Comment on "Frequency response and origin of the spin-$\frac{1}{2}$ photoluminescence-detected magnetic resonance in a π-conjugated polymer"

C. G. Yang,[1] E. Ehrenfreund,[2] M. Wohlgenannt,[3] and Z. V. Vardeny[1,*]
[1]*Department of Physics, University of Utah, Salt Lake City, Utah 84112, USA*
[2]*Department of Physics and Solid State Institute, Technion-Israel Institute of Technology, Haifa 32000, Israel*
[3]*Department of Physics and Astronomy, The University of Iowa, Iowa City, Iowa 52242-1479, USA*
(Received 7 March 2006; revised manuscript received 5 September 2006; published 25 June 2007)

In a recent paper, Segal *et al.* [Phys. Rev. B **71**, 245201 (2005)] advanced a new explanation for the dynamics of spin-$\frac{1}{2}$ photoluminescence-detected magnetic resonance (PLDMR) in films of a π-conjugated polymer, namely, a soluble derivative of poly(phenylene-vinylene) (MEH-PPV), using a model [dubbed triplet-polaron quenching (TPQ)], in which the PLDMR is due to spin-dependent triplet-polaron interactions that reduce the polaron density and consequent quenching of singlet excitons. We studied a fuller PLDMR and photoinduced absorption (PA) and photoinduced absorption detected magnetic resonance (PADMR) dynamics (both frequency and time resolved) of MEH-PPV films as a function of microwave power at various temperatures. We show that (i) the TPQ model in the work of Segal *et al.* is incompatible with the extended frequency dependent spin-$\frac{1}{2}$ PLDMR response; (ii) the spin-$\frac{1}{2}$ PADMR and PLDMR dynamics are not the same, in contrast to the TPQ model; (iii) the TPQ model is not in agreement with the spin-1 PLDMR temperature dependence in relation to that of the spin-$\frac{1}{2}$ PLDMR; and (iv) the TPQ model predicts a much shorter triplet exciton lifetime than that obtained experimentally via PA. In contrast, the alternative model advanced previously [Z. V. Vardeny and X. Wei, in *Handbook of Conducting Polymers*, 2nd ed., edited by T. A. Skotheim, R. L. Elsenbaumer, and J. R. Reynolds (Dekker, New York, 1998), pp. 639–666], namely, the spin-dependent recombination of polarons, is capable of explaining the whole body of experimental results and, in particular, the spin-$\frac{1}{2}$ PLDMR and PADMR dynamics.

DOI: 10.1103/PhysRevB.75.246201 PACS number(s): 78.55.Kz, 76.70.Hb, 73.61.Ph

Segal *et al.*[1] reported the dynamics of spin-$\frac{1}{2}$ photoluminescence-detected magnetic resonance (PLDMR) and photoinduced absorption (PA) in films of the archetypal π-conjugated polymer, namely, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phnylenevinylene] (MEH-PPV) at 20 K. The spin-$\frac{1}{2}$ PLDMR dynamics was also measured using the double modulation PLDMR technique.[1] The authors claimed that the frequency response of the resonance is consistent with a triplet-polaron quenching (TPQ) model, in which the resonance is mediated by spin-dependent interactions between photogenerated triplet excitons (TEs) and polaron pairs in the film, which reduce polaron quenching of singlet excitons.[1] We measured the dynamics of both spin-$\frac{1}{2}$ and spin-1 PLDMR resonances in MEH-PPV films in an extended frequency range, as a function of microwave power, and at various temperatures; for completeness, we also measured the spin-$\frac{1}{2}$ PLDMR and photinduced absorption detected magnetic resonance (PADMR) time-resolved dynamics under resonance conditions. In this Comment, we show that the TPQ model in Ref. 1 is not compatible with our data. We checked that the alternative model, namely, the spin-dependent recombination (SDR) of polarons in organic semiconductors introduced before,[2] readily accounts for all the results.

In the TPQ model,[1] the photogenerated TE interacts with spin-paired polarons by collisions that enhance the polaron recombination. The spin dependence of the TE-polaron annihilation process in this model is a result of *spin conservation*. The spin subsystem of a colliding spin-1 TE and spin-$\frac{1}{2}$ polaron comprises six spin states of equal probability, with four states having spin-$\frac{3}{2}$ and the other two possessing spin $\frac{1}{2}$. After the TE is annihilated, the excited polaron with spin $\frac{1}{2}$ remains; therefore, spin conservation disallows $\frac{2}{3}$ of TE-polaron collisions. In this model, resonant spin-$\frac{1}{2}$ conditions induce rapid transitions between the spin-$\frac{1}{2}$ sublevels of the TE-polaron complex, so that all TE-polaron collisions become allowed.[1] The TPQ model for explaining the spin-$\frac{1}{2}$ PLDMR resonance is therefore viable under three important conditions, *which may be readily checked by the experiment*. (i) In addition to photogenerated polaron density, a substantial density of long-lived photogenerated TE should also exist in the film; (ii) the TE spin-lattice relaxation time should be longer than the TE-polaron collision time, so that their spin state is not randomized before colliding with the paired polarons; and (iii) the underlying mechanism for the spin-$\frac{1}{2}$ PLDMR resonance should be exciton quenching by polarons. Measuring spin-1 and spin-$\frac{1}{2}$, PLDMR and PADMR resonance dynamics, and PA of polarons and TE at various temperatures scrutinizes these three conditions, as reported below.

In addition, Segal *et al.*[1] also calculated the microwave frequency (f_M) response dynamics of the spin-$\frac{1}{2}$ PLDMR resonance based on the TPQ model [Eq. (26) in Ref. 1] and used this calculation to fit the experimental spin-$\frac{1}{2}$ PLDMR dynamics. Alas, only the magnitude ($|\Delta PL|$) of the spin-$\frac{1}{2}$ PLDMR frequency response was measured in Ref. 1, where $|\Delta PL|=[(\Delta PL_I)^2+(\Delta PL_Q)^2]^{1/2}$, and ΔPL_I and ΔPL_Q are the in-phase and quadrature components of the change ΔPL in the photoluminescence (PL) at resonance. Thus, important information on the spin-$\frac{1}{2}$ PLDMR dynamics was missed. In our PLDMR measurements, we obtained *both* ΔPL compo-

nents vs f_M at various microwave powers to ensure that we register a fuller dynamics of the spin-$\frac{1}{2}$ PLDMR resonance. When the extended PLDMR dynamics is unraveled, then it becomes obvious that the TPQ model as described in Ref. 1 fails to reproduce the data. This is important since the PLDMR dynamics can disclose the underlying mechanism for the resonance, and thus, the failure to reproduce the data shows that the TPQ model is not capable of explaining the PLDMR in π-conjugated polymers.

Furthermore, Segal *et al.* also measured the spin-$\frac{1}{2}$ PLDMR dynamics using a version of the double modulation (DM) optically detected magnetic resonance (ODMR) technique,[1] which was the "novelty" basis of a recent letter by the same group.[3] However, the DM-ODMR technique was applied ~20 years back to *a*-Si:H.[4] However, since this technique is rather insensitive and failed to unravel salient features in the ODMR dynamics, it has been abandoned in favor of the time-resolved ODMR,[5,6] which is much more powerful. In the present work, we have applied the time-resolved ODMR technique to study the spin-$\frac{1}{2}$ PLDMR and PADMR dynamics in MEH-PPV. We found that these two signals *do not share the same kinetics* as required in a polaron-exciton quenching model.[1] On the contrary, our results clearly show that the excess polaron recombination that is induced under resonance condition is mainly *radiative*, leading to excess PL emission when the microwaves are turned on. This behavior contradicts the TPQ mechanism,[1] but is, again, well explained by the SDR model in organic semiconductors.[2,7]

The PA and PLDMR measurements were conducted at various temperatures on a MEH-PPV film drop casted from a toluene solution that was mounted in a high Q microwave cavity. The polymer film was excited with an Ar^+ laser at 488 nm with an intensity of ~500 mW/cm^2 subjected to spin-$\frac{1}{2}$ (H=1070 G) or spin-1 (at "half field" H=370 G) resonance conditions at ~3 GHz (S band) microwave frequency.[2] For PA measurements, an incandescent light source was used, and the changes ΔT in the transmission T caused by the laser illumination at various modulation frequencies f_L were measured using a phase-sensitive technique. Both the in-phase and quadrature components of ΔT were routinely recorded. For PLDMR, we measured the changes ΔPL in PL caused by the magnetic resonance, where the microwave intensity was modulated at various frequencies f_M; again both the in-phase and quadrature ΔPL components were measured, where the phase ϕ was set with respect to the microwave modulation. In addition, the PLDMR was studied under variable microwave power conditions P in the range of 2.5–100 mW. We also monitored the transient response of both spin-$\frac{1}{2}$ PLDMR and PADMR under resonance conditions by measuring the time response of the modulated microwave-induced changes in PL and PA using a transient scope.[6] We checked that there are sufficient dynamic ranges in time and signal magnitude to unravel the ODMR dynamics.

Figure 1 shows the spin-$\frac{1}{2}$ PLDMR response vs f_M at 20 K and P=80 mW for the two ΔPL components; the magnitude $|\Delta\text{PL}|$ and the phase ϕ vs f_M were also calculated and shown for completeness. The measured $|\Delta\text{PL}(f_M)|$ response

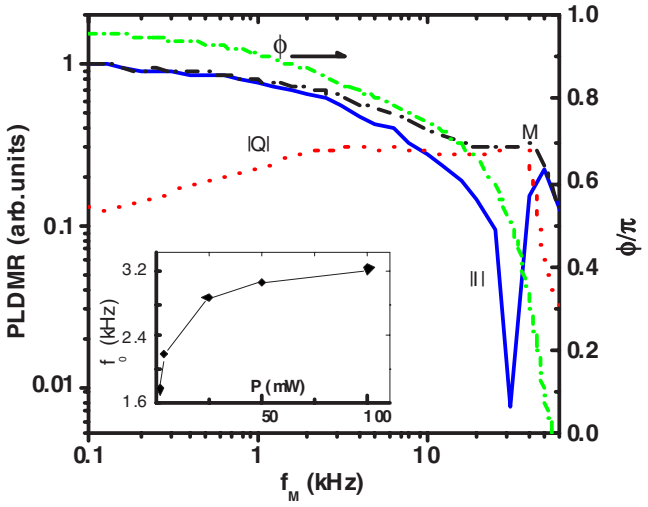

FIG. 1. (Color online) The spin-$\frac{1}{2}$ PLDMR, ΔPL vs the microwave modulation frequency f_M for a MEH-PPV film at 20 K. The in-phase (I, blue solid line) and quadrature (Q, red dotted line) PLDMR components are shown separately, as well as the magnitude $|\Delta\text{PL}|$ (M, black dash-dotted line) and the phase (ϕ, green short dash-dotted line; right scale). Note the zero crossing of the in-phase ΔPL component at $f_0 \approx 30$ kHz for microwave power P =50 mW. The inset shows the dependence of f_0 on P.

is quite similar to the response obtained in Ref. 1, indicating that the polymer sample and resonance conditions in the two laboratories are very similar. However, by measuring the microwave modulation frequency response of both ΔPL components, an unexpected surprise is unraveled; this was completely overlooked in Ref. 1. As seen in Fig. 1, the in-phase component $\Delta\text{PL}_I(f_M)$ *changes sign* at a frequency f_0 of about 30 kHz before decaying away at higher frequencies. Importantly, this response is unique for the in-phase component; the quadrature component retains its sign within the same experimental frequency range. The phase response $\phi(f_M)$ shows the sign change in $\Delta\text{PL}_I(f_M)$ more clearly; it crosses the value $\phi=\pi/2$ at ~30 kHz and continues to decrease thereof as f_M increases.

We checked that this curious PLDMR dynamic behavior is not an artifact of the measuring setup by changing the microwave power P. Figure 1 (inset) shows the dependence of f_0 on P. We found that f_0 increases with P, and thus, cannot be an artifact. Moreover, f_0 changes when varying the laser excitation intensity or when films of different polymers and semiconductors were measured. This bizarre PLDMR f_M response cannot be detected when measuring only the magnitude $|\Delta\text{PL}(f_M)|$; consequently, the *correct* PLDMR dynamics was missed in Ref. 1. Moreover, it cannot be explained by a simple one- or two-oscillator response, as introduced in Ref. 1, for $|\Delta\text{PL}|$ dynamics via the TPQ model. A much more profound understanding of PLDMR dynamic response must be involved to explain the astonishing $\Delta\text{PL}_I(f_M)$ dynamics and its dependence on P.[6]

We first attempt to explain the surprising PLDMR dynamics using the TPQ model introduced in Ref. 1. The spin-$\frac{1}{2}$ PLDMR vs f_M response was fitted in Ref. 1 using the following two-oscillator equation for the complex $\Delta\text{PL}(f_M)$ response [Eq. (26) in Ref. 1]:

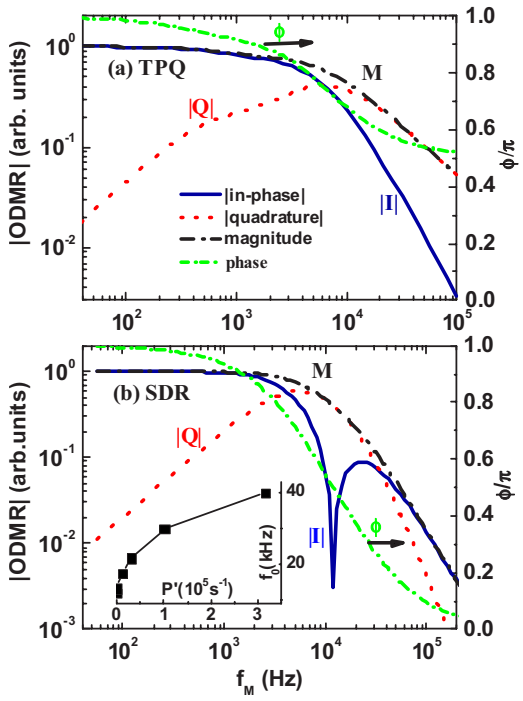

FIG. 2. (Color online) The spin-$\frac{1}{2}$ PLDMR dependence on f_M calculated using (a) the TPQ model [Eq. (1)] and (b) the SDR model [Eqs. (2) and (3)]. The response of the two PLDMR components is shown together with the magnitude $|\Delta PL|$ and the phase; the color codes and symbols are as in Fig. 1. The zero crossing of the in-phase component using the SDR model reproduces the data in Fig. 1. The inset in (b) shows that the calculated zero crossing frequency f_0 in the SDR model increases with the microwave power similar to the data in Fig. 1 (inset). [The abscissa in the inset, P', is proportional to the microwave power applied in the experiment, P, via $P'(1/s) \cong 6.7 \times 10^3 P$ mW.]

$$\Delta PL(f_M)/PL = c_M(i\omega + z_M)/[(i\omega + p_{M1})(i\omega + p_{M2})], \quad (1)$$

where c_M is a scaling factor, $\omega = 2\pi f_M$, and z_M, p_{M1}, and p_{M2} are some effective decay rates, which were determined by the TPQ model. Using the best fitting parameters given in Ref. 1, we calculated the two $\Delta PL(f_M)$ components, as well as the magnitude $|\Delta PL(f_M)|$ and phase $\phi(f_M)$ responses, as shown in Fig. 2(a). It is apparent that the TPQ model *cannot* describe the data in Fig. 1. (i) $\Delta PL_I(f_M)$ does not change sign; this is also seen in the ϕ response that does not decrease beyond $\phi = \pi/2$; (ii) the two bumps in $\Delta PL_Q(f_M)$ response using Eq. (1) are not reproduced in the experimental data; and (iii) there cannot be any dependence on the microwave power P, as seen experimentally, since Eq. (1) above is independent of P. We also tried to change the parameters z_M, p_{M1}, and p_{M2} in Eq. (1) so that a zero crossing occurs in $\Delta PL_I(f_M)$ response. For the unrealistic parameters $z_M > p_{M1} + p_{M2}$, there is indeed a change in sign; however, the sign change in $\Delta PL_I(f_M)$ is followed by a sign change in $\Delta PL_Q(f_M)$ as well, in disagreement with the experimental data in Fig. 1. We conclude that the TPQ model that apparently describes $|\Delta PL(f_M)|$ response in a small frequency range $f_M < f_0$ in Ref. 1 is, in fact, inadequate to describe the more complete $\Delta PL(f_M)$ response. This is *significant* since the more extensive spin $\frac{1}{2}$ PLDMR response gives a clue as to the underlying physical process responsible for the resonance.

On the contrary, the previous model in which the polaron recombination is spin dependent (the SDR model[2]) describes the fuller PLDMR dynamics. This model, also known in the literature as "distant pair recombination model," has been used previously in various inorganic[6,8–11] and organic semiconductors.[2,7,12,13] In the SDR model, polaron pairs with antiparallel spins (having population n_1) recombine faster than polaron pairs with parallel spins (having population n_2). If the polaron pairs are generated with equal initial populations, then "spin polarization" is established by the different recombination rates of parallel and antiparallel pairs, since at steady state conditions $n_1 < n_2$. Microwave absorption reverses the spin sense of some of the polaron pairs so that at saturation $n_1 = n_2$. Therefore, the resonance conditions enhance the overall polaron recombination rate, and consequently, the polaron density decreases as seen in the experiment.[2,13] Whether the PL increases due to reduction in polaron quenching of singlet excitons[1] or/and due to polaron pair radiative recombination[7] is a secondary question, the answer of which is dependent on the polymer film nanomorphology,[14] and thus, has little to do with the spin-$\frac{1}{2}$ PLDMR kinetics.

The spin-$\frac{1}{2}$ PLDMR dynamics in the SDR model is described by a pair of rate equations given by[6]

$$dn_1/dt = G - n_1/\tau_1 - (n_1 - n_2)/2T_{sl} - (n_1 - n_2)P, \quad (2)$$

$$dn_2/dt = G - n_2/\tau_2 - (n_2 - n_1)/2T_{sl} - (n_2 - n_1)P, \quad (3)$$

where G is the generation rate, τ_1 and τ_2 are the lifetimes of polaron pairs with spin antiparallel and parallel, respectively, and T_{sl} is the polaron spin-lattice relaxation time. The coupled Eqs. (2) and (3) were solved numerically, and the change Δn in the polaron density due to the modulated microwave power $P = P_0[1 + \cos(2\pi f_M t)]$ was calculated for various frequencies f_M. The two Δn components, namely, Δn_I and Δn_Q, as well as $|\Delta n|$ and the phase ϕ were obtained as a function of f_M; this procedure was repeated at various P. In addition, an analytical approximate solution to equations close in form to Eqs. (2) and (3) also gives results similar to our numerical solution.[15] A typical spin-$\frac{1}{2}$ ODMR f_M response based on the numerical calculations of Eqs. (2) and (3) is shown in Fig. 2(b). The f_M dynamics was obtained with the following parameters: $\tau_1 = 14$ μs, $\tau_2 = 60$ μs, and $T_{sl} = 10$ μs. In contrast to the TPQ model discussed above, it is seen that the elegant SDR model excellently describes all the PLDMR experimental response features. (i) The in-phase ODMR component correctly changes sign at f_0, followed by the phase ϕ passing the value $\phi = \pi/2$; (ii) the quadrature ODMR component is rather smooth and does not change sign; and (iii) the calculations reproduce the increase of f_0 with P [Fig. 2(b) inset]. The change in sign of the in-phase ODMR is quite natural in the SDR model and does not depend on the parameters used; in fact, it shows that the two spin states (n_1 and n_2) involved in the resonance have indeed

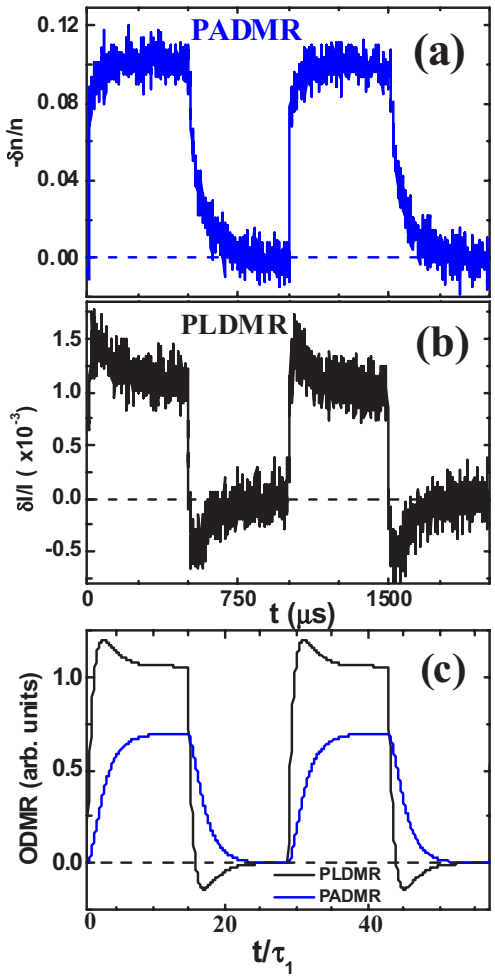

FIG. 3. (Color online) The ODMR transient response upon microwave power modulation at $f_M=1$ kHz for a MEH-PPV film at 20 K and spin-$\frac{1}{2}$ resonance conditions: (a) PADMR(t) in blue and (b) PLDMR(t) in black. The microwave power is turned on at $t=0$, and again at $t=1$ ms. (c) Simulation of the ODMR transient response using the SDR model with the same parameters, as in Fig. 2(b), and adding $\tau_{R1}=50$ μs and $\tau_{R2}=0.7$ ms for n_1 and n_2, respectively. The color codes are as in (a) and (b) above.

different recombination rates.[16] We therefore conclude that the SDR model is capable of describing the spin-$\frac{1}{2}$ PLDMR dynamics in full, whereas the TPQ model does not.

Figure 3 shows the time-resolved spin-$\frac{1}{2}$ ODMR signal under resonance conditions;[6] both PADMR(t) and PLDMR(t) are shown for comparison. Both signals follow the microwave modulation; PA is reduced and PL increases when the microwave power P is turned on. This shows that indeed polaron recombination is enhanced under resonance conditions,[13] and consequently, the PL is also enhanced. However, the two transients *do not share the same dynamics*. It is seen that the PLDMR response is much faster than that of the PADMR response. In particular, PLDMR(t) shows an abrupt peak when P is turned on and off, whereas PADMR(t) does not; this response cannot be explained by a simple quenching model.[1] In the quenching model,[1] where photogenerated polarons quench PL emission by enhancing the singlet exciton recombination or their nonradiative rate, the spin-$\frac{1}{2}$ PLDMR(t) should exactly follow that of PADMR(t), since it is driven by the change in polaron density at resonance. Since PLDMR(t) does not follow PADMR(t), it shows that another physical mechanism is involved in the spin-$\frac{1}{2}$ PLDMR process. The excess peak in PLDMR(t) hints at what this mechanism might be, namely, *radiative recombination of polarons*.[7] We thus explain our results by microwave-induced enhanced polaron radiative recombination under magnetic resonance conditions, as proposed before.[7] Similar time-resolved PLDMR(t) dynamics were recently analyzed in inorganic semiconductors,[6,11] and it was concluded that the enhanced peak at the onset of the microwave transient is indeed due to radiative recombination. Figure 3(c) shows a model calculation based on the SDR parameters used above for explaining the ODMR(f_M) response. By introducing a radiative recombination rate (time) to n_1 that is much larger (shorter) than that for n_2, namely, $\tau_{R1}=50$ μs and $\tau_{R2}=0.7$ ms, we get spin-$\frac{1}{2}$ PADMR(t) and PLDMR(t) responses in agreement with the data. First, PADMR(t) and PLDMR(t) responses do not follow each other. Second, the simulation correctly reproduces the peak in PLDMR(t) at the onset of $P(t)$. We note that the salient but important response of PLDMR(t) at the onset of $P(t)$ cannot be detected in single- or DM-PLDMR measurements as done in Ref. 1; this is unique to the transient response measured here.

Next, we studied the ODMR and PA dynamics as a function of temperature θ. Figure 4(a) shows the temperature dependencies of the spin-$\frac{1}{2}$ and spin-1 PLDMRs, as well as that of the PA of polarons and T. Whereas the spin-1 PLDMR sharply decreases with θ, indicating that the TE spin-lattice relaxation rate dramatically increases with θ, the spin-$\frac{1}{2}$ PLDMR hardly changes with θ. This shows that at high temperatures the TE does not conserve spins, and thus, *cannot participate in spin-dependent collisions between TE and polarons*, as required by the TPQ model.[1] In particular, consider the situation at $\theta>110$ K; the TE spin relaxation rate is so large that the spin state of the TE species is completely randomized [Fig. 4(a)]. Under these conditions, the TPQ that is based on spin conservation simply *cannot be operative*, yet the spin-$\frac{1}{2}$ PLDMR hardly changes at $\theta>110$ K. Figure 4(a) shows that the dramatic increase in TE spin-lattice relaxation rate with θ has no influence over the spin-$\frac{1}{2}$ PLDMR resonance; the polaron and TE spin dynamics are simply *not correlated*, in contrast to the TPQ model requirements.[1]

Figure 4(a) also shows the PA temperature dependence of TE species measured at 1.35 eV and polarons measured at 0.4 eV.[17] In agreement with the spin-$\frac{1}{2}$ PLDMR, the polaron PA hardly changes with θ. In contrast, the triplet PA decreases with θ by more than an order of magnitude up to 200 K. The decrease in TE density with θ apparently does not have much influence on the spin-$\frac{1}{2}$ PLDMR resonance, or polaron PA response; in contrast to the conditions stated above for the TPQ model.[1] In particular, at $\theta>180$ K, the TE density is so small that it is hard to believe that TE still dominates the spin-$\frac{1}{2}$ PLDMR resonance. In fact, the small

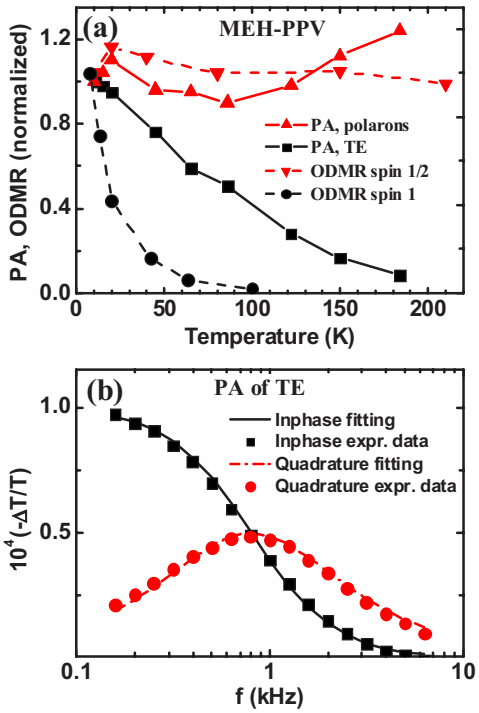

FIG. 4. (Color online) (a) The temperature dependence of the spin-$\frac{1}{2}$ PLDMR (red triangles) and spin-1 (black circles) resonances, plotted together with the temperature dependence of the PA of polarons (red triangles) and triplet excitons (TE; black squares). (b) The PA dependence on the laser modulation frequency f_L for the TE. Both the in-phase (black squares) and the quadrature (red circles) components are shown; the line through the data points is a fit with a single time constant τ=200 μs.

TE density in other polymers, independent of the temperature was also discussed in Ref. 18 as the basis of a separate comment on the TPQ model in Ref. 3.

Finally, we also examined the TE dynamics at low temperatures. Figure 4(b) shows the two components of the PA response at 1.35 eV vs the laser modulation frequency (f_L). It is seen that the TE recombination kinetics is very well described by a *single time constant*, namely, τ=200 μs. This long time constant [Fig. 4(b)] is about an order of magnitude longer than τ=25 μs, extracted for the TE using the TPQ model for the spin-$\frac{1}{2}$ PLDMR and PA dynamics in Ref. 1. Moreover, it also shows that a single, intrinsic time constant is sufficient to describe the TE dynamics, in contrast to Ref. 1 in which the proper description of the TE dynamics requires additional time constants. These show that the TPQ model once again disagrees with the data.

In conclusion, by measuring the full dynamics of the spin-$\frac{1}{2}$ and spin-1 PLDMRs as a function of microwave power and temperature, both in the frequency and time domains, together with the PA dynamics vs temperature, we show here that the TPQ model introduced in Ref. 1 cannot properly describe the PLDMR and PA responses in MEH-PPV films. In contrast, the competing model, namely, the spin-dependent recombination of polarons,[2] which has been extensively used in previous publications, describes well the whole body of experimental results and, in particular the transient ODMR response.

We thank the NSF for support through DMR Grant No. 05-03172 at the University of Utah. E.E. acknowledges the support of the Israel Science Foundation (735/04).

*Corresponding author; val@physics.utah.edu

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