contributions.
VI. CONCLUSIONS

This work concerns the analysis of specific features of experimental trESR spectra of photoexcited spin correlated polaron pairs (P+P−) in polymer:fullerene (P3HT-PCMB) blend at low temperature 100 K (see Sec. I). The analysis is mainly based on exact numerical solution of the SLE within the model of the exponentially decaying polaron pairs, spin-evolution of which is described by the spin-Hamiltonian (2), spin-selective reactivity (7), and spin relaxation of two types: free polaron relaxation (4) and spin-exchange-induced one (8).

According to the analysis, in P+P−-pairs (in polymer:fullerene blend under study) the spin dephasing is much faster than the population relaxation. This relation allows for approximate analytical analysis of trESR spectra, providing deep insight into distinctive properties of the time dependence of spectra. These properties are found to be determined by the specific features of antiphase (APS) and population-relaxation affected ST0-CIDEP contributions. The combined numerical/analytical analysis shows that the generation of the contributions is governed by sophisticated interplay of coherent spin evolution and spin-relaxation/recombination of P+P− pairs.

It is found, in particular, that the observed short time trESR spectra (of the shape of conventional APS with large E/A components) are, actually, the sums of APS and ST0-CIDEP contributions of comparable amplitude. As for the long time spectra, they are determined by the population-relaxation affected spin-selective recombination of P+P− pairs. The contribution of the relaxation/recombination mechanism dominates at times longer than the time τs, defined in eq. (29). For the singlet initial condition this mechanism predicts the change of the sign of both contributions with time, distinctively manifesting itself in trESR spectra.

The analysis also shows that the dissociation of P+P− pairs does not strongly affect the trESR spectra of the system under study at relatively short times t < 10 µs (of main interest in our work). For this reason, in the calculation we have neglected the effect of dissociation. At longer times the contribution of dissociation to trESR spectra becomes important, but, unfortunately, the accuracy of available experimental spectra at these times is not high enough for accurate extraction of the contribution of dissociated pairs to the observed spectra.

At the end of our work it is worth discussing some recent numerical studies of the processes similar to that studied here. As an example, let us discuss one of the most recent and fairly detailed work, concerning the analysis of trESR spectra of geminate pairs of neutral radicals in micelles. Analysis is carried out within the model, which takes into account the spin evolution, accompanied by relative diffusion. The trESR spectra, investigated in this work, do not demonstrate the change of the sign of distortions (of APS and CIDEP-type) at long times. This is, probably, because the radical pairs are created in the triplet spin state.

Certainly, the results of the analysis, presented in ref. [18], are very interesting and insightful. Unfortunately they can hardly be directly applied to the theoretical investigation of considered spin correlated P+P−-pairs in organic solids at low temperatures, first of all because for these systems the diffusion approximation does not seem to be valid, especially taking into consideration strong Coulomb interaction between polarons in non-polar or-
ganic solids, the effect of which is expected to be very important at low temperatures.

Noteworthy is that the direct comparison of parameters of our model with those of model used in the work [18] is hardly possible. It worth also adding, that the proposed decomposition of the trESR spectra into the APS and CIDEP contributions (32) cannot be easily realized in the model proposed in [18].

Concluding our short discussion we would like to emphasize that in spite of great attention, payed to the interpretation of experimental trESR spectra of particular spin-correlated \(P^+P^-\) pairs, the goal of our treatment is more general. The main idea is to develop some new combined numerical/theoretical methods of the analysis of these spectra to get some additional insight into the specific features of \(P^+P^-\)-spin evolution. We belive that the proposed analysis is fairly convincing illustrative example of application of the proposed methods.

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