

## Photoexcitation of Polarons and Molecular Excitons in Emeraldine Base

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We report the first observation of the photoinduced absorption spectrum of the emeraldine base form of polyaniline. The spectrum contains both subgap photoinduced bleaching at 1.8 eV and photoinduced absorptions at 0.9, 1.4, and 3.0 eV, as well as band-edge bleaching above 3.5 eV. The existence of the subgap bleaching peak is consistent with a model of optically excited localized molecular excitons. The energies of the three photoinduced absorption peaks and the dependence of the peak amplitudes on pump power give evidence for the photoexcitation of polaron pairs that recombine bimolecularly.

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Conducting polymers have attracted considerable attention recently because of the presence of nonlinear optical properties in these materials.<sup>1,2</sup> Photoinduced absorption experiments carried out in nearly steady-state conditions have been used to identify and investigate the photoexcitations of materials such as polyacetylene,<sup>3</sup> polythiophene,<sup>4</sup> and polydiacetylene.<sup>5</sup> These experiments, together with light-induced electron-spin resonance (ESR) and photoluminescence experiments, have identified the presence of photoinduced intragap absorptions and have thus aided the application of the concepts of solitons, polarons, and bipolarons to these novel materials.

We report here the first observation of the photoinduced absorption spectrum of a polymer of current interest, the emeraldine base (EB) form of polyaniline. This insulating polymer, illustrated in (i) of Fig. 1(a), differs substantially from earlier studied polymers in several important aspects. First, it is not charge-conjugation symmetric; that is, the Fermi level and band gap are not formed in the center of the  $\pi$  band, so that the valence and conduction bands are very asymmetric.<sup>6</sup> Consequently, the energy-level positions of doping-induced and photoinduced excitations differ from those in charge-conjugation-symmetric polymers such as polyacetylene and polythiophene. Second, both carbon rings and nitrogen atoms are within the conjugation path, forming a generalized "A-B" polymer,<sup>7</sup> unlike polypyrrole and polythiophene, whose heteroatoms do not contribute significantly to  $\pi$ -band formation.<sup>8</sup> Third, emeraldine base can be converted from an insulating to a metallic state if protons are added to the  $=N-$  sites while the number of electrons on the chain is held constant.<sup>9</sup> For example, exposure of emeraldine base to a

protonic acid such as HCl causes a transformation to the emeraldine salt (ES) form of polyaniline, (ii) of Fig. 1(a), which exhibits metallic properties proposed as being due to formation of a polaron lattice in the material,<sup>10-12</sup> in agreement with band-structure calculations<sup>6</sup>

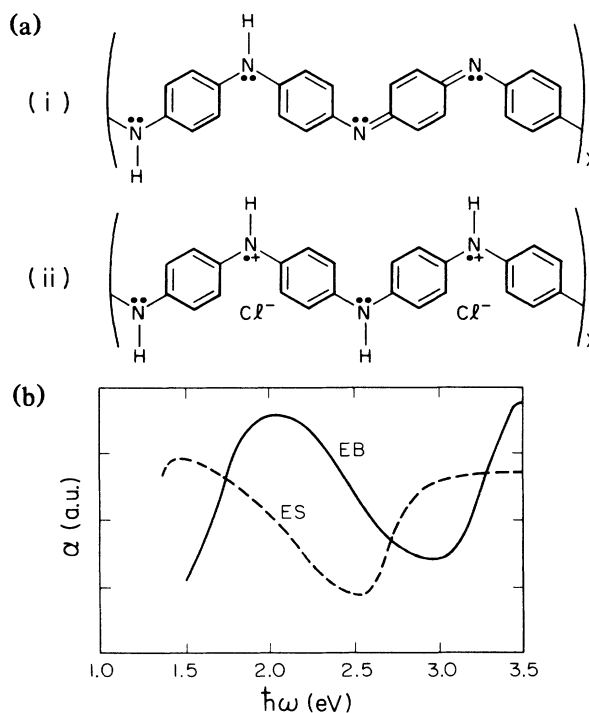


FIG. 1. (a) Repeat unit structure of the (i) emeraldine base (EB) and (ii) emeraldine salt (ES) forms of polyaniline. (b) Absorption spectra of EB and ES.

and optical studies.<sup>6,11,13</sup> Partial protonation leads to phase segregation between protonated and unprotonated regions.<sup>10-14</sup>

The absorption spectra of EB and ES are shown in Fig. 1(b); EB possesses absorption features at 2.0 and 3.5 eV. Our experiments show the presence of five strong photoinduced features in this material: photoinduced absorptions at 0.9, 1.4, and 3.0 eV, and photoinduced bleachings at 1.8 and 3.7 eV. Laser-intensity and modulation-frequency studies demonstrate that the 0.9-, 1.4-, and 3.0-eV induced absorptions and the 3.7-eV induced bleaching have origins different from the 1.8-eV bleaching. The results are discussed in terms of a model of photoexcitation of excitons and polarons in the material.

Upon protonation of EB to form ES, the 2-eV exciton peak vanishes while two new absorptions appear at 1.5 and 3 eV. The 2-eV absorption in EB has been attributed<sup>11</sup> to the formation of a molecular exciton qualitatively described by a charge transfer of  $-|e|/2$  into the quinoid ring from each of the neighboring benzenoid rings.<sup>15</sup> The band-gap transition is at 3.5 eV or above.<sup>15</sup> The disappearance of the quinoid rings upon protonation makes it impossible to form these molecular excitons, consistent with the absence of the 2-eV absorption in ES.

The two absorptions in ES have been identified by Stafström *et al.* as resulting from the new electronic structure that arises from the positive charges that are placed on the polymer chain when EB is protonated.<sup>6</sup> These charges distort the lattice to form positively charged polarons which give rise to two new bands: an almost dispersionless empty band nearly degenerate with the conduction band, and an  $\sim 1$ -eV-wide half-filled band roughly 1.5 eV above the valence band. The asymmetry is a consequence of the lack of charge-conjugation symmetry and the *A-B* character of the polymer. New absorptions at 1.5 and 3.0 eV are assigned<sup>6</sup> to excitations from the highest and second-highest valence bands to the lower polaron band.

Nearly steady-state photoinduced absorption experiments were carried out with use of the light from a tungsten-halogen or deuterium lamp filtered through a monochromator to provide probe photon energies from 0.4 through 4.5 eV and with either an argon laser or a dye laser to excite the sample at excitation energies from 2.0 to 2.7 eV. The laser beam was mechanically chopped at frequencies  $f$  between 4 and 400 Hz; a lock-in amplifier was used to measure the induced change in sample transmission. The sample transmission was measured simultaneously in order to compute  $\Delta T/T$ , which is independent of the response of the measuring apparatus. The samples studied were thin ( $\leq 1 \mu\text{m}$ ) films cast from a solution of EB in dimethyl sulfoxide onto either glass or quartz substrates.

The photoinduced absorption (PA) spectrum of EB, measured at a substrate temperature of 300 K, a laser photon energy of 2.54 eV, and a chopper frequency of 21

Hz, is shown in Fig. 2. Measurements of the temperature dependence of the linear absorption spectrum of EB verified that there were no significant artifacts due to heating of the sample by the laser. The PA spectrum of EB has five distinct features: photoinduced bleaching peaks at 1.8 and 3.7 eV, and photoinduced absorption peaks at 0.9, 1.4, and 3.0 eV. Very weak PA changes in the infrared phonon spectrum of EB have also been observed.<sup>16</sup> The shape of the PA spectrum changes little for pump laser photon energies between 2.0 and 2.7 eV. The relative sizes of the photoinduced peaks do, however, vary with pump-photon energy, with the 1.8-eV bleaching peak being relatively stronger at lower pump-photon energies. At a substrate temperature of 80 K, the low-energy bleaching feature peaks at 2.0 eV and the 1.4-eV absorption peak is increased in magnitude.

The dependence of each peak in  $|\Delta T/T|$  was studied as a function of incident laser intensity, Fig. 3, and chopper frequency, Fig. 4, in order to elucidate their origins. The 1.8-eV induced bleaching behaves differently from the other peaks, its magnitude scaling linearly with laser intensity, which indicates that a unimolecular decay process is involved. The other four PA features all scale as the square root of the laser intensity, suggesting that the excitations responsible for these features decay by a bimolecular recombination process. This clearly indicates that at least two different photoexcitations exist in EB. Table I summarizes the laser-intensity and frequency dependence of the five photoinduced features. The significant frequency dependence indicates that at least some of the photoexcitations have lifetimes on the order of 50 ms. The 1.4- and 3.0-eV photoinduced absorptions have the same chopper-frequency and laser-intensity dependences, suggesting that they have a common origin. The two bleaching features exhibit stronger  $f$  dependences—implying longer-lived excitations—while the 0.9-eV absorption feature has a weaker  $f$  behavior, indicating more rapid temporal decay of the exci-

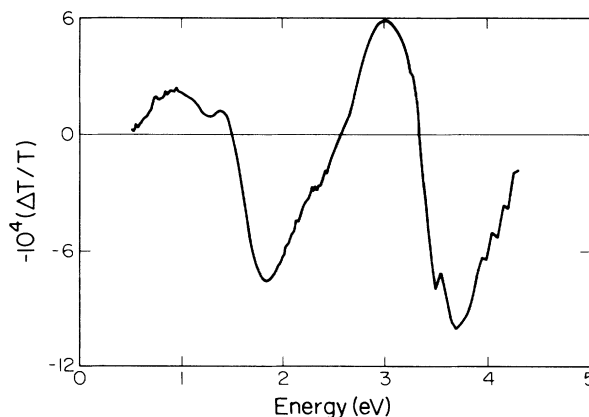


FIG. 2. Photoinduced spectrum of emeraldine base at 300 K taken with a laser intensity of  $0.25 \text{ W/cm}^2$  and a laser photon energy of 2.54 eV.

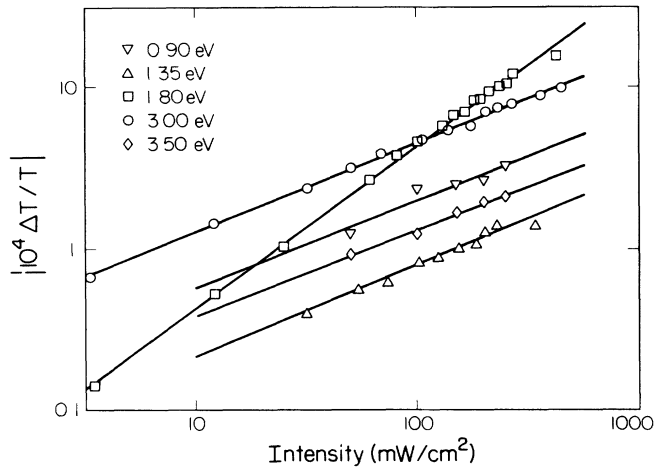


FIG. 3. Log-log plot of the laser-intensity dependence of the five photoinduced features of EB. Lines shown are least-squares fits to the data. The 1.8-eV feature scales linearly with incident laser power, while the other four features scale as the square root of the incident laser power.

tations causing this feature.

The origin of the PA defects is important, especially in the context of the electronic reorganization that occurs in the polymer upon protonation. It is suggested that, when laser light is absorbed by the sample, molecular excitons are created. Picosecond PA experiments indicate that these excitons form in less than 10 ps after light strikes the polymer and that the vast majority decay in less than 2  $\mu$ s.<sup>17</sup> The remaining long-lived excitons may be stabilized through ring rotations or other conformation changes that inhibit recombination. This long-lived component may contribute to the  $f$  dependence of the 3.5-eV PA bleaching.

There are several unimolecular decay channels possible for molecular excitons, including charge recombination and charge separation. Charge recombination involves exciton collapse with the emission of either phonons or photons (luminescence). However, no significant luminescence was observed in EB at room or liquid-helium temperatures. Charge separation involves a rearrangement of charge into pairs of oppositely charged polarons that can separate from each other.

The 1.4- and 3.0-eV photoinduced absorption peaks in the photoinduced spectrum are, by analogy with the ES absorption spectrum, due to the photoproduction of positive polarons  $P^+$  in EB. The identical chopper-frequency behavior of these two peaks confirms that they result from the formation of the same in-gap state, just as was predicted for positive polarons in ES.<sup>6</sup> These  $P^+$  states have their likely origin in the dissociation of a fraction of the excitons into charged polarons, though direct production of  $P^+$  and  $P^-$  may contribute.<sup>18</sup>

The origin of the 0.9-eV photoinduced absorption is less clear. One possibility is that it represents a transi-

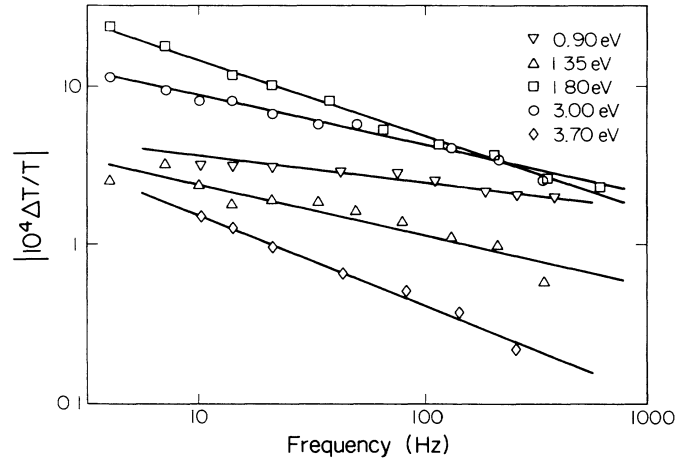


FIG. 4. Log-log plot of the chopper-frequency dependence of the five photoinduced features of EB. Lines shown are least-squares fits to the data. The 1.4- and 3.0-eV features display the same chopper-frequency behavior.

tion from a negative polaron state to the conduction band; this is consistent with the observed laser intensity dependence. The different chopper-frequency dependence of the 0.9-eV peak could result from the existence of different diffusion rates for  $P^+$  and  $P^-$ , consistent with the lack of charge-conjugation symmetry in EB. Alternatively, the 0.9-eV peak may be caused by the formation of some numbers of charged bipolarons or neutral polarons whose lowest optical transition is reduced in energy from that of the polarons.

The band-edge bleaching observed in EB has a different origin than does the bleaching of the exciton absorption; for laser photon energies well below the band-gap energy, direct creation of electrons and holes in the conduction and valence bands cannot occur. As the band-edge varies with laser intensity  $I$  as  $I^{1/2}$ , it is associated primarily with the removal of states from the conduction and valence bands to form polarons. This contrasts with the  $I^1$  behavior observed from the magnitude

TABLE I. Summary of the laser-intensity dependence and chopper-frequency dependence (at 300 K) of each of the five photoinduced features of EB. PA, photoinduced absorption; PB, photoinduced bleaching.

Photon energy (eV)	Peak type	Intensity behavior	Frequency behavior
0.9	PA	$\sqrt{I}$	$f^{-0.17}$
1.4	PA	$\sqrt{I}$	$f^{-0.31}$
1.8	PB	$I$	$f^{-0.47}$
3.0	PA	$\sqrt{I}$	$f^{-0.31}$
3.7	PB	$\sqrt{I}$	$f^{-0.56}$

of the 2-eV bleaching peak.

Spin photoproduction in EB has also been observed in preliminary light-induced ESR experiments.<sup>19</sup> EB powder in an ESR cavity was illuminated with the light from a Hg-Xe arc lamp, which was filtered to ensure that only the exciton absorption was excited. A narrower photoinduced line ( $\Delta H_{pp} \approx 2.2$  G) was found superimposed over the broader ( $\Delta H_{pp} \sim 3.6$  G) dark ESR signal of EB. This supports the assertion that polarons, as opposed to spinless bipolarons, are photoexcited in EB; however, the possibility that triplet excitons are formed has not been ruled out by these results.

In summary, the photoinduced spectrum of the novel emeraldine base polymer has a variety of features, including three induced absorptions, at 0.9, 1.4, and 3.0 eV, as well as two induced bleachings at 1.8 and 3.7 eV. The induced 1.8-eV bleaching is associated with the filling of molecular exciton absorption states by the pumping-laser photons. We attribute the absorptions to the photocreation of polarons on the polymer chains via exciton decay, giving rise to in-gap polaron levels. These polarons recombine bimolecularly, as borne out by the power dependence of the induced absorption peaks. The induced bleaching of the band edge results from states removed from the conduction and valence bands when excitations are formed.

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