Neutral Soliton Formation and Disorder in Pernigraniline Base

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A new long-lived photoinduced absorption near 1.8 eV is reported for pernigraniline base, the Peierls degenerate ground state form of polyaniline. The absence of associated infrared active vibrational modes and the results of light-induced ESR experiments identify the photoexcited defects as disorder confined neutral soliton pairs with a temperature dependent antiferromagnetic exchange interaction. The optical transitions across the Peierls gap are suggested to be broadened by static and quantum fluctuations. The results are in very good agreement with recent predictions of Su and Epstein and McKenzie and Wilkins.

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Though solitons are predicted as stable nonlinear excitations in numerous theoretical models [1,2], their existence has been demonstrated in few condensed matter systems [3,4]. The successful synthesis [5,6] of pernigraniline base (PNB) provides the first degenerate ground state quasi-one-dimensional polymer beyond *trans*-polyacetylene [*trans*-$(CH)_x$] that, in principle, can support solitons [7–9]. Charged solitons have recently been observed in this system [10]. In this Letter, we report the photogeneration of confined neutral solitons in PNB. The difference in their dynamics from those of neutral solitons in *trans*-$(CH)_x$ is attributed to the central role of ring torsion and interchain interaction in PNB. We also report a broadened interband (Peierls gap) absorption in agreement with predictions [11–13] of subgap optical absorption caused by quantum fluctuations and static disorder.

The schematic chemical structure of the dimerized form of PNB is shown in Fig. 1 (inset). In the undimerized form, there is one unpaired electron per N-ring repeat unit of projected length a along the chain axis. The lattice distortion of PNB includes an alternation in the bond length, described by order parameter u [7] and a dimerization in the ring angle described by order parameter ψ [14,15]. X-ray diffraction studies demonstrate that a typical pernigraniline base polymer is only $\sim$ 30% crystalline with a coherence length of $\sim$ 50 Å ($\sim$ 10 ring, N units) [16]. This contrasts with the typical 90% crystallinity and coherence length of $\sim$ 100 Å for *trans*-$(CH)_x$ ($\sim$ 80 C-C units) [17]. Another important distinction is the absence of charge conjugation symmetry [in contrast to idealized *trans*-$(CH)_x$] which implies that neutral soliton pairs can be directly photogenerated [18].

Long-time photoinduced absorption (PA) experiments were carried out using a Nicolet 60SX Fourier transform

infrared (FTIR) spectrometer (500–20 000 cm^{-1} or 0.06–2.5 eV) and a Perkin-Elmer Lambda 19 UV/Vis/NIR spectrometer (0.4–7.2 eV). The Perkin-Elmer Lambda 19 was also used to measure direct absorption spectra. Light-induced electron spin resonance (LESR) experiments to determine the spin associated with the photoexcited defect states were performed with a Bruker 300 ESR spectrometer operating at 9.5 GHz utilizing a standard TE102 cavity with a partial transmission window. The output of a Coherent Innova argon-ion laser (2.4 or 2.5 eV) provided the excitation energy for the photoinduced experiments. The PNB samples used for these studies were in powder form mixed with KBr and pressed under vacuum into uniform pellets that were 0.02%–0.05% PNB by weight. The samples were cooled using a continuous flow liquid helium refrigerator. The long-lived photoin-
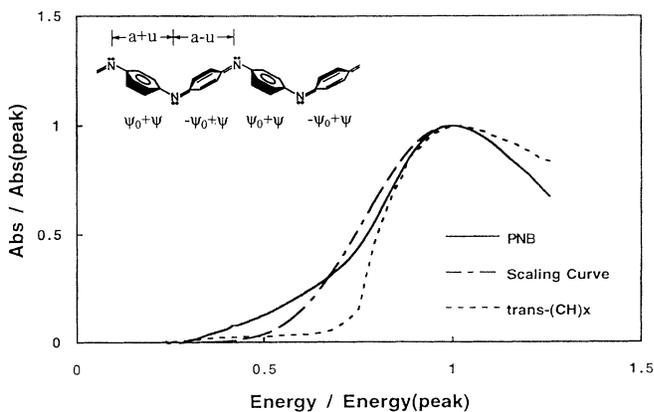

FIG. 1. Optical absorption spectra of *trans*-$(CH)_x$ (dashed line) [19] and PNB (solid line); scaling curve with $\eta = 0.41$ (broken line) [20]. The scaling curve is in units of optical conductivity. Inset: Schematic structure of dimerized PNB.

duced absorption (magnetic) spectra were determined by comparing the optical (ESR) spectra before and after illumination of the sample by the pump beam.

A comparison of the optical absorption spectra of trans-$(CH)_x$ [19] and PNB (Fig. 1) shows that the subgap absorption tail is more significant in the latter. McKenzie and Wilkins recently have shown [11] that for the Peierls-Fröhlich ground state the width of the tail into the gap scales as $\eta^{2/3}\Delta$ where η is a disorder parameter given by $\eta \sim (2\Delta/W)(\delta u/u_0)^2$ with 2Δ the band gap, W the bandwidth, δu the lattice fluctuation, and u_0 being the lattice distortion. This expression must be modified to describe the disorder in PNB as the Peierls gap in PNB is $\sim 60\%$ due to bond length alternation and $\sim 40\%$ due to ring angle dimerization [15]. Thus for PNB,

$$\eta = \eta_{\text{bond}} + \eta_{\text{ring}} \sim (2\Delta/W)[(0.6\delta u/u_0)^2 + (0.4\delta\psi/\psi_0)^2]$$

with $\delta\psi$ the ring angle fluctuation and ψ_0 the ring angle dimerization. It is noted that $2\Delta/W$ for PNB [14,15] is 4 times larger than that for trans-$(CH)_x$ [3]. Considering only effects due to quantum fluctuations, $\eta_{trans\text{-}(CH)_x} \sim 0.15$ while $\eta_{PNB} \sim 0.24$, as there are negligible quantum fluctuations in ψ ($\delta\psi \sim 3°$) due to the large moment of inertia of the rings (~ 89 amu Å^2). Static disorder is much more significant in PNB when compared to trans-$(CH)_x$. The ring angle fluctuation will be more sensitive to this than the bond length fluctuation; assuming δu is essentially unchanged while $\delta\psi \sim \psi_0$ for static disorder, η for PNB will increase to ~ 0.35 when static disorder effects are included. A new method for computing the electronic properties of disordered Peierls systems has recently been developed [20]. Kim et al. [20] show that the optical conductivity, when properly scaled, follows a universal curve. Though the experimental data are optical absorption, we can still use this scaling method to obtain an estimate for η. Fitting the PNB optical absorption to the universal scaling curve [20] (Fig. 1) gives $\eta \sim 0.41$ in reasonable agreement with the η value estimated independently above. In addition to the observed broadening of the Peierls gap, expected effects of this increased disorder in PNB are broadening of optical absorptions due to defect states near the band edges (making them unobservable) and confinement of pairs of photoexcited defects to segments of individual polymer chains.

The long-time PA spectrum of PNB from 0.6 to 6.0 eV obtained after a 20 sec exposure to the pump beam at 150 K is shown in Fig. 2(a). The pump beam energy was 2.54 eV and the intensity was ~ 100 mW/cm^2. The features of this spectrum are PA peaks near 1.5, 1.8, and 3.2 eV as well as photoinduced bleaching (PB) peaks near 2.4, 3.8, and 4.5 eV. This is the first observation of long-lived PA and PB features of energies > 1.6 eV. The bleaching near 2.4 eV shows the expected decrease of the Peierls gap absorption after photoexcitation, while the PB peaks at higher energies are the first observation of bleachings of π - π^* transitions localized to the benzenoid and quinoid units, respectively. Each of the PA and PB features have
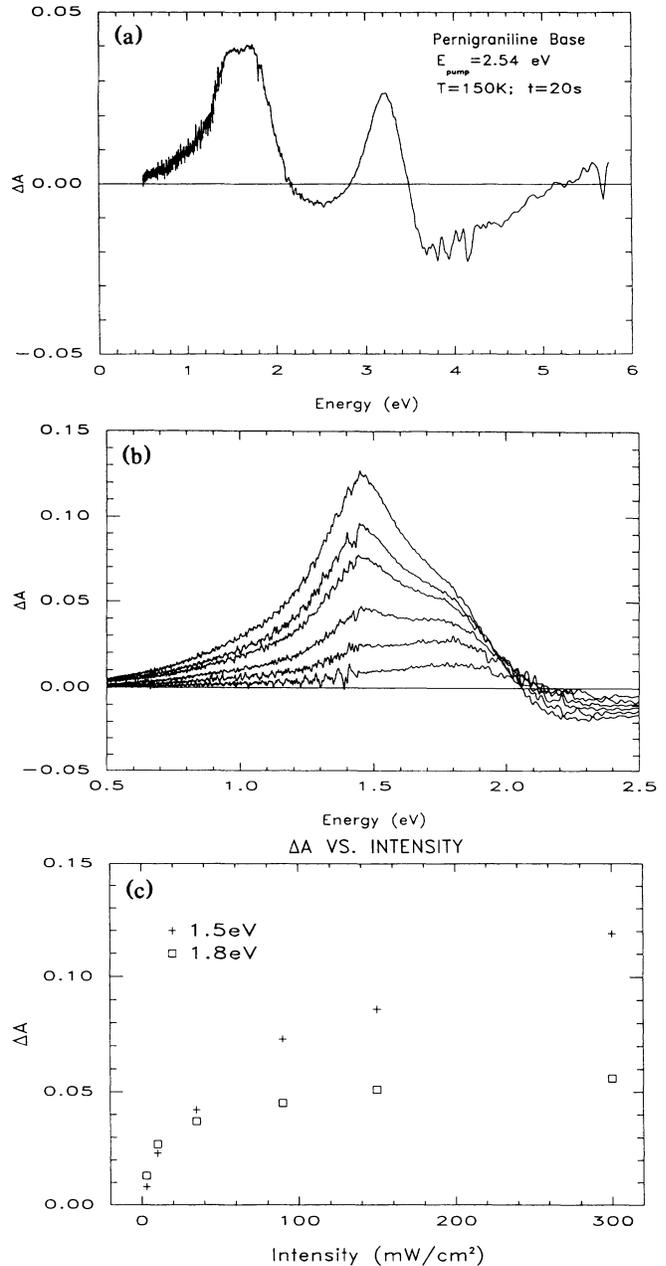

FIG. 2. (a) Long-time photoinduced absorption (PA) spectrum of PNB obtained with pump laser intensity $I = 100$ mW/cm^2, pump energy of 2.54 eV, exposure time of 20 sec, and sample temperature of 150 K. (b) Long-time PA spectra of PNB for 2.54 eV pump intensities of 3, 10, 35, 90, 150, and 300 mW/cm^2 at 80 K. (c) Photoinduced absorption (ΔA) vs intensity for 1.5 and 1.8 eV PA (at 80 K).

lifetimes >24 h at 80 K attributed to the effects [14] of ring torsion angle changes and interchain interactions.

The PA near 1.5 eV, which was reported earlier as having an associated charge and spin 1/2 [10], is consistent with the formation of an electron polaron [9]. The energy levels associated with the corresponding hole polaron are calculated to be near the valence and conduction band

edges [9], and could be obscured by the significant subgap absorption due to disorder that is observed in PNB.

The long-lived subgap absorptions at 1.5 and 1.8 eV are not associated with the same photoinduced defect. Figure 2(b) shows the long-time photoinduced absorption spectra resulting from six separate experiments with all experimental parameters held constant except for the pump beam intensity varying from 3 to 300 mW/cm^2. The sample was warmed to room temperature after each experiment to erase all of the photoexcited defects. The 1.5 eV PA is dominant at high intensities, but at low intensities, the 1.8 eV PA is more prominent [Fig. 2(c)]. A similar experiment was performed to observe the behavior of the two features as the sample temperature was varied. At low temperatures (e.g., 10 K), the 1.5 eV peak is the dominant feature, but at high temperatures (e.g., 200 K), the 1.8 eV peak becomes dominant.

Only the 1.5 eV PA peak is resolvable after a 2 h exposure to the pump beam (2.54 eV) at 50 K, Fig. 3(a). Figure 3(b) shows the infrared active vibrational (IRAV) modes (associated with the 1.5 eV PA) obtained under identical experimental conditions. By shortening the exposure time to 20 sec and increasing the sample temperature to 150 K, the PA and IRAV modes shown in Figs. 2(a) and 3(c), respectively, were obtained. Although both the 1.5 and 1.8 eV peaks are present in the optical PA spectrum obtained under these conditions [Fig. 2(a)], no new IRAV modes are associated with the 1.8 eV absorption, *indicating that the defect producing this absorption is neutral.* It is noted that the 1.8 eV PA is not present in the nondegenerate ground states of polyaniline (leucoemeraldine base and emeraldine base). The results are consistent with the prediction of stable neutral solitons in PNB [9].

In LESR studies of the spin, the sample was cooled to the desired temperature and exposed to the pump beam (2.54 eV, 100 mW/cm^2) for 20 sec. Comparable photoinduced optical measurements repeated for different temperatures in the range from 10 to 80 K [Fig. 4(a)] showed that the 1.8 eV PA increased while the 1.5 eV PA remained constant. However, the effective number of spins, determined by calculating χT, showed a decrease over the same temperature range [Fig. 4(b)]. The absence of an LESR signal at half field dismisses the model that triplet excitons are being photoexcited. Absorption detected magnetic resonance [21] could not be applied due to the long lifetimes of the defects.

Attempts to fit the χT data using a simple spin exchange model with $\chi T = 2N/[3 + \exp(J/T)]$, where N is the number of spins and J an effective antiferromagnetic exchange parameter, were not successful. However, the data can be parametrized by assuming a rapid increase in J, for example, $J = J_0 + bT^3$, with J_0 and b constants, consistent with a decrease in the effective separation between the solitons of a disorder-confined pair.

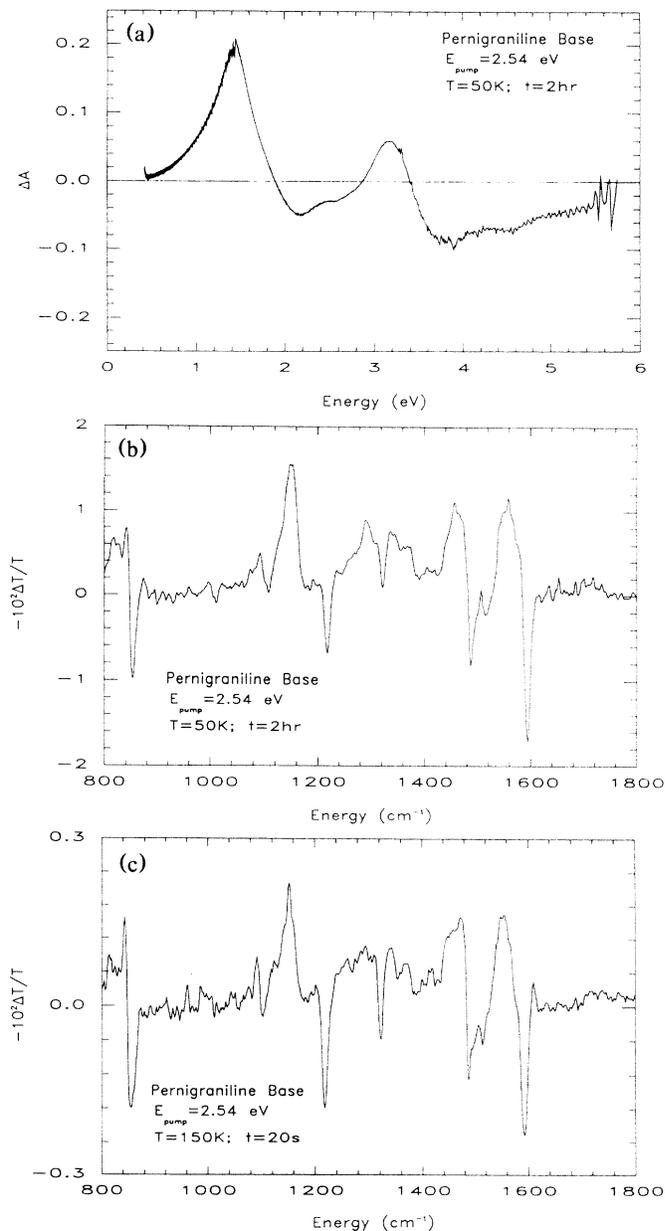In summary, the Peierls gap of PNB is substantially

FIG. 3. Long-time photoinduced spectra for 2.54 eV pump beam intensity of 100 mW/cm^2. (a) Optical absorption after 2 h exposure at 50 K, (b) infrared absorption after 2 h exposure at 50 K, and (c) infrared absorption after 20 sec exposure at 150 K.

broadened by both quantum and static fluctuations compared to that of $trans$-$(CH)_x$. We propose that the new 1.8 eV PA (and a component of the 1.5 eV absorption [9]) in PNB results from the formation of long-lived neutral solitons. LESR measurements show that the neutral solitons are photoproduced in pairs, and that the solitons within each pair are coupled via a temperature dependent antiferromagnetic exchange interaction. The confinement of the pairs and the Peierls optical gap are
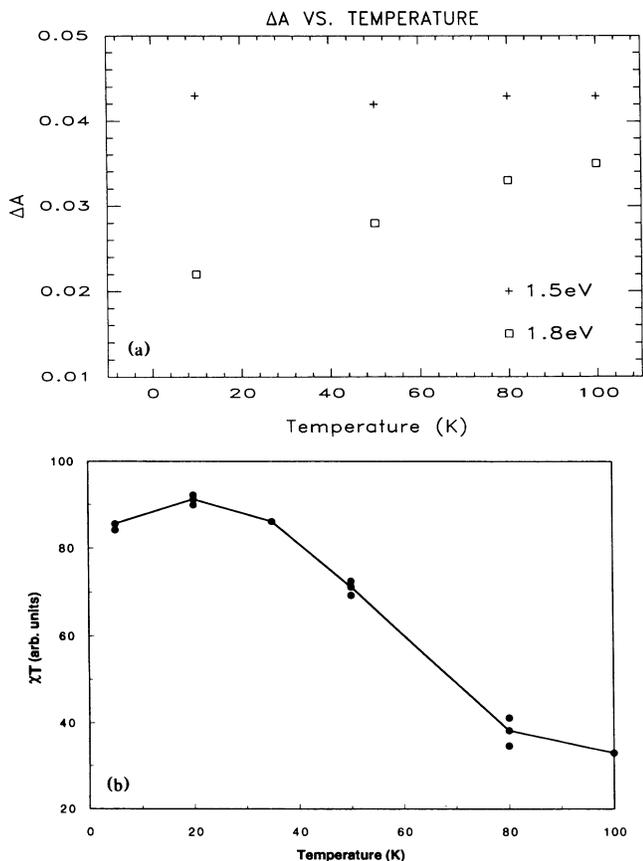
FIG. 4. (a) Photoinduced absorption (ΔA) vs temperature for 1.5 and 1.8 eV PA (100 mW/cm^2), (b) effective number of spins (χT) vs temperature.

suggested to be controlled by the local intrachain and interchain order.

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