

## Photoexcitations in poly(thiophene): Photoinduced infrared absorption and photoinduced electron-spin resonance

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Infrared absorption and electron-spin resonance are used to study the photoexcitations of poly(thiophene). The results indicate photoproduction of both charge- and spin-carrying species.

The intrinsic properties of the nonlinear soliton excitations in *trans*-(CH)<sub>x</sub> have been identified and successfully investigated through photogeneration studies.<sup>1-7</sup> In these experiments, after the initial creation of an electron-hole pair by absorption of a photon at  $\hbar\omega > E_g$  ( $E_g$  is the energy gap), the lattice rapidly ( $\sim 10^{-13}$  s) distorts around the charge carriers leading to a photogenerated soliton-antisoliton pair.<sup>8</sup> Both the lattice distortion within the spatially extended charged solitons and the associated electronic structure of these photogenerated charged species were probed by detecting the small changes in infrared absorption that occur during photoexcitation.<sup>1-6</sup> Similarly the reversed spin-charge relation predicted for solitons was verified through electron-spin resonance (ESR) measurements during photoexcitation.<sup>7</sup> Excitation-profile measurements<sup>6</sup> demonstrated that solitons could be photogenerated by photons with  $\hbar\omega < E_g$  either by a direct absorption process (assisted by quantum fluctuations in the ground state) or by the initial creation of localized electronic excitations through absorption by defect states<sup>9</sup> in the energy gap. Since the characteristic signatures of the charged species observed in photoexcited and doped *trans*-(CH)<sub>x</sub> were found to be in one-to-one correspondence, a principal conclusion of these studies was that in both cases the charge was stored in spinless charged solitons.

The coupling of electronic excitations to nonlinear conformational changes is an intrinsic and important feature of conducting polymers. In the presence of a degenerate ground state, this coupling leads to the novel soliton excitations studied extensively in *trans*-(CH)<sub>x</sub>. Generalization of these concepts and application to the larger class of (nondegenerate ground-state) conjugated polymers has been an obvious goal of the field. Polymers such as poly(thiophene) [Fig. 1(a)] are, therefore, of current interest since the two structures sketched in Fig. 1(b) are *not* energetically equivalent. As a result polarons and bipolarons are expected to be the dominant charged species.<sup>10,11</sup>

In this paper we report the first observation of photoinduced absorption and photoinduced ESR in poly(thiophene). The observation of relatively sharp photoinduced mid-ir peaks (at 1020, 1120, 1200, and 1320 cm<sup>-1</sup>) demonstrates that localized structural distortions are indeed formed, consistent with photogeneration of polarons or bipolarons. The observation of photoinduced spins implies photoproduction of polarons. We find in addition a broad photoinduced absorption peaked at 3600 cm<sup>-1</sup> (0.45 eV) which we attribute to the lowest-energy electronic excitation of the photogenerated polarons.

The poly(thiophene) used in these experiments was syn-

thesized by Kobayashi by condensation polymerization of 2,5-diiodothiophene.<sup>12</sup> The resulting polymer is chemically pure with an estimated molecular weight of about 46 thiophene units (approximately 180 carbon atoms along the backbone), and it is crystalline. Initial physical studies<sup>12</sup> indicate that the polymer is a semiconductor with band gap of about 2 eV. The relatively clean transmission for  $\hbar\omega < E_g$  and the small number of unpaired spins in the  $\pi$ -electron system ( $\sim 65$  ppm per carbon) are consistent with a relatively high-purity material. Samples were prepared by mixing the polythiophene powder with KBr (at a dilute concentration of about 0.3 wt. %) and subsequently pressing the dilute mixture into a red semitransparent pellet. The photoinduced absorption experiments were carried out by Schaffer using an IBM Instruments (Bruker) IR/98 vacuum Fourier-transform interferometer modified to allow an external beam of an Ar<sup>+</sup> laser ( $\hbar\omega = 2.41$  eV) to be incident on the sample simultaneously with the infrared beam. The spin resonance measurements were made by Moraes with an IBM Instruments (Bruker) E-200D ESR spectrometer equipped with an optical access cavity. In this case, the

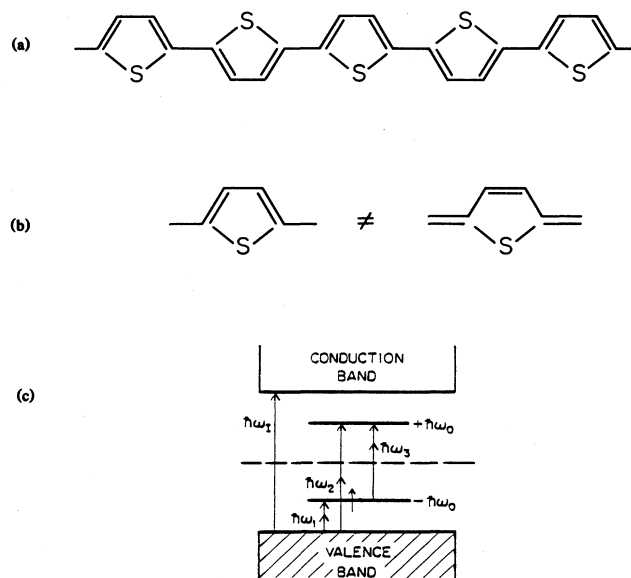


FIG. 1. (a) Chemical structure diagram for poly(thiophene). (b) Two inequivalent structures for the thiophene heterocycle in poly(thiophene). (c) Energy level diagram and allowed transitions for a "hole" polaron.

photoexcitation was pumped with a high-intensity tungsten lamp.

In Fig. 2, we show the photoinduced absorption spectra of poly(thiophene) from 400 to 8000  $\text{cm}^{-1}$  at 80 K. The data are plotted as  $(-\Delta T)/T$  versus frequency where  $T$  is the transmission and  $\Delta T$  is the photoinduced change in transmission ( $-\Delta T > 0$  implies increased absorption). There are two important spectral features evident in the figure: the four relatively narrow lines between 900 and 1400  $\text{cm}^{-1}$  and the broad asymmetric line which peaks at 3600  $\text{cm}^{-1}$ . As shown in the inset the mid-ir lines are at 1020, 1120, 1200, and 1320  $\text{cm}^{-1}$  with full-widths of about 100  $\text{cm}^{-1}$ . The sharp derivativelike features (e.g., at 800  $\text{cm}^{-1}$ ) occur only where there are strong ir absorptions in poly(thiophene). They show up on Fig. 2 as a result of sample heating by the incident laser beam. (If the mode frequency is weakly temperature dependent, then in the presence of modest sample heating the subtraction procedure described above will yield a derivativelike difference curve.) Fortunately, the dark spectrum is clean where the photoinduced peaks in  $(-\Delta T)/T$  occur. Moreover, the line shapes of the four modes listed above are clear maxima rather than derivativelike. We conclude that these four modes are genuine photoinduced absorption lines resulting from the excitation in the poly(thiophene) generated by the laser pump.

In Fig. 3, we show the photoinduced spin resonance in poly(thiophene). The dark signal (from the 64 ppm per carbon neutral defects) is shown superposed on the signal obtained under continuous illumination by white light with an intensity of 800  $\text{mW}/\text{cm}^2$ . These data were obtained with the sample at 50 K using 100-kHz modulation. In Fig. 3 we plot the difference signal (ESR absorption with light on minus ESR absorption with light off) which is a direct measurement of the photogenerated spins. We have checked for saturation; neither the dark signal nor the photoinduced

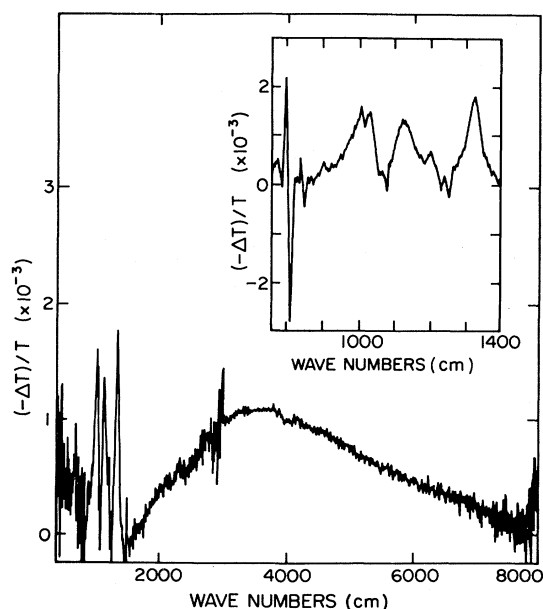


FIG. 2. Photoinduced absorption spectrum of poly(thiophene) with sample at 80 K. Inset shows the mid-ir spectrum in more detail.

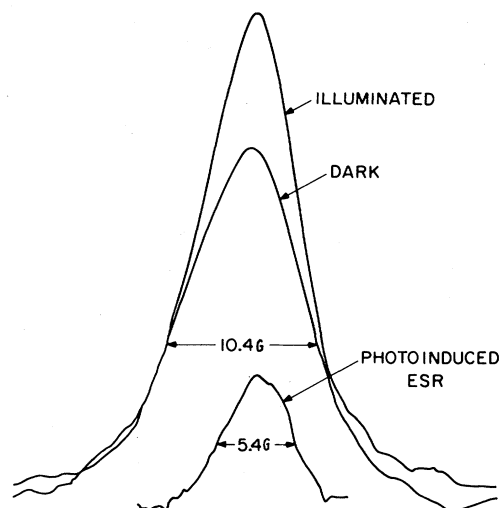


FIG. 3. Photoinduced electron-spin resonance in poly(thiophene). The ESR signal in the dark and under white light illumination are shown, as well as the photoinduced ESR absorption (signal with light on minus signal with lights off).

signal are saturated at the microwave power levels used.

The observed *increase* in the ESR absorption rules out sample heating by the absorbed light as the origin of the photoinduced signal. Care was taken to minimize sample heating by mounting the sample (pressed pellet of polythiophene in KBr) directly in the helium flow of the Helitran apparatus. Note, furthermore, that the linewidths of the dark signal [Fig. 3(a)] and the photoinduced signal [Fig. 3(b)] are different; the photoinduced signal is narrower. Close examination of many traces (derivative and first integral) shows that the photoinduced line is shifted upfield relative to the dark signal by about 0.5 G implying  $\Delta g/g \cong 10^{-4}$ . The *increase* in ESR absorption, the different linewidth, and the *g*-shift demonstrate that the photoinduced ESR signal is real and results from electron-spin resonance of the photoexcitations generated by the absorbed photons.

As noted previously for *trans*-(CH)<sub>x</sub>,<sup>4-6</sup> the general features of  $\Delta T/T$  in the mid-ir range in photoexcited and doped poly(thiophene) are similar. Hotta, Shimotsuma, and Taketani<sup>13</sup> recently reported infrared measurements on polythiophene electrochemically prepared with a variety of dopant species. They find dopant induced absorption bands at 1330–1310, 1200, 1120–1080, and 1030–1020  $\text{cm}^{-1}$ . The close correspondence with the four modes shown in Fig. 2 is evident.

Horowitz<sup>14</sup> has shown quite generally that charge storage via solitons, polarons, or bipolarons will lead to localized infrared modes between each pair of Raman modes in the pristine polymer. Thus, from the ir modes alone, one cannot determine the symmetry of the charge storage state. The existence of photoinduced spins in poly(thiophene) (see Fig. 3) implies that at least some of the charged photoexcitations are polarons with spin- $\frac{1}{2}$ .

We attribute the broad photoinduced absorption peaked at 0.45 eV to the lowest-energy electronic transition of the photogenerated polarons:  $\hbar\omega_1$  on Fig. 1(c). The other two transitions on Fig. 1(c) would be expected to be above 1 eV and thus outside of the spectral range available with the

Fourier transform infrared technique. In the case of charge storage in bipolarons, the expected transitions would be analogous to  $\hbar\omega$ , and  $\hbar\omega_3$  in Fig. 1(c). The strong transition between localized levels is absent for bipolarons since the levels are all either empty or doubly occupied. In our earlier work<sup>15</sup> using *in situ* absorption during electrochemical doping of poly(thiophene) we conclude that in the doped polymer charge ( $2|e|$ ) was stored in bipolaron states. This conclusion was based on the observation of *only* two transitions implying that the two levels are not occupied. If there were electrons in the lower level (as would be the case for a polaron) then a third absorption would be evident arising as a transition between the two localized levels.<sup>11</sup> This was not observed.<sup>15</sup>

Our tentative conclusion is that in the doped polymer charge is stored in charged bipolarons, whereas at least some of the charged photoexcitations are polarons. In the case of photoexcitation, the *neutral*, spin singlet, bipolaron (if formed) would have a short lifetime and weak ir activity,<sup>16</sup> and thus would not contribute to the photoinduced properties. Comparison of the excitation profiles, temperature dependences, and intensity dependences are required to definitively establish that the charge and spin (observed in Figs. 2 and 3) are associated with the same photoexcitation; and magnetic measurements on doped poly(thiophene) are

required in order to determine the spin-charge relation for the doped species. Experiments have been initiated to extend the photoinduced spectral range into the far ir (beyond the cutoff of the KBr pellet) using reflection techniques on high-quality polythiophene films electrochemically polymerized from dithiophene monomer.<sup>15</sup>

In conclusion, from initial measurements of photoinduced infrared absorption and electron-spin resonance, we have demonstrated the photoproduction of charge and spin-carrying excitations in poly(thiophene). These data are to be contrasted with the results obtained from earlier experiments on *trans*-(CH)<sub>x</sub> where the same techniques indicated<sup>1-7</sup> that the charge photoexcitations are spinless solitons.

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