

## Polaron Spin-Lattice Relaxation Time in $\pi$ -Conjugated Polymers from Optically Detected Magnetic Resonance

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We describe a method for obtaining the polaron spin-lattice relaxation time  $T_{SL}$  in  $\pi$ -conjugated polymers by measuring the optically detected magnetic resonance (ODMR) dynamics as a function of microwave power and laser intensity. The peculiar ODMR dynamics is well described by a spin dependent recombination model where both recombination and spin relaxation rates determine together the response dynamics. We apply this method to the spin 1/2 ODMR in films of pristine 2-methoxy-5-(2'-ethylhexyloxy) phenylene vinylene [MEH-PPV] polymer, as well as MEH-PPV doped with various concentrations of radical impurities. We obtained  $T_{SL} \sim 30 \mu\text{s}$  in pristine MEH-PPV, but substantially shorter when the magnetic impurities are added.

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Numerous studies have been recently completed for understanding the spin and magnetic field effects in organic semiconductors (OSEC) [1–4]. The surge in organic spin research stems from the premise of long carrier spin relaxation time  $T_{SL}$  in these materials due to the weak spin-orbit coupling caused by the light atoms of their building blocks; this property is very attractive for potential applications in Spintronics devices [1]. This proposition was recently supported by several demonstrations of organic spin valves using small molecule and polymer films as spacers between two ferromagnetic electrodes, where a relatively large spin-valve magnetoresistance response was measured [2–4]. Also low field magnetotransport response up to 10% was demonstrated in various organic light emitting diodes [5]. One of the important physical parameters in such organic spintronic devices is  $T_{SL}$  that determines the spin randomization rate, and ultimately the spin diffusion length in the OSEC active layer [1,2]. However, at the present time there is no method for determining  $T_{SL}$  of excess carriers (polarons) in OSEC. In this Letter we introduce a simple method for obtaining  $T_{SL}$  of polarons in OSEC, which is based on the dynamics of the optically detected magnetic resonance (ODMR) response in these materials.

Since ODMR involves the spin sublevels response to double excitation, namely, laser illumination (or carrier injection), and microwave (MW) radiation under spin resonance conditions [6]; then this technique is uniquely sensitive to both excess-carrier recombination rate  $\gamma$  and spin-lattice relaxation rate  $\gamma_{SL}$  ( $= T_{SL}^{-1}$ ). In principle ODMR may be described as electron spin resonance (ESR) of the optically generated (or electrically injected) excitations. Whereas the initial spin sublevel populations in ground state ESR measurements is determined by the temperature; under resonant MW radiation at saturation the relative sublevel population dynamics is mainly controlled by  $T_{SL}$  [7]. In contrast to ESR the sublevel populations in

ODMR continuously evolve due to excess-carrier generation and recombination kinetics, so that their MW modulation frequency ( $f$ ) response depends on *both* recombination and spin-lattice relaxation rates [8]. This renders the ODMR frequency response peculiar, and thus distinctly different from that of a single excitation, such as in photo-induced absorption (PA) or photoluminescence (PL).

Specifically, we show in this Letter that unlike the usual response dynamics of pump modulated  $PA(f)$  and  $PL(f)$ , the in-phase ( $I$ ) ODMR( $f$ ) component *reverses sign* at a modulation frequency  $f_0$ . Importantly we found that  $f_0$  depends on  $\gamma$ ,  $\gamma_{SL}$ , and the MW power,  $P_{MW}$ , and thus a thorough analysis of the ODMR dynamics response gives the important rates involved. In particular by analyzing the spin 1/2 ODMR dynamics as a function of  $P_{MW}$  and laser intensity ( $I_L$ ) using a simple spin dependent recombination model, we show that it is possible to obtain both  $\gamma$  and  $\gamma_{SL}$  (and hence also  $T_{SL}$ ) for polarons in OSEC. We demonstrate our powerful analysis for polarons in pristine films of 2-methoxy-5-(2'-ethylhexyloxy) phenylene vinylene [MEH-PPV], as well as MEH-PPV doped with various concentrations of magnetic nanoparticles and radical impurities. Our technique is not restricted to OSEC, or to spin 1/2 excitations; in fact we could equally well analyze the ODMR response in inorganic semiconductors, such as amorphous Si:H [9] with similar success.

The spin 1/2 ODMR (either PADMR or PLDMR) measurements were conducted at various temperatures  $T$  using a MEH-PPV film drop casted from a toluene solution that was mounted in a high  $Q$  ( $\sim 10^3$ ) MW cavity. The polymer film was excited using an  $\text{Ar}^+$  laser at 488 nm with intensities from 50 to 1500 mW/cm<sup>2</sup> subjected to spin 1/2 (i.e.,  $H = 1070$  Gauss) resonance conditions at MW frequency,  $f_{MW} \sim 3$  GHz ( $S$  band) [6]. We measured the dynamic changes  $\Delta PL(f)$  [ $\Delta PA(f)$ ] in PL [PA] caused by the magnetic resonance. Both the in-phase ODMR<sub>*I*</sub> and quadrature ODMR<sub>*Q*</sub> components were measured, where

the phase was set with respect to the MW modulation. In addition, the ODMR was also studied under variable MW power conditions, where  $P_{\text{MW}}$  was varied from 2.5 to 100 mW.

Figure 1(a) shows the spin 1/2 PLDMR response dynamics for the two ODMR components. A unique and peculiar feature is that  $\text{ODMR}_I(f)$  changes sign at a frequency  $f_0$  of  $\sim 30$  kHz, before decaying away at higher frequencies. This response is unique to  $\text{ODMR}_I$ ;  $\text{ODMR}_Q$ , on the contrary, retains its sign. Figure 1(b) shows that  $f_0$  increases with  $P_{\text{MW}}$ ; it increases more sharply at low  $P_{\text{MW}}$

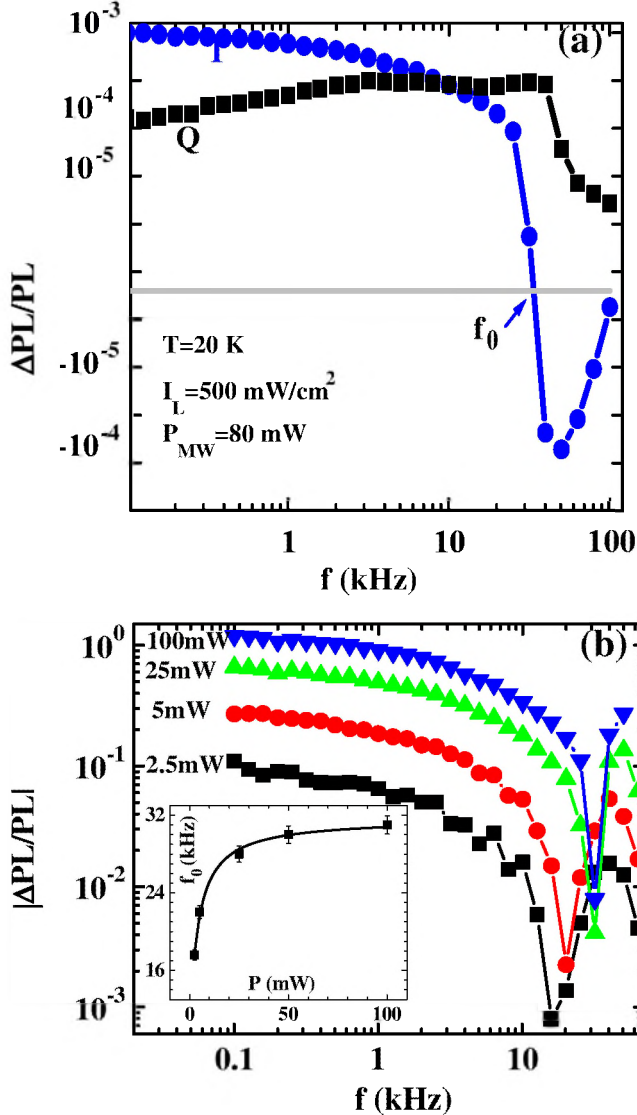


FIG. 1 (color online). (a) In-phase (●, blue or dark gray) and quadrature (■, black) spin 1/2 PLDMR vs the MW modulation frequency  $f$  in MEH-PPV film; zero crossing occurs at  $f_0$ . The positive and negative values are displayed, respectively, on a logarithmic scale above and below the gray horizontal line. (b) Absolute value  $|\text{PLDMR}_I|$  vs  $f$  for various  $P_{\text{MW}}$ , where the dip occurs at  $f_0$ . Inset: the zero-crossing frequency  $f_0$  vs  $P_{\text{MW}}$ .

and saturates at high  $P_{\text{MW}}$ . The  $P_{\text{MW}}$  dependence of the ODMR maximum value ( $[\text{ODMR}]_{\text{max}}$ ) at low  $f$  obtained from several dynamic responses such as in Fig. 1(b), is summarized in Fig. 2;  $[\text{ODMR}]_{\text{max}}$  shows a typical saturation behavior.

The surprising ODMR<sub>I</sub> “zero-crossing” at  $f_0$ , and its dependence on  $P_{\text{MW}}$  can be explained in detail by a spin dependent recombination model for polarons [6,10]. A variation of this model known in the literature as the “distant pair recombination model” [11] has been used previously in inorganic semiconductors [11,12]. In this model, polaron pairs with antiparallel spins (having population  $n_1$  and lifetime  $\tau_1$ ) recombine faster than polaron pairs with parallel spins (having population  $n_2$  and lifetime  $\tau_2$ ), i.e.,  $\tau_1 < \tau_2$ . If the polaron pair spin sublevel populations are formed with equal generation rate  $G$ , then at steady state (SS) conditions (i.e.,  $n_{\text{SS}} = G\tau$ ) without MW radiation (dark,  $d$ ) “spin polarization” is established; namely  $n_{1,d} < n_{2,d}$ . The MW radiation induces spin flips, and a new quasiequilibrium state,  $n_{\text{mw}}$  is established; where the MW induced change  $\Delta n = n_{\text{mw}} - n_d$  in the polaron density,  $n = n_1 + n_2$  is proportional to the ODMR signal [13]. The quantitative  $\Delta n(f)$  response can be then obtained from the solution of the following coupled set of two rate equations, written for the experimental conditions  $T \gg hf_{\text{MW}}/k_B \cong 0.14$  K [12]:

$$dn_i/dt = G - n_i/\tau_i - (n_i - n_j)/2T_{\text{SL}} - (n_i - n_j)P, \quad (1)$$

where  $i \neq j = 1, 2$ , and  $P$  is the MW induced spin-flip rate

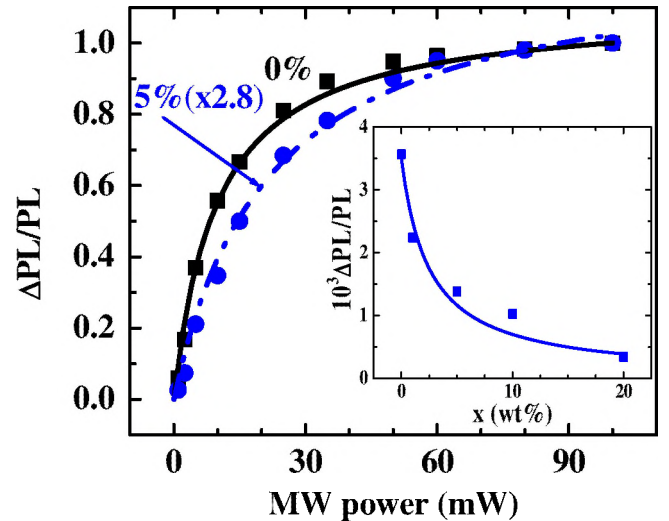


FIG. 2 (color online). ODMR<sub>max</sub> vs  $P_{\text{MW}}$  for pristine (■, black) and doped (●, blue or dark gray) MEH-PPV with  $x = 5$  wt% spin 1/2 radicals. The solid lines are fits using Eq. (2) with  $\gamma_{5\%}^* = 2.2\gamma_{0\%}^*$ , where the  $x = 5$  wt% is normalized to the pristine data. Inset: ODMR<sub>max</sub> vs  $x$  measured at saturation conditions. The solid line is a fit using Eq. (2) with  $\gamma_{\text{SL}}(x) - \gamma_{\text{SL}}(0) \propto x$ .

that is proportional to the modulated  $P_{\text{MW}}$ :  $P = \alpha P_{\text{MW}}$ . Equations (1) were solved numerically in response to the modulated MW radiation, yielding the components  $\Delta n_I$  and  $\Delta n_Q$  vs the modulation frequency  $f$ ; this procedure was repeated at various  $P$ 's.

A typical spin 1/2 ODMR( $f$ ) response based on the numerical calculation of Eqs. (1) is shown in Fig. 3. There are three important quantitative features of the calculated ODMR response that reproduce the data: (i)  $\Delta n_I$  changes sign at  $f_0$ ; (ii)  $\Delta n_Q$  does not change sign; and (iii)  $f_0$  increases with  $P$ .  $\Delta n_I$  sign reversal at  $f_0$  is unique to ODMR, and does not depend on the model or parameters used [8]; in fact it is a manifestation of the different recombination times  $\tau_i$  of the two coupled spin sublevels. This peculiar response occurs since under resonant MW radiation the density of one spin sublevel increases by an initial value  $\delta n$ , whereas the other decreases by the same amount. However,  $\delta n(t)$  decays faster in sublevel 1 than in sublevel 2. It thus follows that  $\Delta n_I(f)$  changes sign at a frequency  $f_0$  that roughly corresponds to the average decay rate of the two sublevels, but is also influenced by  $T_{\text{SL}}$ .

Solving Eqs. (1) using numerical methods, we thoroughly studied the dependence of  $\Delta n(\omega)$  response on the parameters  $G$ ,  $P$ , and  $T_{\text{SL}}$ , while keeping fixed the recombination rate  $\gamma = \frac{1}{2}(\tau_1^{-1} + \tau_2^{-1})$ . Since ODMR is closely related to ESR, we looked for a saturation behavior at large  $P$ . We found that  $\Delta n(\omega \cong 0)$  indeed saturates and may be written approximately as  $\Delta n(\omega \cong 0) \propto P/(\gamma^* + P)$ , where  $\gamma^* = C(\gamma, \gamma_{\text{SL}}, \Delta\gamma)$  [14]  $\cong \frac{2}{3}(\gamma + \gamma_{\text{SL}})$ , where  $\Delta\gamma = \frac{1}{2}(\tau_1^{-1} - \tau_2^{-1})$ . It is thus apparent that saturation

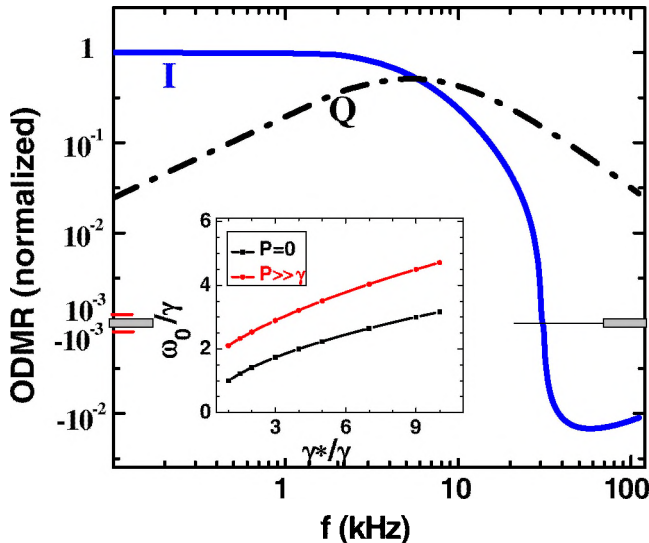


FIG. 3 (color online). The ODMR dependence on  $f$  calculated using Eq. (1) with  $\gamma = 4.4 \times 10^4 \text{ s}^{-1}$  and  $\gamma_{\text{SL}} = 3.6 \times 10^4 \text{ s}^{-1}$ , with same color (or shading) codes and symbols as in Fig. 1(a). The positive and negative values are displayed, respectively, on a logarithmic scale above and below the gray horizontal line. Inset:  $f_0$  vs  $\gamma^*/\gamma$  calculated at small and large  $P_{\text{MW}}$ .

depends on both  $\gamma$  and  $\gamma_{\text{SL}}$  (rather than on  $\gamma_{\text{SL}}$  alone as in ESR measurements). Next, we checked the low frequency response as a function of  $\gamma_{\text{SL}}$  while keeping fixed  $P$  at saturation (i.e.,  $P \gg \gamma^*$ ); we found that  $\Delta n$  is inversely proportional to  $\gamma^*$ . We may thus approximate the low frequency ODMR response by the relation

$$\Delta n(\omega \cong 0) \propto (G/\gamma^*)P/(\gamma^* + P). \quad (2)$$

This relation is in agreement with an approximate analytical solution of Eqs. (1) at low  $f$  [13]. In addition, the dependence of  $f_0$  on  $P$  was also obtained numerically for various  $\gamma^*/\gamma$  values. We found that  $\omega_0 \cong (\gamma\gamma^*)^{1/2}$  for  $P \ll \gamma^*$ . Also at  $P \gg \gamma^*$   $\omega_0$  continuously increases, then saturates at large  $P$ , in agreement with the data [Fig. 1(b)].

By fitting the experimental  $[\text{ODMR}]_{\text{max}}$  (Fig. 2), and  $f_0$  [Fig. 1(b) inset] as a function of  $P_{\text{MW}}$  using Eq. (2) and the  $f_0$  values at low and saturated  $P$ 's, we deduce the rates  $\gamma$  and  $\gamma^*$ . We thus obtained for polarons in pristine MEH-PPV  $\gamma \sim 4.4 \times 10^4 \text{ s}^{-1}$  and  $\gamma_{\text{SL}} \sim 3.6 \times 10^4 \text{ s}^{-1}$  (i.e.,  $T_{\text{SL}} \sim 30 \mu\text{sec}$ ) at  $I_L = 500 \text{ mW/cm}^2$ . The calculated response (Fig. 3) accurately reproduces the “zero crossing” of  $\Delta n_I(f)$  at the measured frequency, whereas  $\Delta n_Q(f)$  does not change sign.

In order to further study the ODMR dynamics we introduced magnetic impurities into the MEH-PPV film by mixing the polymer solution with a predetermined impurity dose [15]. Introducing even a small amount of spin 1/2 radical ions [the free radical used was 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)], or mixing with ferromagnetic  $\text{Fe}_3\text{O}_4$  nanoparticles gives rise to dramatic effects. As shown in Fig. 2 for the radicals: (i) the ODMR signal significantly decreases with the radical concentration  $x$ ; and (ii) the saturation of the ODMR signal occurs at higher  $P_{\text{MW}}$  in the mixed polymer-radical films. From the fit to the  $x = 5\%$  data using Eq. (2) we found that  $\gamma^*$  increases in doped MEH-PPV by a factor of  $\sim 2.2$  relative to the pristine MEH-PPV. Since the magnetic radicals are not expected to have a strong effect on the recombination rate  $\gamma$ , we conclude that the increase in  $\gamma^*$  ( $\propto \gamma + \gamma_{\text{SL}}$ ) is due mostly to a decrease in  $T_{\text{SL}}$  caused by the spin 1/2 radicals. Using the  $\gamma$  and  $T_{\text{SL}}$  values of pristine MEH-PPV obtained above, we find for the MEH-PPV/TEMPO film at  $x = 5\%$  that  $T_{\text{SL}}$  shortens by a factor of  $\sim 4$ .

In addition,  $[\text{ODMR}]_{\text{max}}$  measured under saturating MW power at  $f = 200 \text{ Hz}$  decreases with increasing radical concentration,  $x$  (Fig. 2, inset). This can be well explained by Eq. (2): the solid line (Fig. 2, inset) is a fit assuming that  $\gamma_{\text{SL}}$  increases linearly with  $x$ :  $\gamma_{\text{SL}}(x) - \gamma_{\text{SL}}(0) \propto x$ . Such a linear increase may occur via *spin-spin dipolar interaction* between the photogenerated polaron and radical spins, which randomizes their spins.

The variation in the ODMR dynamics with the laser intensity  $I_L$  provides additional insights as seen in Fig. 4: (i)  $f_0$  increases with  $I_L$ , and (ii)  $[\text{ODMR}]_{\text{max}}$  saturates at higher  $P_{\text{MW}}$  for higher  $I_L$ . From the fit to the ODMR

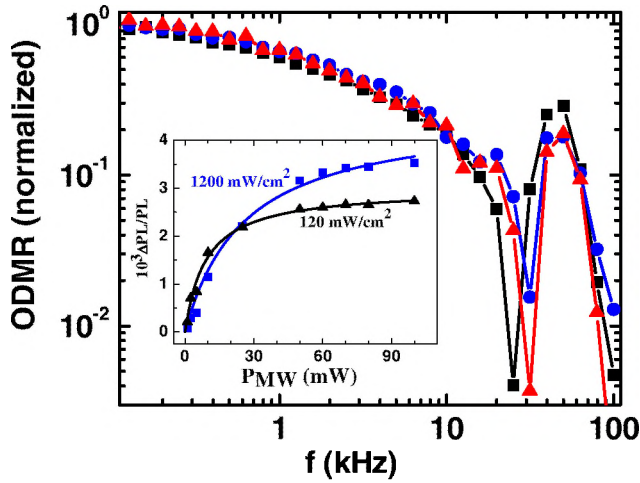


FIG. 4 (color online). Spin 1/2 PLDMR dynamics in pristine MEH-PPV for various laser excitation intensities,  $I_L$  at  $T = 20$  K and  $P_{MW} = 100$  mW.  $I_L = 90$  (■, black),  $500$  (●, blue or dark gray), and  $1500$  (▲, red or gray)  $\text{mW}/\text{cm}^2$ . Inset:  $\text{PLDMR}_{\text{max}}$  vs  $P_{MW}$  measured at  $f = 200$  Hz for  $I_L = 1200$  (■, blue or dark gray) and  $120$   $\text{mW}/\text{cm}^2$  (▲, black). The solid lines are fits obtained using Eq. (2), with  $\gamma_{1200}^* = 2.8\gamma_{120}^*$ .

saturation behavior at two  $I_L$  using Eq. (2), we obtained  $\gamma_{1200}^* = 2.8\gamma_{120}^*$ . The increase in  $\gamma^*$  also explains the corresponding increase of  $f_0$  with  $I_L$  seen in Fig. 4.  $\gamma^*$  increase with  $I_L$  may be explained by an increase in  $\gamma_{\text{SL}}$  via spin-spin dipolar interaction, similar to the mixed MEH-PPV/TEMPO discussed above; where the increased density of unpaired spin 1/2 polarons at large  $I_L$  plays the role of magnetic impurities. The obtained increase in  $\gamma^*$  may be also explained by an increase in  $\gamma$  caused by nonlinear recombination kinetics, where the magnetically coupled pair dynamics at high  $I_L$  is affected by neighboring paired and unpaired polarons. Our results thus indicate that  $T_{\text{SL}}$  of polaron pairs formed in organic light emitting diodes upon current injection should depend on the injected current

density, which is actually equivalent to introducing spin 1/2 magnetic impurities into the active film.

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