Studies of Charged Excitations in π-Conjugated Oligomers and Polymers by Optical Modulation

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We have studied photogenerated charged excitations in sexithiophene and a variety of π-conjugated polymers by photoinduced absorption (PA) and PA-detected magnetic resonance. We found distinct spin signatures for polarons and bipolarons, which enabled us to separate their contributions to the PA spectrum. In all cases, we find that polarons have two subgap optical transitions, whereas bipolarons have one. Having unambiguously identified the energy levels of polarons and bipolarons, we show that bipolarons are stable photoexcitations, with negative effective correlation energy. [S0031-9007(96)00966-0]

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The nature of charged excitations in π-conjugated polymers has been extensively studied. Charges added to the polymer chain by doping, current injection, or photogeneration are self-localized and have states deep in the gap. In nondegenerate ground state polymers, two kinds of charged excitations can be formed: singly charged, paramagnetic ($S = 1/2$) polarons and doubly charged, diamagnetic ($S = 0$) bipolarons. The occupation of states allows three subgap optical transitions for polarons and two for bipolarons [1]. Hence, the observation of two subgap absorption bands due to charged excitations in polymers [2–5] has been generally interpreted as due to bipolaron formation.

In contrast, the doping and photoinduced absorption (PA) spectra of various π-conjugated oligomers show that polarons have only two subgap optical transitions and bipolarons have only one [6,7]. Calculations of oligomer electronic states [8,9] have shown that the parity of levels alternates between even and odd (see Fig. 1, insets). As optical transitions are dipole allowed only between levels of opposite parities, this model correctly predicts that polarons have two subgap optical transitions, whereas bipolarons have one. These results cast doubt on the previous assignment of two absorption bands as due to bipolarons.

In this paper, we have combined the techniques of photoinduced absorption (PA) and PA-detected magnetic resonance (PADMR) to unambiguously determine the absorption spectra of polarons and bipolarons. We first examine sexithiophene (6T), a model π-conjugated oligomer, and then extend our studies to PT, poly(3-butylthiophene) (P3BT), poly(thienylene vinylene) (PTV), and 2,5-dioctoxy poly(p-phenylene vinylene) (DOO-PPV). In all cases, we find that the absorption spectrum of polarons consists of two subgap bands whereas that of bipolarons has only a single band. Hence, dipole selection rules are shown to hold for both π-conjugated oligomers *and* polymers. Based on our identification of the polaron and bipolaron absorption bands, we show that bipolarons are stable excitations, with negative effective correlation energy ($U_{\mathrm{eff}} < 0$).

PA spectroscopy uses standard phase-sensitive lock-in techniques with a modulated Ar^{+} laser beam as a pump and an incandescent light source as a probe. Photoinduced changes ΔT in the sample transmission T are recorded to obtain the normalized changes in transmission ($-\Delta T/T \approx n\sigma d$, where n is the photoexcitation density, σ the absorption cross section, and d the sample thickness). In PADMR, the sample is mounted in a high Q microwave cavity (at 3 GHz) equipped with a superconducting magnet and illuminated by the pump and probe beams. Microwave resonant absorption leads to small changes, δT, in the probe transmission. This δT is proportional to δn, which is induced by transitions in the microwave frequency range that change spin-dependent recombination rates. Two types of PADMR spectra are possible: the H-PADMR spectrum, in which δT is measured at a fixed probe wavelength λ as the magnetic field H is varied, and the λ-PADMR spectrum, in which δT is measured at a constant H, in resonance, while λ is varied.

All samples studied were thin films on sapphire substrates. 6T was well purified and then films were prepared by vacuum sublimation onto a substrate at room temperature (s-6T) or by evaporation from solution onto a heated substrate (e-6T). PT and PTV samples were polymerized onto the substrate; P3BT and DOO-PPV samples were cast from solution.

The PA spectrum of the s-6T film, measured at 140 K and shown in Fig. 1(a), consists of two sharp bands, P_1 at 0.80 eV and P_2 at 1.54 eV, each of which is accompanied by a high-energy vibronic sideband. Upon further cooling the sample to 10 K [Fig. 1(b)], a third PA band (BP_1) arises with a peak at 1.10 eV and a vibronic sideband at 1.24 eV. The P_1 and P_2 PA bands are correlated by temperature, frequency, and intensity dependence [10]. When 6T in solution is lightly doped, absorption bands form at 0.84 and 1.60 eV due to a paramagnetic species [6]. At high dopant concentrations, the subgap absorption

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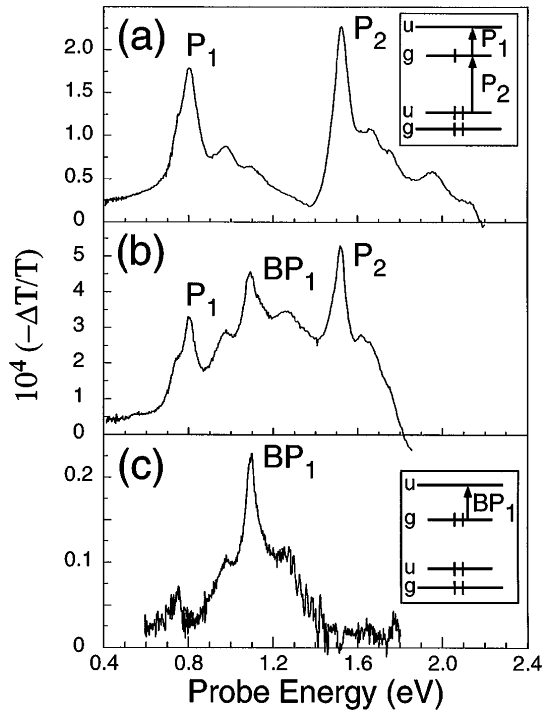

FIG. 1. PA spectrum of s-6T film at (a) 140 K and (b) 10 K. (c) PA spectrum of e-6T film at 80 K. Inset: schematic diagrams of energy levels, parities, and optical transitions of (a) 6T and (c) $6T^{2-}$ defects.

spectrum is dominated by a single band at 1.24 eV due to a diamagnetic species [6]. Hence, we assign the P_1 and P_2 PA bands to spin 1/2 polarons and the BP_1 PA band to bipolarons. The clear correlation between doping, ESR, and PA make 6T an ideal material for investigations of charged excitations.

The PA spectrum of e-6T [Fig. 1(c)] is strikingly different from that of s-6T. Deposition onto a heated substrate improves structural order in 6T films [11]. As a consequence, the PA spectrum of this sample *is dominated by bipolarons.* We observe a clearly resolved shoulder at 1 eV, which has not been observed in studies of heavily doped 6T [6,10]. We further note a shoulder at 0.76 eV [[1(b)], below the P_1 polaron band, which has been absent in lightly doped 6T. Doping produces charged excitations of only one sign, whereas photogeneration creates equal populations of positive and negative excitations. These data are evidence of differences between positive and negative charged excitations, i.e., charge conjugation symmetry violation.

We next examine PT, the polymer analog of 6T. The PA spectrum of PT, shown in Fig. 2(a), consists of bands P_1 at 0.4 eV and P_2 at 1.3 eV, respectively, and a series of sharp infrared active vibrational modes (IRAV's), which are signatures of charges on the chains [12]. In contrast, the PA spectrum of a PT film annealed at 300 °C for 30 min, shown in Fig. 2(b), is dominated by a single band BP_1 at 0.9 eV, also correlated with IRAV's. Heat treatment of PT significantly increases the crystallinity of the film and improved coherence in the crystalline regions [13]. The PA spectra of regular and improved PT resemble those of the two 6T films described above, redshifted by ≈ 0.3 eV due to greater conjugation lengths in the polymer film. These similarities lead us to conclude that the PA spectrum of the regular PT film is dominated by polarons, whereas that of the improved film is dominated by bipolarons. Hence, dipole selection rules hold for charged excitations in *both* 6T and PT.

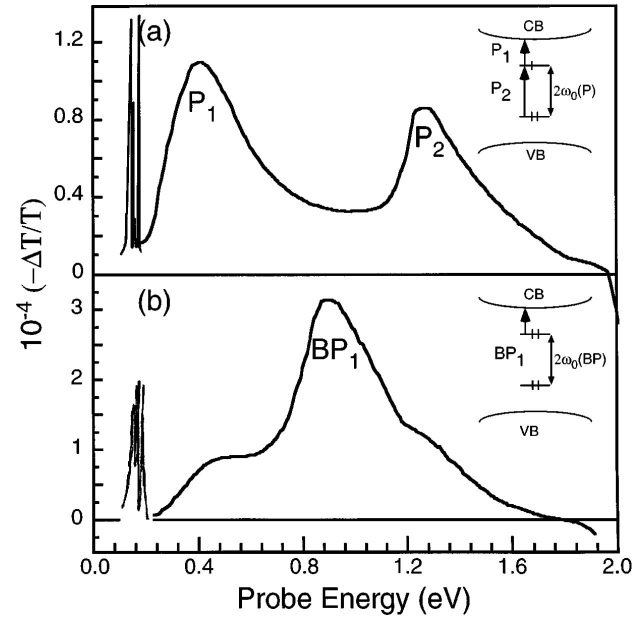

FIG. 2. PA spectra of (a) regular and (b) improved PT films. Inset: schematic diagrams of negative (a) polarons and (b) bipolarons and their optical transitions.

The identification of charged excitations in many π-conjugated polymers is complicated by the presence of long-lived neutral excitations such as triplet excitons. However, we can use the technique of PADMR to separate the absorption spectra based on the spin of the photoexcitation. The H-PADMR spectrum of s-6T (Fig. 3, inset) has a resonance at 1074 G due to spin 1/2 excitations. The λ-PADMR spectrum of s-6T, measured at 1074 G and shown in Fig. 3(b), contains sharp, PA-quenching PADMR bands at 0.80 and 1.54 eV, respectively, and a broad, PA-enhancing signal between 1.0 and 1.45 eV. The two sharp negative PADMR bands coincide in energy with the P_1 and P_2 polaron PA bands. Hence, these two bands are due to spin 1/2 polarons. A negative PADMR means that magnetic resonance reduces the steady-state population of polarons $[\delta n(P) < 0]$. The probe energies of the $\delta n > 0$ band in λ-PADMR and BP_1 band in PA coincide, which suggests that magnetic resonance increases the steady state population of bipolarons $[\delta n(\mathrm{BP}) > 0]$.

In order to explain these results, we consider spin-dependent recombination processes of photogenerated

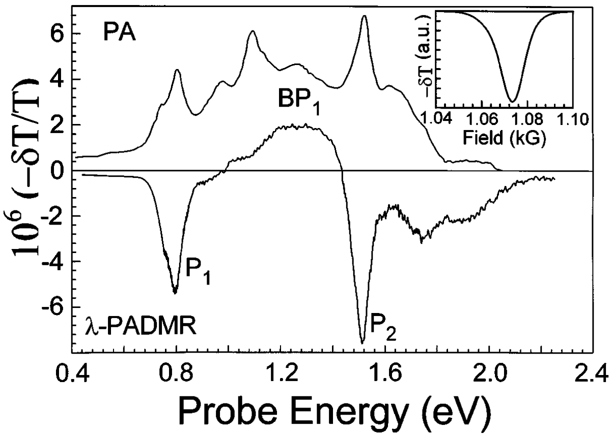

FIG. 3. Scaled PA and spin 1/2 ($H = 1070$G) λ-PADMR spectra of s-6T at 10 K. Inset: H-PADMR spectrum of s-6T for $\lambda = 800$ nm.

charged excitations which can be affected by magnetic resonance:

$$P^{\pm} + P^{\mp} \rightarrow \mathrm{GS}, \tag{1}$$

$$P^{\pm} + P^{\pm} \rightarrow \mathrm{BP}^{2\pm}, \tag{2}$$

where GS is the ground state. Two spin 1/2 polarons will produce pairs with spins either parallel (p) or antiparallel (ap). For nongeminate pairs, p and ap pairs will form with initially equal probability, but the recombination rate of ap pairs is higher, leading to steady state populations with $n_P > n_{ap}$. Microwave-induced spin flips convert p pairs into ap pairs, increasing the recombination rate of *oppositely charged* pairs to the ground state and reducing polaron populations at resonance [$\delta n(P) < 0$]. If $U_{\mathrm{eff}} < 0$, magnetic resonance will also enhance bipolaron formation [$\delta n(BP) > 0$] from *like-charged* pairs. We emphasize that polarons and bipolarons have distinct spin signatures. Thus, PADMR spectroscopy can unambiguously identify polarons and bipolarons and separate their PA bands.

The spin 1/2 λ-PADMR of P3BT, shown in Fig. 4(b), consists of $\delta n < 0$ bands at 0.55 and 1.4 eV and a $\delta n > 0$ band between 0.9 and 1.25 eV. Based on the PA spectra of regular and improved PT (Fig. 2) and the λ-PADMR of 6T (Fig. 3), we assign the $\delta n < 0$ bands to transitions of polarons and the $\delta n > 0$ band to transitions of bipolarons. Our conclusions are consistent with those of a recent Raman scattering study comparing doped 6T and PT [14]. However, they vary from the original assignment of the absorption spectrum of doped PT to bipolarons [2,3]. This assignment was based on ESR measurements [15], which found no appreciable increase in the spin density of PT as the material was progressively doped. An alternative explanation to bipolarons is spin pairing between like-charged polarons on different chains. Spin pairing has been observed in 6T, where the spin density of lightly doped 6T decreases as the temperature decreases [16]. This was attributed to the formation of spinless complexes known as π dimers from pairs of 6T$^+$ polarons.

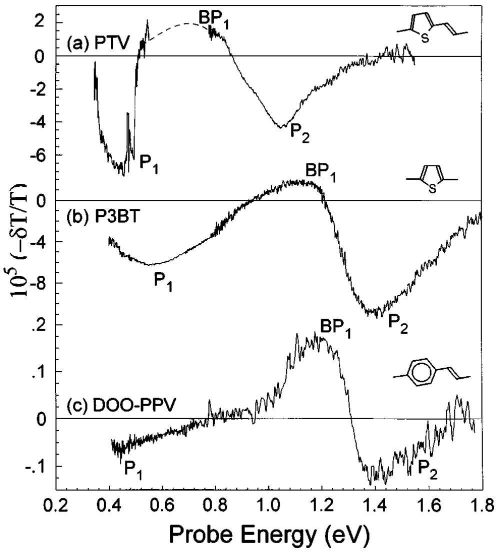

FIG. 4. Spin 1/2 λ-PADMR spectra of (a) PTV, (b) P3BT, and (c) DOO-PPV at $T < 10$ K.

We extend our studies to PTV, a nonluminescent conjugated polymer, and DOO-PPV, which is luminescent. The spin 1/2 λ-PADMR spectra of PTV and DOO-PPV are shown in Figs. 4(a) and Fig. 4(c), respectively. For both polymers, we find two $\delta n < 0$ bands characteristic of the transitions of polarons as well as a single $\delta n > 0$ band characteristic of bipolarons. We thus find that bipolarons are stable excitations in all of these polymers. The absence of a strong bipolaron absorption band in the PA spectra of these polymers can be explained by the polaron pair model [17,18]. As photogenerated polarons originate from the fission of singlet excitons, it has been suggested >90% of polarons remain bound by Coulomb attraction as geminate polaron pairs. These polaron pairs will not easily separate to form bipolarons and thus dominate the PA spectrum.

U_{eff} plays an important role in determining the electronic properties of deep defects in semiconductors. In general U_{eff} is the difference between the Coulomb repulsion U and the lattice relaxation energy E_r ($U_{\mathrm{eff}} = U - E_r$). If U_{eff} is positive, as for dangling bonds in amorphous silicon and solitons in *trans*-CH$_x$ [19], defect states in equilibrium are singly occupied. However, if $U_{\mathrm{eff}} < 0$, as for defects in chalcogenide glasses such as $\mathrm{As_2S_3}$ [20], defect states are unoccupied or occupied by two electrons. We can calculate U_{eff} from the transition energies of polarons and bipolarons measured above. Since both of these transitions are into (from) the conduction (valence) band, U_{eff} is simply the difference in the transition energies of the two states [19]. However, we must take into account that polarons and bipolarons have *two* levels in the gap [1]. The singly occupied level of P$^-$ is pushed up by $\omega_0(P)$ [Fig. 2(a), inset] and the HOMO

TABLE I. Transition energies in eV for polarons (P_1 and P_2) and bipolarons (BP_1) and the resulting U_{eff} for the polymers studied.

	P_1	P_2	BP_1	U_{eff}
e-PT[1]	0.45	1.25	0.85	−0.20
P3BT[2]	0.55	1.4	1.1	−0.35
DOO-PPV[2]	0.5	1.3	1.0	−0.30
PTV[2]	0.45	1.05	0.7	−0.05

[1] From PA in Fig. 2.
[2] From PADMR in Fig. 4.

level of the BP^{2-} is pushed up by $\omega_0(BP)$ [Fig. 2(b), inset]. Hence, U_{eff} is given by the following relation:

$$\begin{aligned} U_{\text{eff}} &= [P_1 + \omega_0(P)] - [BP_1 + \omega_0(\text{BP})] \\ &= P_1 - BP_1 + \Delta\omega_0 \end{aligned} \tag{3}$$

For a reasonable choice of the polymer confinement parameter γ, Choi and Rice [21] estimated $\omega_0(\text{BP}) \cong 0.5$ eV for PPV. For DOO-PPV, we measured $\omega_0(P) = P_2/2 \cong 0.7$ eV, giving $\Delta\omega_0 \cong 0.2$ eV. Assuming $\Delta\omega_0 \approx 0.2$ eV, we find that U_{eff} is *negative* and of order 0.2 eV for all polymers studied (Table I).

In summary, we measured the absorption spectra of polarons and bipolarons in 6T, a model π-conjugated oligomer, and both luminescent (PT, P3BT, and DOO-PPV) and nonluminescent (PTV) π-conjugated polymers. Dipole selection rules are shown to hold for all materials. Hence, the absorption spectrum of polarons consists of two subgap bands, whereas that of bipolarons has only a single band. The observation of bipolaron formation by PADMR proves that bipolarons are stable excitations, with negative effective correlation energy. We have estimated $U_{\text{eff}} < 0$ from the transition energies of polarons and bipolarons in several π-conjugated polymers.

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