



# Time-domain shape of electron spin echo signal of spin-correlated radical pairs in polymer/fullerene blends



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## ABSTRACT

Temporal shape of electron spin echo (ESE) signal of photoinduced spin-correlated radical pairs (SCRPs) in composite of conductive polymer P3HT and substituted fullerene PCBM is studied in details. ESE signals of radical pairs (RP)  $P3HT^+/PCBM^-$  are calculated in realistic model, taking into account finite microwave pulse length. Inhomogeneous broadening of resonant lines and interradical distance distribution are included. Experimentally observed ESE time-domain shape was found to contradict predictions of conventional SCRPs theory, which would be valid in the case of very fast electron transfer. Thus, instantaneous formation of singlet SCRPs is not the case for  $P3HT^+/PCBM^-$  pair, and spin system has enough time to evolve coherently during sequential electron transfer. While it is impossible to reproduce experimental data within simple singlet SCRPs model, assumption of presence of additional – with respect to what is predicted by singlet SCRPs theory – AE (absorption/emission) spin polarization gives convincing accordance with the experiment. Density matrix of RP  $P3HT^+/PCBM^-$  is a superposition of two contributions, namely the parts reflecting (i) antiphase polarization of original singlet-born SCRPs and (ii) additional AE-polarization which is generated during initial stage of charge separation. AE-polarization affects experimental ESEEM (electron spin echo envelope modulation) traces, as well as ESE shape, making impossible their interpretation via simple singlet SCRPs model. However, this effect can be eliminated by averaging of ESEEM traces over EPR spectral positions. Finally, choosing the optimal gate for ESE time-domain integration and proper microwave detection phase tuning are considered.

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## 1. Introduction

Polymer/fullerene blend is the most widely used active media for organic photovoltaics (OPV) devices. The power conversion efficiency (PCE) of OPV cells is determined, to the large extent, by the yield of photoinduced charge separation. For many polymer/fullerene blends, including the benchmark composite of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl- $C_{60}$ -butyric acid methyl ester (PCBM), this yield is close to unity [1,2]. However, the origin of such a high efficiency of charge separation is still unclear, despite numerous studies [3,4]. The main reason for this is lack of information about the structure and dynamics of the intermediates of charge separation at polymer/fullerene interface. These intermediates are usually called light-induced primary charge-

separated (CS) states [5] or charge-transfer states (CTS) [6,7]. To determine the mechanism of charge separation in polymer/fullerene (or, more generally, in donor/acceptor) composites, knowledge of the distance between charges in CTS is needed. Since CTS can be caught at low temperature, when the charge separation is slowed down, EPR becomes a suitable method to study CTS structure.

Initially, CW EPR spectrum of separated charges in continuously illuminated polymer/fullerene composites were obtained [8]. This experiment proved the efficiency of light-induced charge separation in polymer/fullerene composites. However, lack of temporal resolution limits CW EPR experiments severely, and only thermalized separated charges are accessible for this method. Later, time-resolved (TR) EPR spectra were obtained for CTS in polymer/fullerene composite [5–7,9,10] under pulse laser illumination. It was established that light-induced CTS in P3HT/PCBM composite is spin-correlated radical pair (SCRPs), consisting of two weakly interacting radicals (polarons)  $P3HT^+$  and  $PCBM^-$ , created in the singlet spin state upon exciton dissociation. However, because of limited data set and complexity of the system the interpretation of TR EPR spectra is ambiguous.

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Electron spin echo (ESE), in particular, out-of-phase (OOP) ESE can provide more detailed information about the electronic structure of this SCRPs [11]. Previously, this technique was successfully used to determine the structure of the intermediates of light-induced charge separation in bacterial photosynthetic reaction centers (RCs) [12–14] and plant photosystems [13]. For these systems out-of-phase ESE gives the unique possibility to determine the interspin distance in SCRPs in nanometer range with angstrom precision. This distance nearly coincides with the distance between electron donor and acceptor molecules of RC, determined from X-ray structure [12,15]. Lately, out-of-phase ESE was used to study intramolecular light-induced charge transfer in artificial donor-spacer-acceptor systems [16,17].

Recently, out-of-phase ESE spectroscopy was employed for polymer/fullerene composites [18,19]. It was shown experimentally that time-domain shape of OOP ESE signal in P3HT/PCBM composite is nearly antisymmetric having negative and positive parts. At the same time OOP ESE signal in photosynthetic RCs, obtained under similar conditions [20], is bell-shaped, the signal sign is the same in every point and its maximum is well defined. Therefore, while obtaining electron spin echo envelope modulation (ESEEM) signal is straightforward in the case of RCs, it becomes tricky and ambiguous for the case of P3HT/PCBM composite: it is not clear how to derive properly ESE intensity upon time-domain integration in the latter case. Result of ESEEM experiment, being critical for interradsical distance measurement, depends significantly on choice of integration interval of ESE signal.

There is another pitfall that is worth to point out. Interpretation of ESEEM data in the frame of SCRPs theory is based on well known analytic expression for ESE modulation frequency [21]. Nevertheless, unusual time-domain ESE shape, obtained for radical pairs (RP) in P3HT/PCBM composite, makes questionable applicability of the SCRPs theory for such systems. Thus, ESE data for RPs in polymer/fullerene composites cannot be interpreted in strictly the same way, as it was done for photosynthetic SCRPs.

This work is devoted to systematic study of ESE signal in SCRPs P3HT<sup>+</sup>/PCBM<sup>-</sup> by numerical simulation of spin dynamics. The aim is to check whether the predictions of SCRPs theory, which are valid for photosynthetic SCRPs [21], are also valid for SCRPs in polymer/fullerene composites. We analyzed the time-domain shape of ESE and derived the recommendation for choosing the interval for ESE integration in ESEEM experiments. Finally, the predictions of SCRPs theory and results of ESE experiments with P3HT/PCBM under laser flash illumination are compared. We found that it is impossible to reproduce ESE time-domain shape and ESEEM data within the framework of conventional singlet SCRPs theory. In order to explain this discrepancy we assume additional spin polarization to be generated at initial steps of photoinduced charge separation. Thus, spin state of P3HT<sup>+</sup>/PCBM<sup>-</sup> RPs differs from pure singlet. We will call RPs, which carry this additional polarization, *AE-polarized*. The polarization itself is named, accordingly, *AE-polarization*. Individual radicals, which AE-polarized RP is composed from, carry net polarization, whether absorptive (A) or emissive (E), of opposite sign and the same magnitude. The origin of AE-polarization is coherent evolution of RP spin state prior to ESE experiment.

## 2. Theory and calculation method

The spin-Hamiltonian of a radical pair in the high-field approximation ( $J, D \ll \mu g B_0$  for both spins) can be written as

$$\mathcal{H}_{\text{lab}} = \mu g_A B_0 S_{Az} + \mu g_B B_0 S_{Bz} + J(\mathbf{S}_A \cdot \mathbf{S}_B) + \frac{D}{2}(3 \cos^2 \theta_D - 1) \left( S_z^2 - \frac{1}{3} \mathbf{S}^2 \right). \quad (1)$$

Here spin operators of radicals are denoted as  $\mathbf{S}_i$  ( $i = A, B$ ),  $\mathbf{S} = \mathbf{S}_A + \mathbf{S}_B$ ,  $\mu$  is a Bohr magneton,  $B_0$  represents strength of the magnetic field,  $J$  and  $D$  are the values of exchange and dipolar interaction correspondingly,  $\theta_D$  is an angle between line connecting spins and direction of the external magnetic field  $\mathbf{B}_0$  and, finally,  $g_A$  and  $g_B$  denote effective g-factors of two species in radical pair. In Hamiltonian (1) we omit possible nonaxiality of dipole interaction tensor and use point-dipole approximation. The Hamiltonian (1) does not contain hyperfine interactions because number of interacting nuclei is too large. Instead of writing down all the terms explicitly they are taken into account by inhomogeneous broadening of individual resonant lines. Anisotropy of g-tensors in the treated systems is small, so effective g-factors of each radical can be evaluated as

$$g_i = g_{iXX} \sin^2 \theta \cos^2 \phi + g_{iYY} \sin^2 \theta \sin^2 \phi + g_{iZZ} \cos^2 \theta, \quad (2)$$

where  $g_{iXX}$ ,  $g_{iYY}$ ,  $g_{iZZ}$  are principal values of corresponding g-tensor and polar and azimuthal angles  $\theta$ ,  $\phi$  define an spatial orientation of g-tensor.

It is convenient to express equations in terms of angular frequency. Then Hamiltonian (1) in the rotating frame can be written as

$$\mathcal{H} = \omega_A S_{Az} + \omega_B S_{Bz} + J(\mathbf{S}_A \cdot \mathbf{S}_B) + \frac{D}{2}(3 \cos^2 \theta_D - 1) \left( S_z^2 - \frac{1}{3} \mathbf{S}^2 \right). \quad (3)$$

Here  $\omega_i = (g_i/g - 1)\omega + \Delta\omega_i$ , where  $\omega$  is a spectrometer microwave frequency,  $g_i$  is calculated using (2) and resonant g-factor  $g$  is defined by condition of resonance  $g\mu B_0 = \omega$ . The term  $\Delta\omega_i$  corresponds to spreading of Larmor frequency within inhomogeneously broadened EPR line of a radical. It is supposed that other quantities in (3) are also evaluated in angular frequency units.

Calculations can be performed with convenience in basis set which is a direct product of two spin  $S = \frac{1}{2}$  basis sets, i.e.  $|\alpha\alpha\rangle$ ,  $|\alpha\beta\rangle$ ,  $|\beta\alpha\rangle$  and  $|\beta\beta\rangle$ . Spin operators for two-spin system in this basis can be easily obtained as Kronecker product of corresponding one-spin operators.

CTS which can be observed in the experiment is a weakly coupled secondary RP<sub>2</sub> formed from strongly coupled primary precursor RP<sub>1</sub> by sequential electron transfer as shown on the scheme Fig. 1(a). On the Fig. 1(a)  $k_Q$  is the rate of formation of the secondary pair RP<sub>2</sub>, parameters  $j_1$ ,  $Q_1$  and  $j_2$ ,  $Q_2$  are the parameters controlling frequencies of singlet-triplet interconversion within RP<sub>1</sub> and RP<sub>2</sub>. For both pairs  $2Q_k$  is the difference of resonant frequencies  $\omega_A$  and  $\omega_B$  of two radicals,  $j_k$  arises from exchange and dipolar interactions [22].

It is important to note that saying “weakly coupled RP” we imply the case when  $|\omega_A - \omega_B| \gg J, D$ . For “strongly coupled RP” the inverse condition  $|\omega_A - \omega_B| \ll J, D$  is fulfilled.

Since primary pair RP<sub>1</sub> is formed from photoexcited molecular singlet it has antiphase, or multiplet, polarization. Polarization of observable weakly coupled pair RP<sub>2</sub> may differ from polarization of RP<sub>1</sub> owing to prior evolution of its spin state: if parameter  $j_1$  for primary RP<sub>1</sub> and formation rate  $k_Q$  are comparable, initial spin state of RP<sub>1</sub> has enough time to evolve.

We will split polarization and density matrix of secondary pair RP<sub>2</sub> into two conceivable contributions. For the sake of simplicity these two contributions will be treated separately. Such separation is allowed as far as density matrix obeys linear equation of motion, but actually there are no differently polarized observable pairs RP<sub>2</sub>, and polarization of RP<sub>2</sub> is a composition of these two contributions.

The first contribution to density matrix of RP<sub>2</sub> originates from spin-correlated state of primary precursor, i.e. pure singlet  $\rho_0^S = |S\rangle\langle S|$ . As  $S = (|\alpha\beta\rangle - |\beta\alpha\rangle)/\sqrt{2}$ , density matrix  $\rho_0^S$  is given by

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