

## Studies of Photoexcited States in Polyacetylene and Poly(paraphenylenevinylene) by Absorption Detected Magnetic Resonance: The Case of Neutral Photoexcitations

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Photoexcited states in *trans* polyacetylene [ $t\text{-(CH)}_x$ ] and in alkoxy derivatives of poly(paraphenylenevinylene) (PPV) have been studied by the technique of absorption detected magnetic resonance. In addition to the stable *charged* photoexcitations, which are charged solitons in  $t\text{-(CH)}_x$  and bipolarons in PPV, we clearly identify *neutral* photoexcitations with *nonzero* spins. In  $t\text{-(CH)}_x$  these are spin- $\frac{1}{2}$  neutral solitons  $S^0$  ( $\bar{S}^0$ ) with an optical transition at 1.35 eV. The neutral photoexcitations in PPV form triplet excitons which cannot dissociate into  $S^0\bar{S}^0$  pairs due to the confinement caused by the nondegenerate backbone structure.

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Photoexcited states and their relaxation processes in conducting polymers with degenerate and nondegenerate backbone ground-state structures have generated considerable experimental and theoretical studies in the last decade [1]. This has been stimulated by the possibility that various types of nonlinear excitations such as solitons, polarons, bipolarons, and breathers can be photogenerated [2]. Most of the studies, however, have been focused on *charged* photoexcitations because of the relatively easy comparison with available spectroscopic data on nonlinear excitations produced by doping [2], and more recently by field injection [3]. A relatively simple picture has emerged for charged photocarriers: They form solitons ( $S^\pm$ ) in the degenerate polymer *trans* polyacetylene [ $t\text{-(CH)}_x$ ], whereas in nondegenerate ground-state polymers, such as polythiophene and poly(paraphenylenevinylene) (PPV), photocarriers form polarons ( $P^\pm$ ) and bipolarons ( $BP^{2\pm}$ ); this picture is based on noninteracting model Hamiltonians, such as that of Su, Schrieffer, and Heeger (SSH) [4].

On the other hand, there is now accumulating experimental evidence [5-7] of the importance of the  $\pi$ -electron Coulomb interaction  $U$  in this class of conducting polymers, which places  $U$  at the intermediate level,  $3 \text{ eV} < U < 7 \text{ eV}$ . The reversed order of the even ( $2A_g$ ) and odd ( $B_u$ ) excited-state symmetries in short polyenes [8] is thought to result from the strong Coulomb correlation. Interestingly, more recent calculations of photoexcitations within interacting model Hamiltonians using nonperturbative [9-11] methods and numerical renormalization-group methods [12] show that *neutral* photoexcitations compete with charged excitations in the photophysics of conducting polymers. In this picture the lowest excited state ( $2A_g$ ), if reached, decays into *triplet* neutral excitations; in degenerate ground-state polymers such as  $t\text{-(CH)}_x$ , the triplet excitations dissociate further [11] into spin- $\frac{1}{2}$  *neutral* soliton-antisoliton ( $S^0\bar{S}^0$ ) pairs. Thus, in addition to the stable charged photoexcitations

predicted in the  $U=0$  limit ( $S^\pm$ ,  $P^\pm$ , and  $BP^{2\pm}$ ) these models predict stable triplet ( $S=1$ ) and doublet ( $S=\frac{1}{2}$ ) neutral photoexcitations which may be observed with spin-sensitive experimental techniques.

In the present work we have applied such a spin-sensitive technique, absorption detected magnetic resonance (ADMR), to investigate the spin and charge states of photoexcitations in degenerate [ $t\text{-(CH)}_x$ ] and nondegenerate (PPV) ground-state conducting polymers. In  $t\text{-(CH)}_x$  we have found that the well-known 1.35-eV spectral feature [13] is associated with spin- $\frac{1}{2}$  neutral photoexcitations, which we identify as neutral solitons  $S^0$ . In alkoxy derivatives of PPV, on the other hand, we have identified both charged and neutral excited states. The charged photocarriers form  $BP^{2\pm}$  with two optical transitions at 0.3 and 1.25 eV, respectively, which are a correlated bound pair of spin- $\frac{1}{2}$   $P^\pm$ . The neutral photoexcitations, however, are triplet ( $S=1$ ) excitons with an optical transition in the triplet manifold at 1.35 eV.

In ADMR we detect changes in the steady-state photomodulation (PM) spectrum associated with induced changes in the photoexcitation recombination kinetics. This is caused by resonant microwave absorption among Zeeman-split electronic energy levels in a moderately strong magnetic field. This technique is similar to another optical detected magnetic resonance, phosphorescence detected magnetic resonance (PDMR) [14], except that in ADMR, changes in PM intensity are detected, whereas in PDMR, changes in photoluminescence (PL) intensity are recorded.

Our ADMR setup consists of a pump beam, from an  $\text{Ar}^+$  laser at 488 nm, and a probe beam from an incandescent light source dispersed by a monochromator. The sample was placed in a high- $Q$ -value microwave cavity with resonance at about 3 GHz ( $S$  band), equipped with optical windows for transmission. The cavity was placed in a Dewar in a superconducting magnet with a field  $H$  up to 3 T. We used an rf field with power up to 200 mW

which was modulated at 500 Hz. After proper signal averaging, the sensitivity of our apparatus  $\delta T/T$  (where  $T$  is the transmission and  $\delta T$  is its spin modulation) was  $\delta T/T \approx 3 \times 10^{-8}$  in the Si-detector spectral range, which decreased to  $2 \times 10^{-7}$  in the InSb ir range. Two types of ADMR and PDMR spectra were obtained: the  $H$ -ADMR spectrum for which  $H$  was swept at a fixed probe wavelength, and the  $P$ -ADMR spectrum for which the probe wavelength was changed at a constant  $H$ , in resonance. The samples studied were three Shirakawa polymerized  $t$ -(CH) $_x$  thin films and two solution-cast films of alkoxy derivatives of PPV:DOO [poly(2,5-octoxy-PV)] and DHO [poly(2,5-hexoxy-PV)] [15], all deposited on sapphire substrates.

The PM spectrum of  $t$ -(CH) $_x$  at 4 K is shown in Fig. 1. Two photoinduced absorption (PA) bands at 0.45 eV (LE) and at 1.35 eV (HE) dominate the PM spectrum [13]. The LE band was identified [2] as due to  $S^\pm$ ; associated with it is a prominent oscillation above 1.4 eV, identified [16] as due to electroabsorption (EA) caused by  $S^\pm$ . The HE band, associated with neutral photoexcitations [16], however, has still remained a mystery for over a decade; singlet [17] and triplet [9] solitonic excitons, breather modes [18], and  $A_g$  states [16] are only a few of the explanations given for the HE band that can be found in the literature. The ADMR spectra shown in Fig. 1 can elucidate its origin. The  $H$ -ADMR signal at 1.35 eV (at the HE peak) is shown in Fig. 1 (inset). A reduction of PA ( $\delta n < 0$ ), with  $\delta n/n \approx 3 \times 10^{-3}$ , where  $n$  is the steady-state population and  $\delta n$  is its change, is observed at 1067 G ( $S = \frac{1}{2}, g \approx 2.003$ ). This is caused by enhanced recombination associated with the HE excitations with unthermalized spins. This eliminates the singlet excitons [17] and breather modes [18] for which  $S = 0$ , as

well as triplet excitons [9], as valid explanations for the HE band.

The  $P$ -ADMR spectrum of  $t$ -(CH) $_x$  at a fixed  $H$  of 1067 G is also shown in Fig. 1. It consists of a relatively large reduction  $\delta n$  in the HE photoexcitation density [ $\delta n/n(\text{HE}) \approx -3 \times 10^{-3}$ ], a smaller increase in the  $S^\pm$  population at the LE band [ $\delta n/n(\text{LE}) \approx 10^{-3}$ ], and a EA oscillation that is barely observable in the ADMR spectrum, in agreement with the small value of  $\delta n/n(\text{LE})$ . Moreover, the  $\delta n$  signals at the LE and HE bands are correlated with each other as verified by studying the dependencies of  $\delta n$  on the pump excitation intensity  $I_L$ , sample temperature  $\Theta$ , and the rf modulation frequency  $f$ . In addition to having the same  $H$ -ADMR spectrum (Fig. 1, inset),  $\delta n$  for both LE and HE bands increases with  $I_L$  as  $\delta n \sim I_L^{0.65}$ . Also both  $\delta n$  signals decrease with  $f$  in the same way, and at  $f = 500$  Hz,  $\delta n(\text{HE})$  and  $\delta n(\text{LE})$  have the same phase lag in the lock-in amplifier. In particular, Fig. 2 shows the PM and ADMR temperature dependencies of the two PA bands. Whereas in the PM spectrum the HE and the LE PA bands do not decrease with  $\Theta$  in the same way; their  $\delta n$  signals, however, decrease with  $\Theta$ , together. The experimental correlation between the two  $\delta n$  signals shows, therefore, that a part of the photogenerated  $S^\pm$  in  $t$ -(CH) $_x$  is correlated with the HE species, in spite of their many distinct different properties in the PM spectrum [16].

Recent careful light-induced ESR (LESR) studies [19] of  $t$ -(CH) $_x$  showed conclusively the photogeneration of spin- $\frac{1}{2}$  species. It was also speculated [19,20] that these are neutral solitons  $S^0$  associated with the HE band; our ADMR results provide the experimental proof. In fact, we show that the HE band is due to neutral spin- $\frac{1}{2}$  photoexcitations that are correlated with  $S^\pm$ . We conjecture, therefore, that the HE band is due to photogenerated  $S^0$ . However, neutral solitons cannot be directly pho-

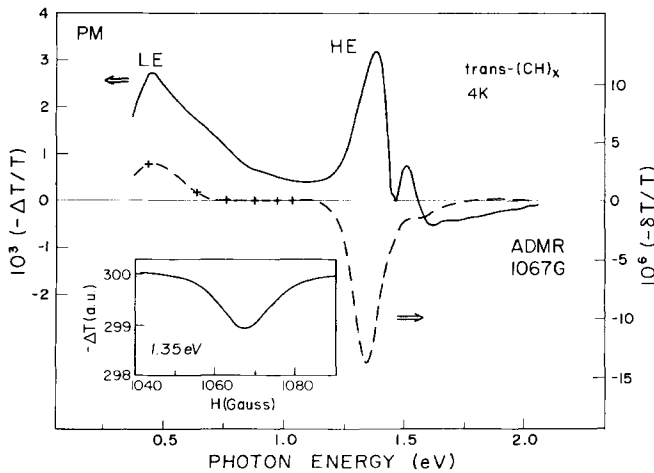


FIG. 1. PM spectrum (solid line) and  $P$ -ADMR spectrum (broken line) at 1067 G of  $t$ -(CH) $_x$  at 4 K. Inset: The  $H$ -ADMR spectrum at 1.35 eV (HE peak). The ADMR resolution is  $3 \times 10^{-8}$  for  $\hbar\omega > 1.1$  eV,  $6 \times 10^{-8}$  for  $0.8 < \hbar\omega < 1.1$  eV, and  $2 \times 10^{-7}$  for  $\hbar\omega < 0.8$  eV.

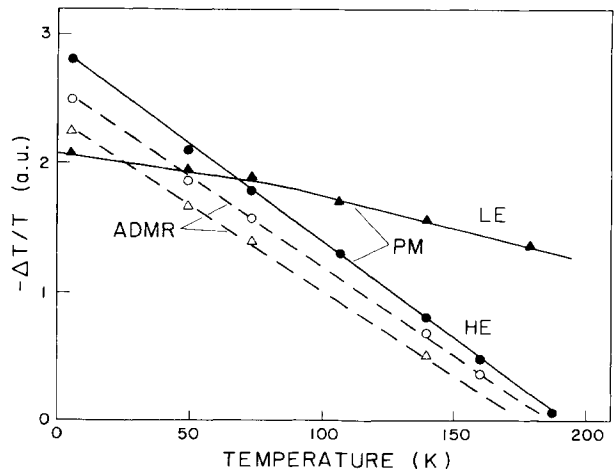


FIG. 2. The temperature dependencies of the LE and HE PA bands of  $t$ -(CH) $_x$  in the PM spectrum (solid lines) and in  $P$ -ADMR at 1067 G (broken lines).

togenerated since the photoexcited singlet  $B_u$  state cannot decay into a  $S^0\bar{S}^0$  pair [10–12]. Either a parity change transition between  $B_u$  and  $2A_g$  states occurs first [20] and then the  $2A_g$  state decays into a  $S^0\bar{S}^0$  pair [10–12], or an intersystem crossing from the singlet to the triplet manifold takes place, followed by a triplet exciton fission into a  $S^0\bar{S}^0$  pair [21]. In any case the magnitude and sign of  $\delta n(\text{HE})$  indicate that at 4 K the  $S^0$  spins are unthermalized at the rf modulation frequency and that the microwave resonant absorption enhances the recombination kinetics of  $S^0$  by flipping the direction of one  $S^0$  spin  $\frac{1}{2}$ .

The experimental correlation found between  $\delta n(\text{HE})$  and  $\delta n(\text{LE})$  shows that a conversion process from  $S^0\bar{S}^0$  into  $S^+\bar{S}^-$  pairs may occur in  $t\text{-(CH)}_x$ , even though  $S^0\bar{S}^0$  is the more energetically favorable pair. An important possibility is a fusion process of two  $S^0\bar{S}^0$  pairs into an excited  $S^+\bar{S}^-$  pair:  $2S^0\bar{S}^0 \rightarrow S^+\bar{S}^-$  [22], similar to the fusion process of two triplet excitations into an excited singlet exciton, commonly found in molecular crystals [23]. A different explanation for the positive  $\delta n(\text{LE})$  signal, which does not involve the energetically unfavorable conversion of neutral to charged solitons, is that photo-generated  $S^0\bar{S}^0$  pairs act as recombination centers for the long-lived  $S^+\bar{S}^-$  pairs, promoting their conversion into  $S^0\bar{S}^0$  pairs. Then fewer  $S^0\bar{S}^0$  pairs, caused by microwave absorption, may consequently reduce the charged to neutral soliton conversion, resulting in a correlated  $\delta n(\text{LE}) > 0$  signal [22].

The photoexcitation dynamics in polymers with nondegenerate ground state, such as PPV and its alkoxy derivatives, is very different from that of  $t\text{-(CH)}_x$ . Triplet excitons, formed either via the decomposition of the  $2A_g$  state [10–12] or through an intersystem crossing from the singlet manifold [21], cannot further produce  $S^0\bar{S}^0$  pairs

because of the confinement of the backbone structure [10–12]. We expect therefore that triplet excitons would dominate the PM and ADMR spectra for neutral excitations. This is shown in Fig. 3 for the DOO derivative of PPV at 4 K; we obtained identical results for the DHO derivative. The PM spectrum is composed of two main PA bands: a  $\text{LE}_1$  band at 0.35 eV and a HE band at 1.36 eV; a shoulder ( $\text{LE}_2$ ) is also evident at about 1.3 eV. We have also observed in PPV a strong PL band with 0-0 transition at 2 eV, and this is also shown in Fig. 3. The  $\text{LE}_1$  and HE PA bands in PPV do not share any common origin as evidenced by their distinct  $I_L$ ,  $\Theta$ , and modulation frequency dependencies; the latter is shown as an inset to Fig. 3. In fact the  $\text{LE}_1$  band is due to charged photoexcitations, whereas the HE band is due to neutral excitations; this was proven by the lack of any ir activity in the phonon spectral range associated with the HE band [24].

The  $H$ -ADMR spectrum at 1.36 eV (the HE peak) is shown in Fig. 4 together with the  $H$ -PDMR spectrum at 2 eV (the PL peak). We note that the ADMR signal is negative, whereas the PDMR signal is positive [25]. Both spin-dependent spectra, however, show a symmetric band at 1067 G ( $g \approx 2.003$ ) due to spin- $\frac{1}{2}$  excitations and an asymmetric band at 405 G. We identify the later as  $\Delta m_s = \pm 2$  transitions associated with triplet excitons having zero field splitting ( $D, E \neq 0$ ) [14,25]. The signal of a triplet "powder pattern" associated with the  $\Delta m_s = \pm 1$  transitions, which usually appears together with the  $\Delta m_s = \pm 2$  band in the  $H$ -ADMR spectrum, was below the noise level for our system equipped with microwaves at 3 GHz. Such a powder pattern signal, however, was recently observed in PDMR measurements of the same PPV derivatives using microwaves at 9 GHz

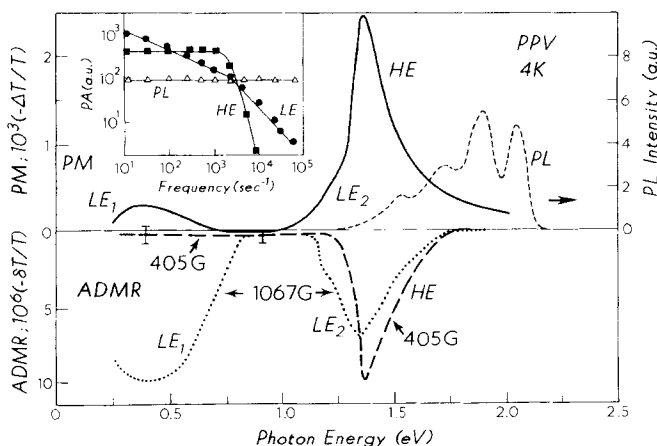


FIG. 3. PM spectrum (solid line) and  $P$ -ADMR spectra at 405 G (broken line) and at 1067 G (dotted line), of DOO-PPV at 4 K. The PL band is also shown (right panel) and the different PA bands ( $\text{LE}_1$ ,  $\text{LE}_2$ , and HE) are labeled. Inset: The modulation frequency dependencies of the various PA and PL bands up to  $10^5$  Hz.

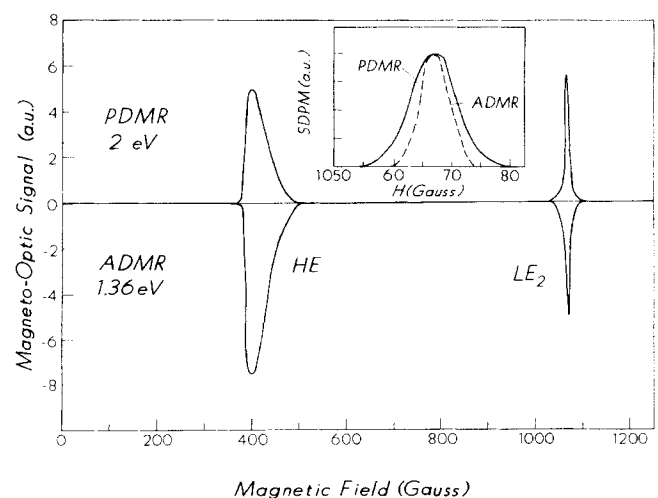


FIG. 4. The  $H$ -ADMR and  $H$ -PDMR spectra at 1.36 eV (HE band) and 2 eV (PL band), respectively, of DOO-PPV at 4 K. Inset: The two spectra at  $H$  around 1067 G are shown in more detail.

[25]; the  $H$ -PDMR signal was spread over 1.2 kG and was an order of magnitude smaller than the  $g=2$  signal. We have recently succeeded [26] in detecting all three triplet ADMR allowed transitions in *oriented* PPV derivatives at 3 GHz; this was done with  $H$  parallel and perpendicular to the chain axis. From our measurements [26], we obtained for the triplet Hamiltonian in PPV,  $D=630$  G ( $0.059$  cm $^{-1}$ ) and  $E=90$  G ( $0.008$  cm $^{-1}$ ).

The  $P$ -ADMR spectra taken at 1067 G ( $S=\frac{1}{2}$ ) and at 405 G ( $S=1$ ) are shown in Fig. 3. The triplet ADMR spectrum contains a single band peaked at 1.36 eV with the same spectral shape as the HE band in the PM spectrum. The spin- $\frac{1}{2}$  ADMR spectrum, however, contains two bands peaked at 0.3 and 1.3 eV which are equivalent to the  $LE_1$  band and  $LE_2$  shoulder, respectively, in the PM spectrum. We therefore identify the  $LE_1$  and  $LE_2$  PA bands as due to optical transitions associated with photogenerated bipolarons ( $BP^{2\pm}$ ), at somewhat lower energies compared to the doping-induced BP [15]. The HE band, on the other hand, is due to optical transitions in the triplet manifold, associated with photogenerated triplet excitons in PPV [24].

The photoexcitation dynamics in PPV, similar to that of  $t$ -(CH) $_x$ , also shows two competing processes associated with the distinct  $B_u$  and  $2A_g$  states (or singlet and triplet manifolds). An excited  $B_u$  state can decay into spin- $\frac{1}{2}$  polarons ( $P^\pm$ ) [12], which are not topological defects and are therefore relatively mobile in the sample. Although we cannot discern a PA band in the PM spectrum associated with  $P^\pm$ , their  $BP^{2\pm}$  by-products are observable in the PM spectrum. Polaron recombination is a spin-dependent process with faster recombination for polaron pairs with antiparallel spins [14]. This leads to excess  $P^\pm$  pair population with parallel spins, which is partially transformed by microwave resonant absorption into  $P^\pm$  pairs with antiparallel spins with enhanced recombination. The enhanced  $P^\pm$  recombination explains the positive PDMR signal [25] (more PL) and the negative ADMR signal for  $BP^{2\pm}$  ( $LE_1$  and  $LE_2$  in Figs. 3 and 4). This originates from the smaller  $P^\pm$  steady-state density under the microwave resonance conditions. On the other hand, if an intersystem crossing from  $B_u$  to  $2A_g$  (or from the singlet to the triplet manifold) occurs [20], triplet excitons are formed [10–12] with a strong transition at 1.36 eV. These excitons become spin polarized due to different recombination dynamics of each of the triplet sublevels [27]. Under microwave absorption, transitions among the triplet sublevels enhance recombination. This results in a PDMR enhancement and an ADMR reduction due to a decrease in the triplet steady-state population; both changes are in agreement with the measurements presented in Figs. 3 and 4.

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