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The report of doping of polyacetylene to form a highly conducting polymer opened the question concerning the nature of the electronic states of the polymer backbone that are formed upon charge transfer between the polymer and dopant backbone. Extensive study of polyacetylene has demonstrated that this system is a degenerate Peierls semiconductor with a bandgap introduced through bond alternation. Pernigraniline is a semiconductor analogous to *trans*-polyacetylene. However, it differs from polyacetylene in that the overlap between adjacent sites can be modulated by both changes in bond length and changes in ring torsion angle. It is shown that as a result of these two independent order parameters there are differing types of charge excitation possible on pernigraniline backbone, with both bond order excitations such as bond order solitons and ring torsion excitations such as ring torsion polarons possible. Recent photoexcitation spectroscopy studies have confirmed the presence of both bond order solitons and ring rotation polarons.

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THE PEIERLS GROUND STATE, SOLITONS AND POLARONS IN RING-CONTAINING POLYMERS

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Abstract

The report of doping of polyacetylene to form a highly conducting polymer opened the question concerning the nature of the electronic states of the polymer backbone that are formed upon charge transfer between the polymer and dopant backbone . Extensive study of polyacetylene has demonstrated that this system is a degenerate Peierls semiconductor with a bandgap introduced through bond alternation. Pernigraniline is a semiconductor analogous to *trans*-polyacetylene. However, it differs from polyacetylene in that the overlap between adjacent sites can be modulated by both changes in bond length and changes in ring torsion angle. It is shown that as a result of these two independent order parameters there are differing types of charge excitation possible on pernigraniline backbone, with both bond order excitations such as bond order solitons and ring torsion excitations such as ring torsion polarons possible. Recent photoexcitation spectroscopy studies have confirmed the presence of both bond order solitons and ring rotation polarons.

A. Introduction

The interconnection of chemical and electronic structures has been extensively studied for π conjugated polymers such as polyacetylene, polydiacetylene, and polythiophene (Hanack et al. 1991; Aldissi 1989; Shirakawa et al. 1987). The Su-Schrieffer-Heeger (SSH) Hamiltonian and its variants (Heeger et al. 1988) have been widely used to study the electronic structure of the carbon backbone polymers, being particularly successful in describing the ground state of such systems in terms of a Peierls distortion augmented by extrinsic contribution to the ground state energy gap, that is, one electron effects, in the case of the nondegenerate ground state polymers like polythiophene. The SSH model includes the electron-lattice interaction based on the coupling of the charge transfer integral to the separation between adjacent sites. It was found that the charge storing states are soliton, polaron and bipolaron defects in the ground state pattern of bond alternation. Later studies show the important roles of Coulomb interaction and interchain coupling (Hanack et al. 1991; Aldissi 1989; Shirakawa 1987).

The successful preparation of the pernigraniline-based polymer has created the opportunity to test the concepts of electron lattice interaction in polymers which contain both a heteroatom and a ring within the repeat unit. Dos Santos and Brédas (1989a; 1989b; 1990) predicted that the pernigraniline base polymer, Fig. 1a, will act as a degenerate polymer similar to *trans*-polyacetylene. They calculated the effects of bond-length changes (resulting in the formation of alternating benzenoid- and quinoid-like rings) and predicted the formation of charged excitations of this polymer which have soliton and polaron features.

Ginder and Epstein (1990a; 1990b) suggested an alternate perspective on the ground state and defect states in pernigraniline by emphasizing the important role of ring rotational dimerization. Central to this perspective is the ring rotational degree of freedom of the C_6 rings of the polyaniline with respect to the plane formed by the backbone of nitrogen atoms. Rotation of the C_6 rings by a dihedral angle ψ out of this plane leads to a reduction of the carbon-nitrogen p_z transfer integral by a factor $\cos\psi$. Hence a Peierls distortion can be introduced into this polymer through two mechanisms, changes in effective bond length and change in effective ring torsion angle. Figure 1b schematically illustrates the chemical structure of pernigraniline base after bond length and ring torsion angle dimerization. Later calculations (Brédas et al. 1991) demonstrated that the two order parameters contribute independently to the Peierls gap with the ring torsion dimerization contributing about 40% of the full bandgap value and the bondlength dimerization contributing approximately 60% of the full bandgap value.

The near-steady-state (millisecond time scale) and long-lived (second to hour) photoinduced absorption experiments have recently been carried out for pernigraniline polymer (Leng et al. 1991a; 1991b). These experiments are made possible by the recent synthesis of well characterized pernigraniline base (Sun et al. 1990). The sample was photoexcited by the output of an argon ion laser pumping at 2.4 eV, above the ~2.2 eV Peierls gap. Figure 2 summarizes the photoinduced absorption results for pernigraniline obtained in the near-steady-state experiment at 10K and in the long-lived experiment at 80K. The presence of two very different kinds of electronic excitations are clearly observed. The near-steady-state shows the presence of both a low energy peak (~1.0 eV) and a second weaker peak at 1.5 eV. Photoinduced infrared active vibrational modes (IRAV) are found at 1100, 1220, 1320, and 1580 cm^{-1}. In contrast in the long time photoinduced absorption experiment photoinduced absorption is observed at 1.5 eV. The photoinduced IRAV modes at long times are much weaker and found at 1153 and 1554 cm^{-1} and photoinduced bleaching peaks at 1219, 1323, 1487,1591 cm^{-1}. The defect masses can be estimated for the relative oscillator strengths of the electronic transitions and the IRAV utilizing in the amplitude mode formalism (Horovitz 1982; Ehrenfreund et al. 1987). We conclude that the defect masses are ~300 and 5-10 m_e for the 1.5 eV and the 1.0 eV defects, respectively. Also, the lifetimes of the two defects are very different. The 1.5 eV and associated IRAV peaks are observed to have an effective lifetime of several hours or longer at 80K while the 1.0 eV peak and associated IRAV has a lifetime in the millisecond range even at 10K. Based on these and related experimental results, it was proposed (Leng et al. 1991b) that the low energy peak originates from bond length order solitons induced in pernigraniline base while the 1.5 eV peak results from ring rotation polaron defects induced in the ring rotation order parameter of the system. This analysis assumes that the ring rotation and the bond length order parameter are independent. However, the long time photoinduced absorption involves vibrational modes of the benzenoid and quinoid groups indicating there is some coupling between bond length and ring rotation parameters. The defect mass associated with the 1.5 eV feature is therefore an effective mass as the corresponding IRAV are coupled to the bond length parameter.

The early study of π conjugated polyacetylene and related materials led to the introduction of a number of important concepts especially relating to the interaction of charge with the polymer backbone. The study of ring containing polymers su [illegible] the pernigraniline base form of polyaniline now has shown that multiple order parameters play an important role in determining the response of ring containing polymers to the presence of electronic charge.

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FIGURE CAPTIONS

Fig. 1: Schematic chemical structure of (a) undimerized and (b) bond length and ring torsion angle dimerized pernigraniline base polymer. (From Leng et al. 1991b).

Fig. 2: Photoinduced absorption spectra of pernigraniline base polymer as powder mixed with KBr, obtained with pump laser intensity $I_0 = 250$ mW/cm^2. Left scale: Near-steady-state (22.4 Hz light modulation) at 10 K. Right scale: Long-lived (reduced by a factor ~ 400) at 80 K. (From Leng et al. 1991b).

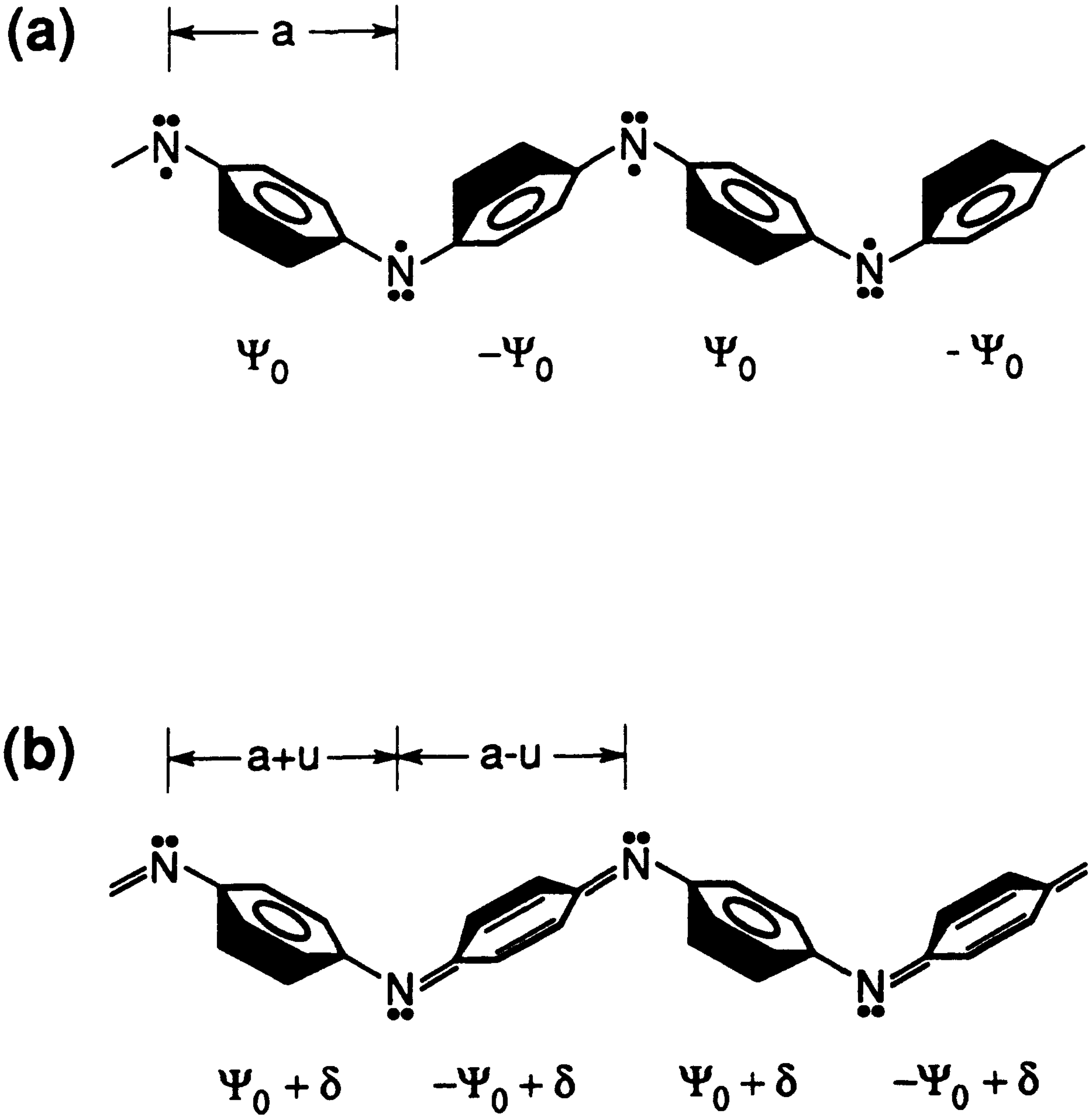
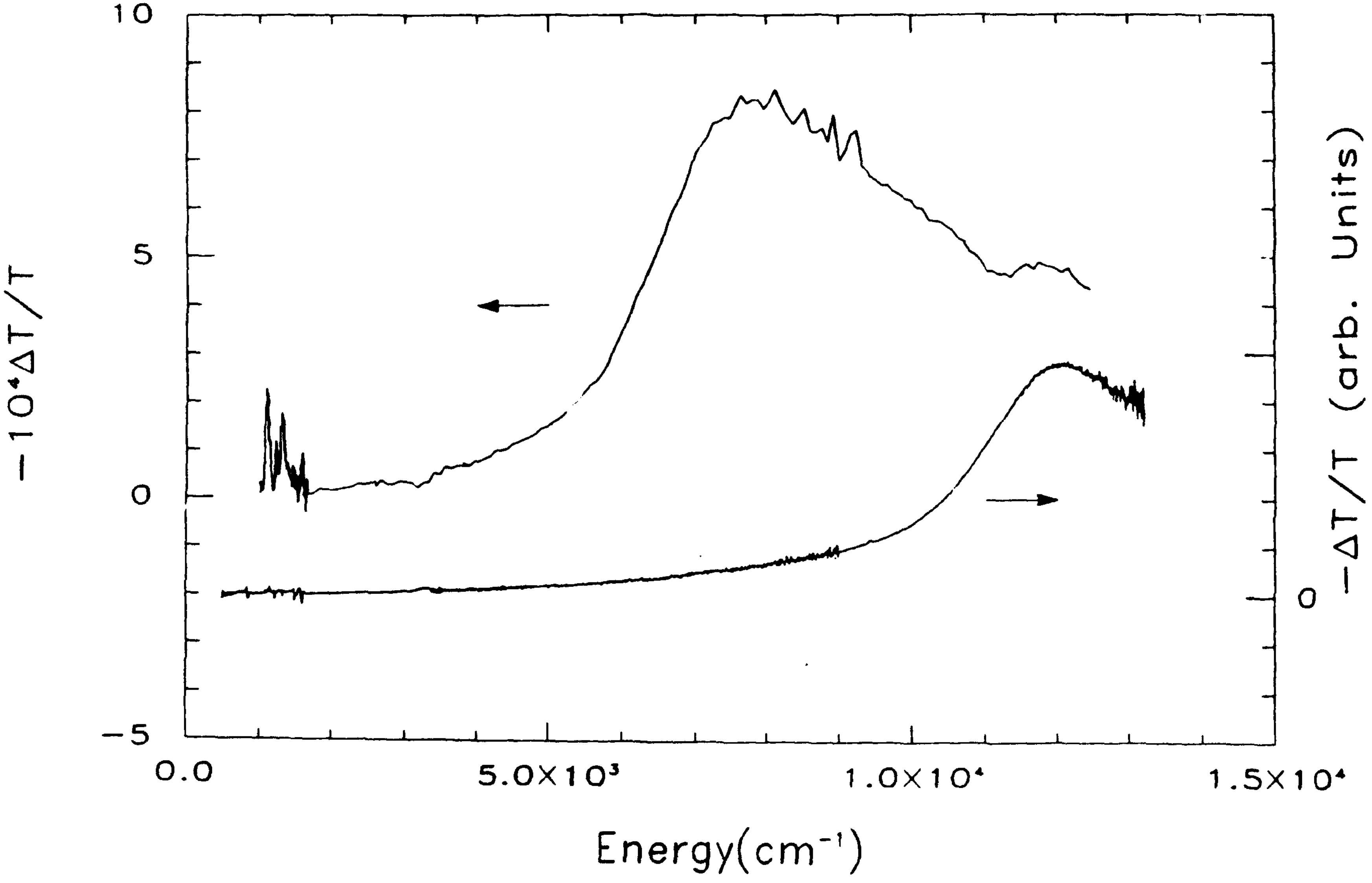


Fig. 1, A.J. Epstein



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