

Spin and spectral signatures of polaron pairs in π -conjugated polymers

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ABSTRACT

We have studied polaron pair photoexcitations in a variety of π -conjugated polymer films by photoinduced absorption (PA) and optically-detected magnetic resonance (ODMR). An exchange interaction between polarons broadens the ODMR spectrum, permitting the unambiguous identification of the polaron pair species. Both isotropic and anisotropic exchange interactions have been observed. An isotropic exchange interaction broadens the spin-1/2 resonance associated with polarons, whereas an anisotropic exchange interaction gives rise to both full-field and half-field powder patterns. We have successfully modelled the observed spin-1/2 ODMR spectra and estimate the strength of the isotropic exchange interaction J . Both polarons and polaron pairs are characterized by two absorption bands. The high energy PA band of polaron pairs is blueshifted with respect to that of isolated polarons.

Keywords: Polaron pair conjugated polymer ODMR photoinduced absorption

1. INTRODUCTION

The initial report of electroluminescence from poly(*p*-phenylene vinylene) (PPV) thin films¹ has stimulated extensive studies of photoexcitation dynamics in π -conjugated polymers.² For both practical and theoretical reasons, decay processes which affect the radiative quantum yield η are of great interest. The primary photoexcitations in π -conjugated polymers are intrachain singlet excitons, formed with nearly unit quantum yield^{3,4} and having binding energies of a few tenths of an eV.⁵⁻⁷ The exciton thermalizes within 1 ps by relaxation in the polymer chain followed by migration to chain segments with the lowest energy (longest conjugation).⁸⁻¹⁰ Photoluminescence (PL) arises from radiative decay of singlet excitons. Nonradiative decay channels include intersystem crossing to form triplet excitons and interchain charge transfer leading to the formation of polarons or polaron pairs.¹¹⁻¹³

The PL efficiency of polymer films is significantly lower than that of solutions or dilute blends with inert polymers.¹⁴ The drop in η is accompanied by changes in fast (ps) photoexcitation dynamics. The PL of solutions and blends of PPV derivatives decays nearly exponentially, whereas the PL of most films exhibits nonexponential decay with long-lived components.¹² It has been suggested that interchain polaron pairs bound by Coulomb attraction are the primary photoexcitations in polymer films.¹¹⁻¹² Much speculation has focused on the transient photomodulation (PM) spectra, which contain both stimulated emission and photoinduced absorption (PA) bands. The difficulty in identifying polaron pair photoexcitations lies in the complexity of PM spectra. In the ps time domain, the existence of electronic states with energies above the gap gives rise to PA bands with dynamics matching those of the PL.¹⁵ Moreover triplet excitons and polarons may also contribute to the PM spectrum. Similar difficulties exist in the analysis of the steady state (ms) PM spectra. Hence, arguments regarding assignment of the PM spectra have been indirect.

We have studied polaron pairs in π -conjugated polymer films using PA and optically detected magnetic resonance (ODMR). Studies of the magnetic field effect on the photoconductivity of π -conjugated polymer films have led Frankevich *et al.*¹⁶ to suggest that exchange coupling between polarons plays a significant role in the dissociation of pairs to create charge carriers. The exchange interaction results from a coupling of the spatial coordinates of an ion (polaron) pair to their spins.¹⁷ While the exchange interaction depends upon the coordinates of the electrons forming the pair, the complete wave function of the system must be antisymmetric with respect to electron exchange. Hence, the orbital and spin functions are coupled and the spins act

as indicators of the nature of the orbital states. The exchange interaction modifies the magnetic resonance spectra of polaron pairs, but not that of isolated or loosely correlated polarons. Hence, ODMR can thus be used to identify polaron pairs and measure their absorption spectra.

We have studied the following π -conjugated polymers: electrochemically polymerized polythiophene (e-PT), 2,5-dioctyloxy poly(*p*-phenylene vinylene) (DOO-PPV), and 2,5-dibutoxy poly(*p*-phenylene ethynylene) (DBO-PPE). We also measured C_{60} -doped films of DOO-PPV and DBO-PPE. Doping concentrations are stated in relation to the number of C_{60} molecules per repeat unit of the polymer (mol%). All samples measured are thin films either cast from solutions onto sapphire substrates or directly polymerized onto the substrates. Fullerene-doped films were prepared by dissolving C_{60} with the polymer in solution and spin-casting the film onto the substrate.

Photoinduced absorption (PA) spectroscopy uses standard phase-sensitive lock-in techniques with a modulated Ar^+ laser beam as a pump. Photoinduced changes ΔT in the sample transmission T are recorded to obtain the normalized changes in transmission ($\Delta T/T \propto \Delta\alpha d$, where d is the sample thickness and αd its optical density). The ODMR spectra were measured by monitoring microwave induced changes in PL (PLDMR) or PA (PADMR). PADMR combines the advantages of PA (spectral information) and electron spin resonance (spin selectivity) and is ideally suited to investigate polaron pair photoexcitations. The PADMR technique uses a cw pump beam and an IR probe beam to constantly illuminate the sample, which is mounted in a high Q microwave cavity (at 3 GHz) equipped with optical windows and a superconducting magnet producing a field H . Microwave resonant absorption, which are nominally modulated at 800 Hz, leading to small change, δT , in the probe transmission. This δT is proportional to δn , the change in the photoexcitation density n produced by the Ar^+ pump beam. δn is induced by transitions in the microwave frequency range that change spin-dependent recombination rates. Two types of PADMR spectra are obtained: the H-PADMR spectrum, in which δT is measured at a fixed wavelength λ , and the λ -PADMR spectrum, in which δT is measured at a constant H , in resonance, while the probe wavelength is varied.

2. MAGNETIC RESONANCE SPECTRA OF POLARON PAIRS

The spin-1/2 PLDMR¹⁸ and H-PADMR spectra of DBO-PPE are shown in Figure 1. The spectra consist of a Gaussian-shaped line with FWHM ≈ 12 Gauss superimposed upon a broad ($\sim 70G$ wide) resonance line. The two lines have the same dependence on temperatures, microwave power, and probe wavelength and are hence correlated. No half-field resonance is correlated with the $\sim 70G$ wide resonance, which rules out magnetic dipole interactions.¹⁹ The $\approx 1000G$ wide resonance due to triplet excitons has been previously measured.¹⁹ The narrow resonance is due to spin-1/2 excitations, i.e., charged polarons. We show below that the broader component of the spin-1/2 resonance can be explained by an isotropic spin exchange interaction between two polarons with dissimilar g values.

DOO-PPV has a high PL quantum yield¹⁵ and shows little evidence of polaron pair formation. However, charge transfer in fullerene/polymer blends will create a high steady state population of positive polarons on the polymer chains and negatively-charged C_{60} anions. The steady state excitation density of any excitation is given by the relation $N_{SS} = G\eta\tau$ where G is the generation rate per cubic cm, η is the quantum yield and τ the excitation lifetime. For our system, $G = 6 \times 10^{23} \text{ cm}^{-3} \text{ sec}^{-1}$. If we assume a unit quantum yield for exciton dissociation and an excitation lifetime of $\tau > 1$ ms below 100K, we find $N_{SS} \geq 6 \times 10^{20} \text{ cm}^{-3}$. This actually exceeds the density of fullerene molecules in the film. Fullerene doping also results in quite dramatic changes to the PLDMR spectrum. The spin-1/2 PLDMR spectra of pristine and 10 mol% C_{60} :DOO-PPV is shown in Figure 2. The PLDMR of the doped sample is roughly 10 times as intense as that of the undoped sample. The most striking difference between the two spectra is the appearance of a $\sim 200G$ wide resonance about $g \approx 2$ with clearly resolved shoulders at 1045 and 1095G. The broad resonance in C_{60} -doped DOO-PPV is accompanied by a weak "half-field" PLDMR signal has been observed at 530G in doped DOO-PPV (not shown).

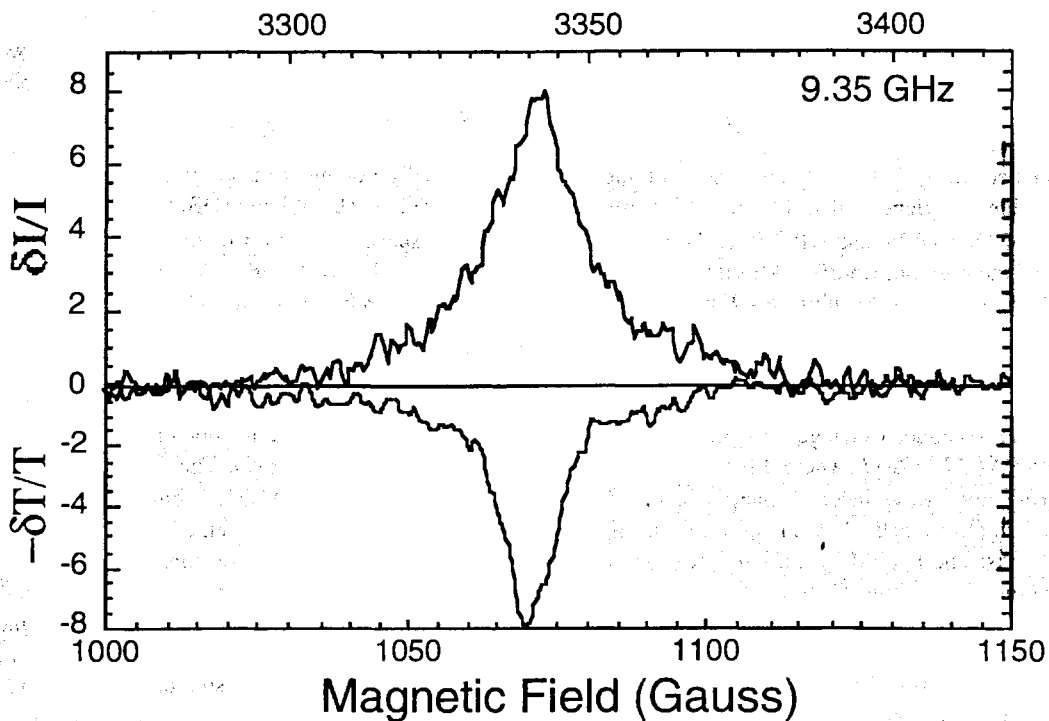


Figure 1. (a) PLDMR and (b) H-PADMR spectra of DBO-PPE.

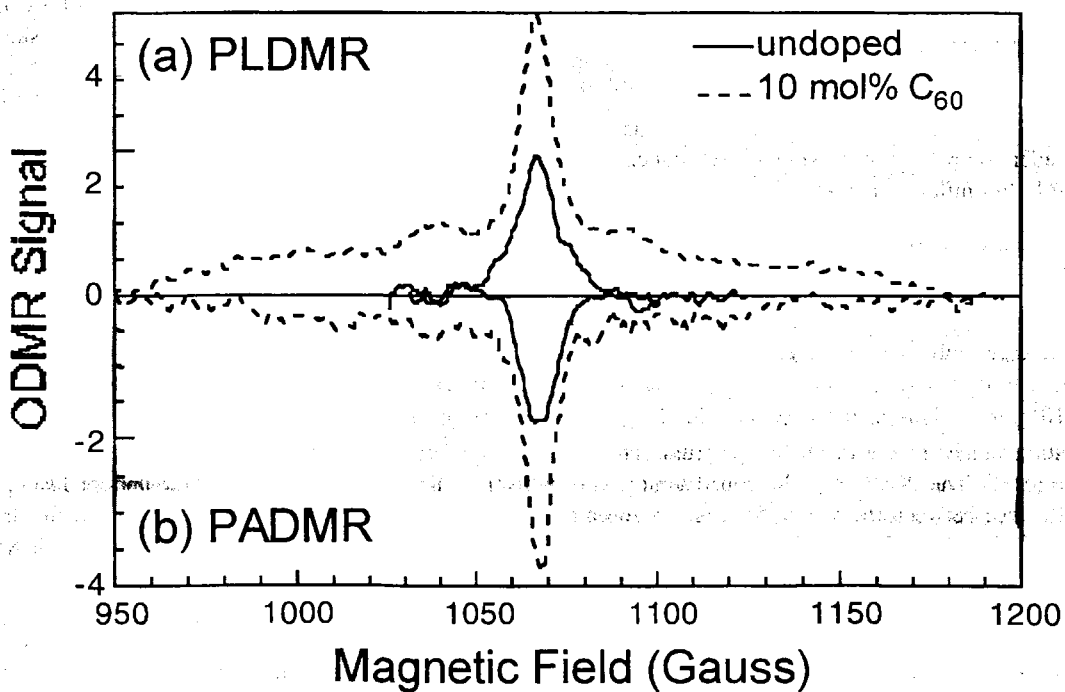


Figure 2. (a) PLDMR and (b) H-PADMR spectra of pristine and 10 mol% C₆₀:DOO-PPV.

There are several possible explanations for the observed broad resonant spectrum (BRS) and its accompanying "half-field" resonance. This excitation must have spin 1 (else no half-field resonance) and cannot be triplet excitons native to PPV as the BRS is much narrower than that previously observed by ODMR.^{20,21} The observed BRS does resemble that of photoexcited C_{60} triplets,²² but this explanation is problematic. The PL of the composite film is due to emission from singlet excitons on DOO-PPV. Hence, any excitation on C_{60} could only indirectly influence the PL. Moreover, magnetic resonant enhancement of $^3C_{60}$ decay would lead to the creation of more PPV^+/C_{60}^- defect centers, yielding a PL-quenching resonance, not an enhancing one. Spin-correlated polaron pairs can explain the BRS feature and its "half-field" companion. For a fullerene-polymer blend, the PPV^+ polaron could be bound to either a PPV^- polaron on the polymer chain or a C_{60}^- molecule. We have not observed a similar resonance in pure DOO-PPV; it is therefore reasonable to suggest that the BRS and its half-field companion are due to bound P^+/C_{60}^- complexes.

The broad, spin-1/2 resonances observed in Figures 1 and 2 can be understood as due to spin exchange interactions between the polarons composing the pair. We first consider an isotropic exchange interaction. The spin Hamiltonian is written:

$$H_{S-S} = g_e \beta \vec{H} \cdot \vec{S}_e + g_h \beta \vec{H} \cdot \vec{S}_h + J \vec{S}_e \cdot \vec{S}_h \quad (1)$$

where β is the Bohr magneton, $\vec{S}_{e,h}$ are the spins of the positive and negative polarons, the gyromagnetic tensors \vec{g}_e and \vec{g}_h are assumed to be isotropic, and \vec{H} is the magnetic field. This Hamiltonian has four eigenstates. In the case where $g_e = g_h$, the singlet spin sublevel has quantum numbers $S=0$, $m_S=0$ and energy $E_S = +3J/4$ and the triplet sublevels have quantum numbers of $S=1$, $m_S = -1, 0, +1$ and energy $E_T = -J/4 + g\beta H m_S$. Transitions between singlet and triplet sublevels are forbidden and the magnetic resonance spectrum has a single triplet-triplet transition at $H_0 = h\nu / g\beta$. However, if $g_e \neq g_h$, the two $m_S = 0$ spin sublevels have mixed singlet and triplet character. The magnetic resonance spectrum consequently has contributions from singlet-triplet transitions which occur at $H \equiv \frac{1}{2}(g_e + g_h)\beta / h\nu \pm J$ for $J \gg \delta g\beta H$. The transition rate R_{ij} between two coupled states is given by Fermi's Golden Rule²⁵ $R_{ij} = \langle i | \mathcal{C} | j \rangle^2$, where \mathcal{C} is the microwave perturbation. The transition fields and amplitudes are plotted in Figure 3 as a function of J . The two outer lines, associated with singlet-triplet transitions, move further away from H_0 and rapidly weaken as J increases. It is important to note that the $\Delta m_S = 2$ transition is *strictly forbidden* for an isotropic spin-exchange interaction, so there is no half-field resonance.

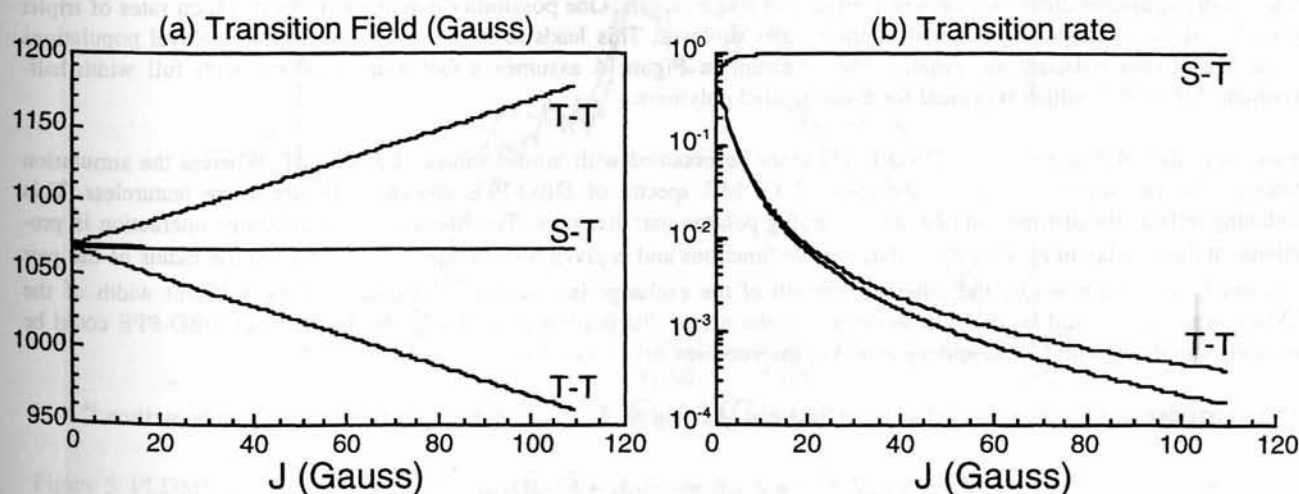


Figure 3. Magnetic resonance (a) resonant fields and (b) transition rates for an isotropic exchange interaction and 3 Ghz microwaves. Triplet-triplet (T-T) and singlet-triplet (S-T) transitions are marked.

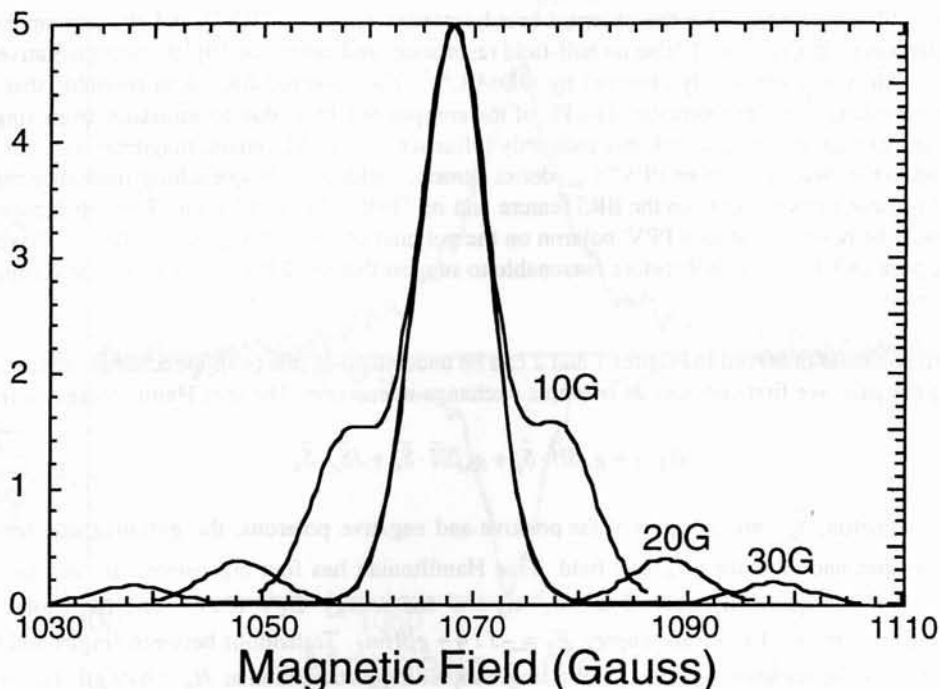


Figure 4. Simulated ODMR spectra for polaron pair with J varying between 10 and 30 G.

Figure 4 shows a simulated ODMR spectrum resulting from an isotropic exchange interaction between a pair of dissimilar ($g_e \neq g_h$) polarons with $J = 10, 20,$ or 30 G. We take into account the g -value of the polarons, generation and recombination rates for each spin sublevel, and the width of the polaron resonance itself. In most conjugated polymers, contributions from the negative and positive polarons cannot be resolved. We therefore take $\delta g \beta H \cong 1G$, which corresponds to g -values of 2.001 and 2.003, respectively, for the interacting positive and negative polarons. For the isotropic spin-exchange interaction to result in a significant broadening of the polaron resonance, population differences among the triplet sublevels must be much smaller than population difference between triplet and singlet levels. One possibility is that the recombination rates of triplet sublevels may be much slower than that of the singlet sublevel. This leads to high steady state triplet sublevel populations and the desired spin polarization. Finally, the spectrum in Figure 4 assumes a Gaussian lineshape with full width half-maximum $\Delta H = 10G$, which is typical for π -conjugated polymers.

A good fit to the ODMR spectra of DBO-PPE cannot be obtained with single values of J and ΔH . Whereas the simulation spectra exhibit two distinct satellites, the spin-1/2 ODMR spectra of DBO-PPE shown in Figure 1 are featureless. This broadening reflects the distribution of J due to varying polaron pair distances. The strength of the exchange interaction is proportional to the overlap integral of the polaron wave functions and is given by $J = J_0 e^{-2r/r_0}$, where r is the radius of the pair and r_0 and J_0 are determined by the inherent strength of the exchange interaction.^{23,26} Because of the inherent width of the ODMR spectrum, it would be difficult to determine the actual distribution of J . The ODMR spectra of DBO-PPE could be adequately simulated with $J=12G$ and a FWHM of the satellites $\Delta H=25G$.

We now consider anisotropic spin exchange interactions. As long as $\delta g \beta H \ll J$, the spin Hamiltonian can be written:²⁴

$$\begin{aligned}
 H_{SS} &= g_e \vec{H} \cdot \vec{S}_e + g_h \vec{H} \cdot \vec{S}_h + J \vec{S}_e \cdot \vec{S}_h + \vec{S}_e \cdot \vec{D}_J \cdot \vec{S}_h \\
 &= \bar{g} \beta H m_S + J \left[S^2 - 3/2 \right] + \frac{1}{2} (J_x S_x^2 + J_y S_y^2 + J_z S_z^2)
 \end{aligned}
 \tag{2}$$

where S and m_S are the spin quantum numbers. Eq. (2) has an even (singlet) solution at $E_S = -\frac{3}{4}J$ and three odd (triplet) solutions centered at $E_T = \frac{1}{4}J$. As \bar{D}_J is traceless, H_{SS} can be written in terms of two independent parameters: $D = \frac{3}{4}J_z'$ and $E = \frac{1}{4}(J_x' - J_y')$. D' and E' are referred to as the zero-field splitting (ZFS) parameters due to the exchange interaction. The spin Hamiltonian ${}^3H_{SS}$ for the odd solutions now reads:

$${}^3H_{SS} = \bar{g}\beta H m_S + J[S^2 - 3/2] + D(S_z^2 - \frac{1}{3}S^2) + E(S_x^2 - S_y^2) \quad (3)$$

This spin Hamiltonian has the same form as that of a regular triplet exciton with a singlet-triplet splitting of J and ZFS parameters D' and E' . Due to this similarity, it would be difficult to distinguish between triplet powder patterns due to magnetic dipole interactions from those due to spin-exchange interactions. The full-field power pattern will have

singularities at
$$H = H_0 \pm (D - 3E)/2 \quad (8a)$$

shoulders at
$$H = H_0 \pm (D + 3E)/2 \quad (8b)$$

and steps at
$$H = H_0 \pm D \quad (8c)$$

We simulated the magnetic resonance spectrum of C_{60} :DOO-PPV by adding a Gaussian line at $g \approx 2$ due to non-interacting polarons to an anisotropic spin-exchange triplet powder pattern with ZFS parameters $D = 122G$ and $E = 15G$. The simulation, shown in Figure 5, is in good agreement with the experimental data.

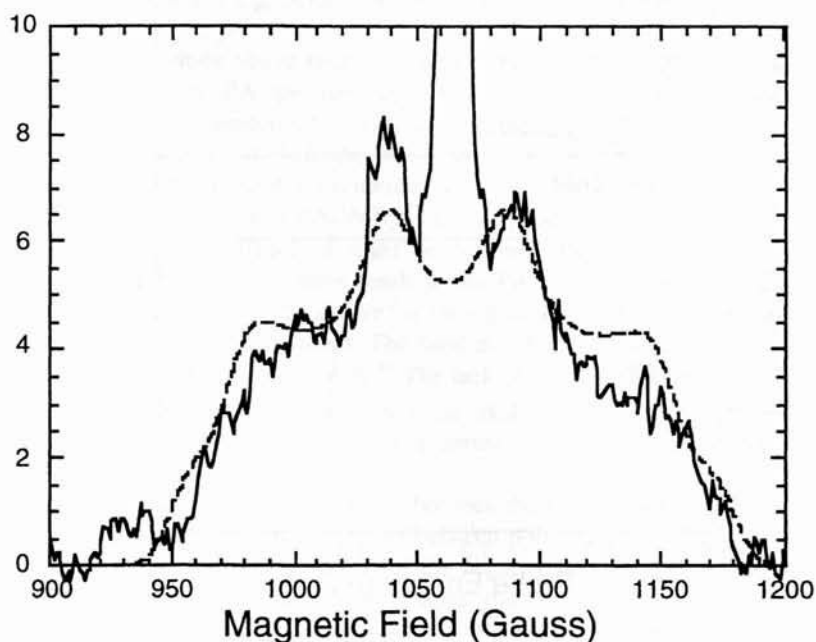


Figure 5. PLDMR spectrum of 10 mol% C_{60} :DOO-PPV (solid line) and anisotropic spin exchange spectrum (dashed line).

3. SPECTRAL SIGNATURES OF POLARON PAIRS

Having identified polaron pairs by a spin exchange interaction, we can now use PA and λ -PADMR to measure their absorption spectra. The PA spectrum of DBO-PPE [Figure 6(a)] consists of a weak band at 0.4 eV and strong PA above 1.2 eV with bands at 1.35, 1.55 and 1.75 eV, respectively. The bands at 0.4 and 1.75 eV correspond to the polaron pair λ -PADMR spectrum [Fig. 6(b)], measured at either the peak of the narrow line ($H=1070G$) or on the broad resonance ($H=1050G$). We note that the PP_2 band is much stronger than the PP_1 band. While the triplet resonance was too weak to directly measure its spectrum by λ -PADMR, C_{60} doping completely quenches the triplet PLDMR spectrum.¹⁸ The resulting PA spectrum [Figure 6(a)] contains the polaron pairs bands PP_1 and PP_2 and a weaker feature at 1.3 eV due to polarons (P_1). We therefore attribute the band at 1.6 eV to triplet excitons and the band at 1.35 eV to isolated polarons.

The H-PADMR of the 10% C_{60} :DOO-PPV sample is affected by the spin exchange interaction (Figure 2), enabling us to separately measure the absorption spectra of isolated polarons at $H=1072G$ and P^*/C_{60}^- complexes at $H=1050G$. These spectra are shown in Figure 7. The polaron λ -PADMR consists of two bands with maxima at 0.45 and 1.4 eV, respectively. The polaron pair λ -PADMR also contains two bands, labelled PP_1 and PP_2 as above. The PP_2 band is blue-shifted by about 0.4 eV with respect to P_2 of isolated polarons and is much stronger than the PP_1 band. We do not see transitions of C_{60}^- molecules at 1.2 eV or their magnetic resonance at $g=1.995$.

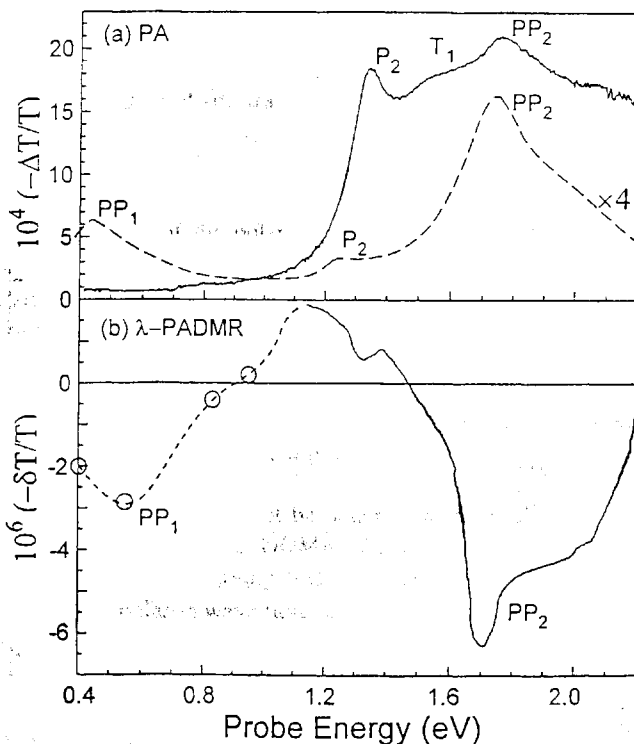


Figure 6. (a) PA spectra of pure (solid line) and 1 mol% C_{60} doped DBO-PPE (dashed line). (b) λ -PADMR spectrum of DBO-PPE film measured at 1070 Gauss. Transitions of polarons, polaron pairs, and triplet excitons are marked.

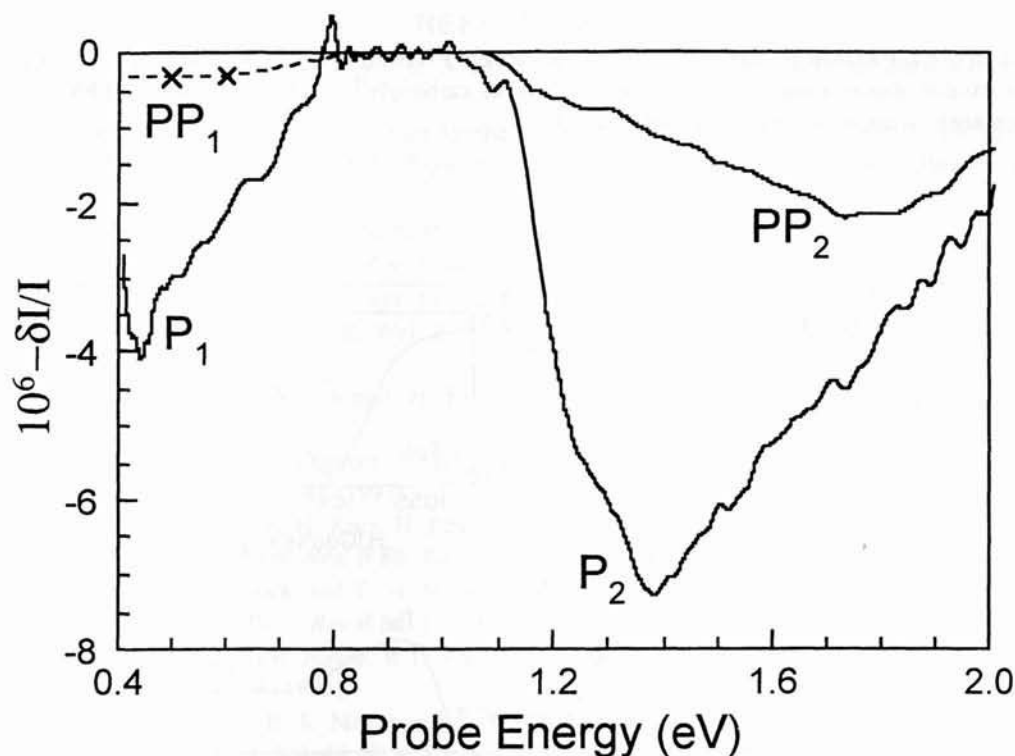


Figure 7. λ -PADMR spectra of 10 mol% C_{60} :DOO-PPV measured at 1070 G (polarons) and 1050 G (polaron pairs).

Measurements of e-PT are consistent with the above results on DBO-PPE and DOO-PPV. e-PT is only weakly luminescent ($\eta < 10^{-3}$), due to a high defect density.³⁰ The PA spectrum of e-PT is shown in Fig. 8(a). It contains three PA bands: P_1 at 0.45 eV, P_2 at 1.25 eV, and PP_2 at 1.8 eV, respectively.³¹ We note that the P_1 and P_2 bands are correlated with infrared active vibrations (IRAVs) whereas the PP_2 band is not.³⁰ Hence, the P_1 and P_2 bands must be associated with charged excitations, whereas the PP_2 band must be associated with neutral excitations. The H-PADMR spectrum of e-PT, measured at the peak of the three PA bands, is shown in Fig. 8 inset. The H-PADMR is negative, contains a narrow resonance about $g=2$ due to spin-1/2 excitations, but no half-field resonances. Hence, \bar{J} must be isotropic. The λ -PADMR spectrum of e-PT, measured at 1067 G and shown in Fig. 8(b), contains the same three bands as the PA spectrum, but with different relative intensities.³¹ We also find a positive band, which we have recently shown³² is the signature of bipolarons. We assign the P_1 and P_2 bands to polarons and the $\delta n/n > 0$ λ -PADMR band to bipolarons. The band at 1.8 eV cannot be due to a third optical transitions of polarons, as these should follow a sum rule of $P_1 + P_2 = P_3$.³³ The lack of a triplet PADMR rules out triplet excitons as its origin. We therefore suggest an assignment of polaron pairs, most likely resulting from dissociation of singlet excitons at defect centers. This interpretation is consistent with the low PL quantum yield and high defect density in these films.

The shift of the energy levels is due to the Coulomb attraction between the oppositely-charged polarons composing the pair. Mizes and Conwell¹¹ have shown that a Coulomb interaction between polarons composing the pair shifts the energy level positions. Due to their mutual attraction, the energy levels of the negative polaron shift upwards and those of the positive polaron shift downwards. Mizes and Conwell predict three transitions; the highest energy pair transition (PP_2) is blue-shifted with respect to the high energy P_2 transition. If the transition which transfers an electron between the partially occupied levels of the two polarons is weak or forbidden, their calculations are in agreement with our experimental results. Our results may explain the PA bands observed in several ps transient measurements of films of PPV derivatives at energies around 1.8 eV.^{12,15,27-29} In good PPV films the transient PA spectrum shows a PA band of excitons at 1.5 eV whose dynamics match those of the PL and stimulated emission (SE).¹⁵ However, in measurements made at high excitation densities²⁸ or of oxidized¹² or C_{60} -doped^{15,27,29} films, there appears a new PA band at about 1.8 eV whose dynamics are not correlated with those of the PL

and SE. Based on our λ -PADMR results here, we attribute the new PA band at 1.8 eV to polaron pair excitations. These may be created via exciton dissociation at extrinsic defects such as carbonyls¹² or photoinduced C_{60}/PPV^+ complexes²⁷ or by exciton-exciton annihilation at high excitation intensities.²⁸

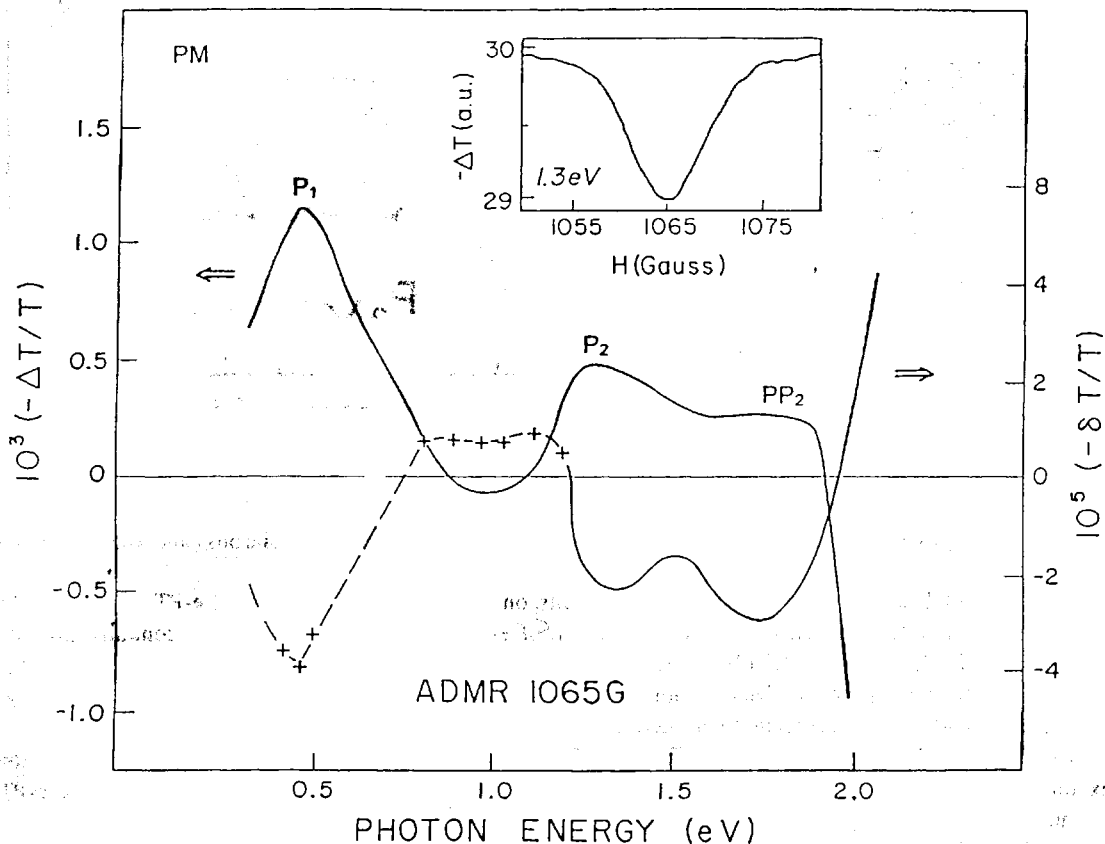


Figure 8. (a) PA and (b) spin-1/2 λ -PADMR spectra of polythiophene. Inset: H-PADMR spectrum at 1.3 eV.

SUMMARY

We have shown that polarons and polaron pairs can be distinguished from isolated or weakly coupled polarons. A spin exchange interaction broadens the spin-1/2 ODMR spectra and Coulomb interactions blue-shift the high energy polaron band. We first show experimental evidence (via PADMR and PLDMR) for a spin-exchange interaction between polarons composing Coulomb-bound polaron pairs. An exchange resonance broadens the spin-1/2 ODMR associated with polarons; both isotropic and anisotropic exchange interactions have been observed. An isotropic exchange interaction results in a broadening of the spin-1/2 resonance associated with polarons, whereas an anisotropic exchange interaction will give rise to both full-field and half-field powder patterns. Both interactions have been successfully modelled by incorporating the parameters of the exchange interaction and generation and recombination rates for each magnetic sublevel. The absorption spectra of polaron pairs were measured by PA and λ -PADMR spectroscopy. Both polarons and polaron pairs have two optical transitions; the polaron pair transition PP_2 occurs at a higher energy than the P_2 transition and the pair transition PP_1 is relatively weak.

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