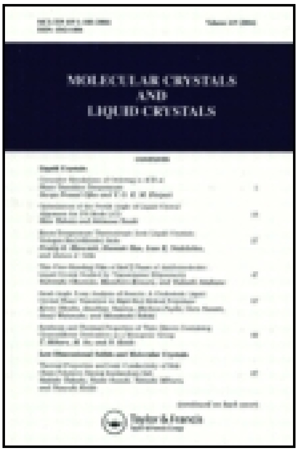

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PHOTOEXCITATION STUDIES OF SOLITONS IN A SHORT POLYACETYLENE

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Abstract We report new experimental results of photoexcitation and doping studies on a chain of short polyene system, poly(phenylacetylene). We found that charged solitons are elementary excitations in short polyenes and confined within the conjugate polyene segments. Effective correlation energy at soliton site is estimatedto be ~ 0.6 eV corresponding to bare on-site Coulomb energy $U_0 \leq 4.0$ eV.

Keywords: Photoexcitation, soliton, infrared-active vibrational modes, pinning, coulomb interaction, polyacetylene

INTRODUCTION

The inherent structural instability against structural distortions in a quasi-one-dimensional electronic system strongly modifies the electronic structure; the system stabilizes further by lowering its energy by spontaneously breaking symmetry leading to the chain dimerization, and opening an energy gap at the Fermi level making a semiconductor. Therefore, a π-conjugated polymer backbone composed of a chain of monomer can be dimerized in two distinct patterns of short and long bond order. When the ground state energies of each different dimerization pattern are the same, the system can support a domain wall-like nonlinear excitation (called soliton) connecting the two phases with opposite bond alternation.

Trans-polyacetylene (t-$(CH)_x$) is a prototype quasi-one-dimensional semiconductor with a two-fold degenerate dimerized ground state and known to support solitons as the important excitations[1]. The soliton can accomodate a charge in the form of negatively or positively charged soliton and has spin-charge reverse relationship. Spinless charged solitons ($S^{\pm}$) can be generated in t-$(CH)_x$ either by chemical charge transfer doping or through charge separation following photoexcitation[2]. Since the soliton creation energy (E_S) is less than the energy required to create a band excitation, the decay channel from a photogenerated electron-hole pair into a positively and negatively charged soliton pair is very effective as predicted by Su and Schrieffer[3] and verified by time-resolved picosecond and subpicosecond photoexcitation studies of t-$(CH)_x$[4].

When charges are added to t-$(CH)_x$), the excess charge disrupt the dimerization pattern, and create charged solitons. Because the presence of charged solitons spontaneously breaks the symmetry of translational degree of freedom[5] the optical phonon spectrum is strongly modified as well as the local electronic state. Therefore, there must exist a zero-frequency mode (the Goldstone mode) and other localized modes due to a localized perturbation to the continuum density of states by charged solitons. These localized, infrared-active vibrational (IRAV) modes are the specific fingerprint of charged solitons, and directly related to the Raman-active modes.

The amplitude mode formalism proposed by Horovitz[6] has been successful in connecting the IRAV modes to the resonant Raman scattering (RRS) modes by introducing a phenomenological pinning parameter, α_p. The corresponding IRAV modes can be found from the solutions of the equation given by $D(\omega) = -1/(1-\alpha_p)$, where $D(\omega)$ is the phonon response function. Typical pinning parameters found from experiments are in the range of $0<\alpha_p<2\lambda$ (2λ = electron-phonon coupling constant) due to counter dopant ions (for doping-induced solitons) and impurities and structural defects (for photoinduced solitons). $\alpha_p = 0$ is expected for the freely mobile solitons with the zero-frequency Goldstone mode and $\alpha \approx 2\lambda$ implies that the charged states are immobile.

In this paper, we experimentally studied the nature of nonlinear excitations and Coulomb interactions of charged states in a chain of short polyene system, *trans*-poly(phenylacetylene) (*t*-PPA). We chose *t*-PPA as a model system of short polyenes of average π-electron conjugation length of ~10 carbon-carbon as estimated from the optical absorption spectrum[7] eventhough its molecular weight is ~ 1.5 x 10^4. Our aim is to answer specific questions such as whether the lattice relaxation associated with charge excitations is improtant and what is the nature of elementary excitations in a short polyene with degenerate ground state by probing the infrared photoinduced spectra and by directly comparing with *t*-$(CH)_x$.

EXPERIMENTAL

T-PPA is a derivative of *t*-$(CH)_x$ with the replacement of a hydrogen atom by a phenyl group in every other hydrogen sites in *t*-$(CH)_x$. *T*-PPA was obtained by polymerizing a monomer solution prepared by mixing phenylacetylene and toluene with a solution of WCl_6 in toluene at 30 °C. Detailed synthesis and characterization procedures can be found elsewhere[8]. The resulting *t*-PPA polymer is soluble in common nonpolar organic solvents and fairly stable in air.

Due to the steric hindrance effect, the polymer strand is significantly twisted into a chain of short conjugated segments containing ≈10 carbon sites as estimated from the optical absorption peaked at ~3.0 eV (Δ~ 1.5 eV)[9]. Although the optical spectrum suggests that there is a possibility of having N=6 segments which would give ~ 5 eV absorption, this is irrelevant to the physics involved in this study because we cannot create charges in N=6 segments with 2.53 eV optical pumping. Therefore, *t*-PPA polymer strand can be modeled as a chain of decapentaenes.

Photoinduced absorption spectrum was obtained by measuring fractional changes (-ΔT/T) in the infrared transmission (T) of the pristine *t*-PPA thin film sample on a KBr substrate in response to the external laser excitation coincident with the infrared probe beam on the sample for 4 seconds. A Bruker 113v infrared spectrometer modified to allow access for the optical pumping source (Ar$^+$ ion laser) for frequencies between 600 cm^{-1} (0.07 eV) to 8000 cm^{-1} (1 eV) was used. The spectral resolution was set to 2 cm^{-1}.

Figure1(a) shows the photoinduced absorption spectra for *t*-PPA obtained in the spectral range from 600 cm^{-1} to 8000 cm^{-1} at 4.2 °K, with the inset showing the photoinduced IRAV mode in greater detail. We found four major photoinduced IRAV modes at 874, 1180, 1328, and 1482 cm^{-1} and directly compared with the doping-induced IRAV modes at 867, 1184, 1328, and 1465 cm^{-1} shown in the inset of Figure 1(a). Note that the both photoinduced and doping-induced IRAV modes at near1180 and 1482 cm^{-1} are significantly disturbed by bleachings of the vibrational modes of the phenyl group implying some structural softening in the phenyl ring upon charge injection into the polymer backbone. In addition, <u>two</u> broad electronic absorption peaks at ~ 4200 cm^{-1} (0.52 eV) and ~7000 cm^{-1} (0.87 eV) were observed, which correspond to the electronic absorption due to the soliton state in *t*-(CH)$_x$ at ~ 0.47 eV (~3800 cm^{-1}) (see Figure 1(b)).

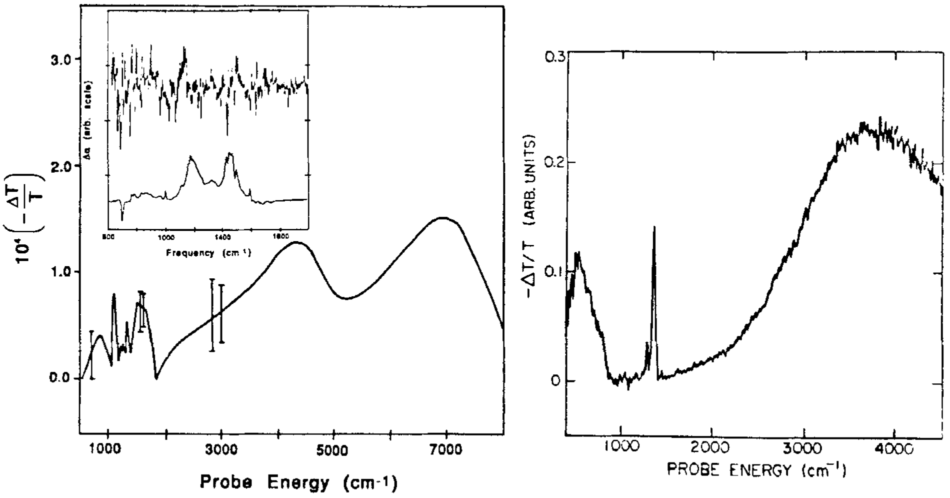

FIGURE 1 (a) Photoinduced absorption spectrum of t-PPA at 4.2 °K (2.53 eV pump at 50 mW/cm^2); inset shows direct comparison of photoinduced infrared spectrum (upper plot) with the difference absorption spectra (lower plot) before and after doping. (b) A photoinduced absorption spectrum of t-(CH)$_x$ (from Ref.10).

DISCUSSION

The observed photoinduced IRAV modes at 1180, 1328, and 1465 cm^{-1} in *t*-PPA correspond to the photoinduced IRAV modes in *t*-$(CH)_x$ at 518, 1280, and 1364 cm^{-1} respectively (see Figure 1(b))[10]. We identify the new weak and broad IRAV mode at 874 cm^{-1} as the pinned Goldstone mode (localized mode associated with the Raman-active mode involving the additional degree of freedom due to the phenyl group in the system) as inferred from the amplitude mode formalism[6]. In *t*-$(CH)_x$, the 518 cm^{-1} mode has been identified as the pinned Goldstone mode of photogenerated charged solitons with pinning parameter α_p=0.079 obtained from the amplitude mode analysis[10]. Note that very small pinning of photogenerated charged solitons in *t*-$(CH)_x$ gives rise a finite frequency gap from the zero-frequency Goldstone mode. The physical origin of small pinning in pristine *t*-$(CH)_x$ is not clearly known at present time.

The observed photoinduced and doping-induced IRAV modes of *t*-PPA are quite close to Raman (A_g) frequencies of short *t*-$(CH)_x$ segments probed by RRS study with 2.6 eV[11]. The result implies that the charged excitations in *t*-PPA are basically immobile ($\alpha_p \approx 2\lambda$) for both photoinduced and doping-induced cases according to the amplitude mode analysis[12]. Strong localization of the charged solitons in *t*-PPA is due to physical confinement by the conjugated segment.

The ~ 0.35 eV splitting in the photoinduced electronic absorption in *t*-PPA can be understood as following. Because of the topological nature, solitons must be created in soliton (S) and antisoliton ($\bar{S}$) pairs implying that we must have two likely charged solitons in each short polyene in order to produce the observed doping-induced and photoinduced spectra. Solitons in a fully extended chain (*t*-$(CH)_x$) has electronic coherence length ξ~7a with $\Delta \approx$ 0.7 eV (a=lattice constant and ξ tend to get shorter as Δ increases within Su, Schrieffer, and Heeger (SSH) model[1a]) and the electronic states for three different solitons (S° and $S^\pm$) are degenerate at the center of the gap ($\hbar\omega_s \approx \Delta$) due to the electron-hole symmetry when two solitons are far apart. When we bring two solitons together, the overlap between two solitons lifts the degeneracy into $\hbar\omega_1 = \hbar\omega_s - E_0/2$ and $\hbar\omega_2 = \hbar\omega_s + E_0/2$. From the photoinduced absorption data, we find the confinement energy ($E_0 = \hbar\omega_2 - \hbar\omega_1$) by the conjugation length to be $\approx$0.35 eV much smaller than the typical confinement energy ($E_0 \approx$1.3eV) of a bipolaron state in a system with non-degenerate ground state, which is an extreme overlap case[13]. The surprisingly small soliton overlap in a short polyene is consistent with ξ~2a for Δ ~1.5 eV calculated within SSH model[1a].

The effective on-site repulsive Coulomb interaction at the soliton state, $U_S \approx U_0 a/3\xi$ (U_0: bare on-site Coulomb energy) tends to lift the degeneracy[14,15], which is responsible for the observed red-shift in the photoinduced electronic absorption from Δ. The change in the Coulomb interaction energy (U_c) between two solitons in the absorption process from the initial ($\bar{S}^+$ and S^+) to final ($\bar{S}^o$ and S^+or $\bar{S}^+$ and S^o) states also contributes to the red-shift for an interacting soliton pair. U_c can be estimated from the doping-induced absorption data since the Coulomb binding energy of S^+ to the dopant-ion and the Coulomb correlation energy U_s approximately cancel since they both depend on the spatial extension of solitons[13]. Using $U_c \approx 0.2$ estimated form the doping-induced electronic absorption peaked at $\approx$1.3 eV for *t*-PPA[7], we find $U_s \approx$0.6 eV from the total red-shift (due to U_s+U_c) in the photoinduced absorption peak from Δ, which is somewhat larger than that found in *t*-$(CH)_x$ mainly due to the reduction in the soliton size as the energy gap increases. Here we have taken $(\hbar\omega_s)_{photoinduced} \approx 0.7$ eV at the mid-point of the two absorption peaks. With $\xi \approx 2a$ and estimate the corresponding bare on-site Coulomb energy $U_o \approx 3.6$ eV which is consistent with other experimental findings[2]. Therefore U_o can be treated as perturbation even in a short polyene as in SSH model ($U_o/4t \ll 1$).

In summry, we have demonstrated that charged solitons are elementary excitations in short polyenes. We found that pairs of likely charged solitons are confined within the conjugated segments and their interaction via overlap is surprisingly small. We estimated the bare on-site Coulomb energy $U_o \leq 4.0$ eV which ensures that SSH picture is still applicable in short polyenes.

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