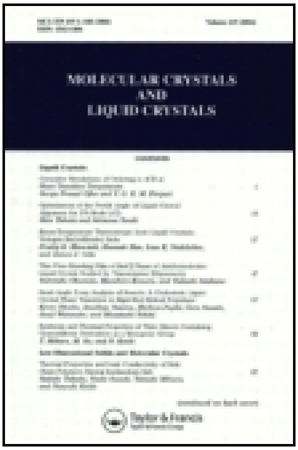

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Z. Vardeny [a], E. Ehrenfreund [a] & O. Brafman [a]
[a] Physics Department and Solid State Institute, Technion, Haifa, Israel

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PHOTOINDUCED ABSORPTION SPECTROSCOPY OF GAP STATES IN POLYACETYLENE

Z. VARDENY, E. EHRENFREUND AND O. BRAFMAN
Physics Department and Solid State Institute, Technion,
Haifa, Israel

Abstract We measured steady-state photoinduced absorption in trans and in cis-rich $(CH)_x$ from 0.1 to 2.5 eV. By assigning the s^0 optical transitions to the 1.45 eV band we can fully account for both the bleaching and absorption parts of the spectrum. The e-e correlation energy involved in the soliton defects is found to be ~ 0.5 eV.

INTRODUCTION

The optical absorption of photoexcited gap states can be directly detected by the photoinduced absorption (PA) technique.[1] The application of PA to polyacetylene has produced a wealth of new information in recent years.[1-7] The PA spectrum in trans-$(CH)_x$ is due to photoinduced IR active vibrations (IRAV)[2-3] and the electronic transitions involving photoexcited gap states.[1,4] While the IRAV spectrum is now quite well understood,[5] the electronic PA bands origin is still an open question.

In this work we report steady-state PA measurements in trans- and cis-rich $(CH)_x$ in an extended energy range from 0.1 to 2.5 eV. In addition to the various PA bands with $\Delta\alpha > 0$ ($\Delta\alpha$ is the photoinduced change in the optical absorption constant α), we pay special attention to the bleaching part of the spectrum with $\Delta\alpha < 0$. The latter shows the energy from which the different bands derive their oscillator strength.[6] The following mechanism is consistent with the data: (i) photoexcitation in trans-$(CH)_x$ mainly produces bound neutral soliton-antisoliton pairs. (ii) Some electron hole pairs which are excited on neighboring chains[6] are trapped at neutral soliton defects and thus create charged solitons. The steady-state PA spectrum of a cis-rich sample is shown to arise only from the trans isomer segments in the sample.

EXPERIMENTAL

The experimental setup for steady-state PA is described elsewhere.[5] For excitation we used an Ar^+ laser at 2.7 eV with an intensity of 20 mW cm^{-2}. For measuring $\Delta\alpha$ spectrum we used broad energy range lamps followed by a monochromator. The samples were held in a cryostat and measurements were taken from 10 to 300K. The samples were thin films grown on KBr or sapphire substrates, initially polymerized as cis-$(CH)_x$ and subsequently isomerized to trans-$(CH)_x$ by heat treatment of 180°C for 10 min. One sample was held at 200°C for 2 h; we refer to it as super-isomerized (SI) trans-$(CH)_x$.

RESULTS AND DISCUSSION

The PA spectrum ($-\Delta T/T \sim \Delta\alpha$) of trans-$(CH)_x$ at 10K is shown in Figure 1 together with the regular absorption $\alpha(\omega)$ spectrum. The low-energy (LE) PA band at 0.45 eV and its associated oscillations in the PA spectrum from 1.4 to 1.8 eV, were identified[2,4] as due to photoexcited charged defects, most probably charged solitons[3,7] (s^+,s^-). Since a double peak is not observed in the LE band, the transitions from s^- to the conduction band (CB) and from the valence band (VB) to s^+, are identical. This confirms the charge conjugation symmetry in trans $(CH)_x$.[8] The high-energy (HE) PA band at 1.4 eV is due to neutral excitations.[4] In trans-$(CH)_x$ the HE band completely disappears from the PA spectrum for temperatures $\Theta > 200K$.[1] This gives a unique opportunity to measure the photoinduced bleaching associated with the LE band as shown in Figure 2 for $\Theta = 210K$.

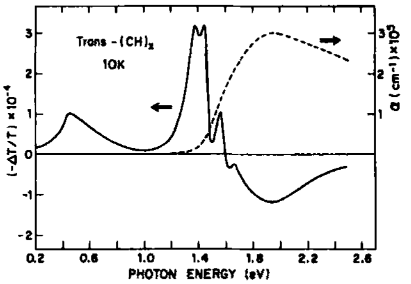

FIGURE 1 PA spectrum of trans-$(CH)_x$ at 10K.

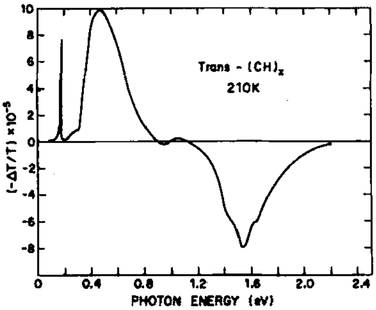

FIGURE 2 PA spectrum of trans-$(CH)_x$ at 210 K.

The interband transitions in trans-$(CH)_x$ peak at 1.95 eV, as seen in Figure 1 for $\alpha(\omega)$. However, as seen from the bleaching part of the spectrum in Figure 2, the LE band derives its strength from a below band-gap optical transitions centered at about 1.45 eV. This proves that an extrinsic defect is the source of the LE band. Further supports for this assignment are: (i) the LE band saturates at moderately high laser intensities.[2,3] (ii) Its strength depends on sample preparation,[6] as shown in Figure 3 for the SI trans-$(CH)_x$ sample. The LE band (and its associated oscillations) practically disappear from the PA spectrum. (iii) The quantum efficiency (QE) of the LE band[6] increases monotonically with the excitation photon energy $\hbar\omega_L$, while the QE for the HE band is approximately independent of $\hbar\omega_L$.[7] A possible candidate for the defect associated with the LE band is the neutral soliton defect s^0, known to exist in trans-$(CH)_x$ with a sample preparation dependent concentration around 10^{19} cm^{-3}. With this assignment, charged solitons can be created by photoexcitation only via the process: $2s^0 \rightarrow s^+ + s^-$.[6]

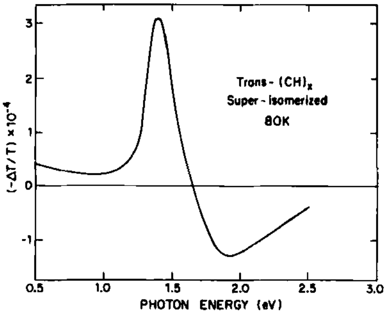

FIGURE 3 PA spectrum of SI trans-$(CH)_x$ at 80K.

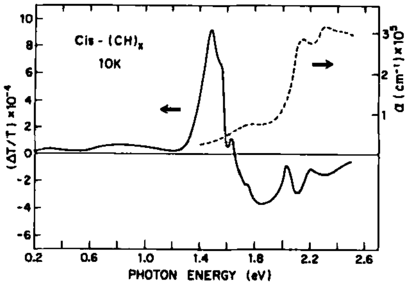

FIGURE 4 PA spectrum of 80% cis-$(CH)_x$ at 10K.

Allowing for lattice relaxation with energy E_r and coulomb repulsion with energy U,[8] but not for lattice dynamics, the optical transitions from s^- to the CB are peaked at $\Delta_0 - U^-$ (where U^- is the effective correlation energy of the fully relaxed s^- and $2\Delta_0$ is the dimerization gap). Symmetrically, the transitions from the VB to s^+ are peaked at $\Delta_0 - U^+$ and because of charge conjugation $U^+ = U^-$. Analogously, the optical transitions from s^0 to the CB and from the VB to s^0 are peaked at $\Delta_0 + U^0$, where U^0 is the effective correlation energy of the fully relaxed s^0. Now, using the LE PA band at 0.45 eV ($s^\pm$) and its associated s^0 bleaching at 1.45 eV, we derive $2\Delta_0 + \Delta U = 1.9$ eV ($\Delta U = U^0 - U^\pm$), and $U^0 + U^\pm =$ 1 eV. Assuming that E_r for s^0 and $s^\pm$ are identical and $2\Delta_0 = 1.7$ eV,[9] we get $U = 0.5$ eV and $E_r = 0.1$ eV.

The HE band, on the other hand, is an intrinsic excitation of the polymer chain, for the following reasons: (i) the bleaching part of its spectrum can be isolated in the SI sample and as seen in Figure 3 it is peaked at 1.95 eV, as the $\alpha(\omega)$ spectrum (Figure 1). This shows that the HE band derives oscillator strength from the interband transitions rather than from a defect level. (ii) The HE band does not saturate. In fact $\Delta T/T$ at 1.4 eV reaches 0.1 in the picosecond time domain, much higher than in Figure 1.[10] (iii) The HE band intensity does not depend on sample preparation. (iv) Starting from 1.4 eV its QE spectrum is rather flat.[7] Since the HE band peaks around 1.4 eV (Figure 3 and Figure 1) it is reasonable to assign this PA band as due to transitions involving s^0 and the photoexcitation is a bound ss pair composed of neutral solitons rather than two separate charged solitons.[11] A possible binding mechanism are 3D effects[12] and localization due to unavoidable remnant cis bonds in the trans chains.[13] Further support for this assignment can be inferred from the PA spectrum of a cis-rich sample.

The PA spectrum of a 80% cis-rich $(CH)_x$ at 10K, together with the $\alpha(\omega)$ spectrum are shown in Figure 4. The LE PA band is about 10 times weaker than the corresponding peak in trans-$(CH)_x$. This is consistent with an order of magnitude reduction of s^0 density for this sample. The HE band (at 1.47 eV) and the oscillations up to 1.8 eV belong to the trans segments in the sample for the following reasons: (i) the bleaching part of the spectrum peaks at 1.9 eV, where the peak in $\alpha(\omega)$ of the trans segments in the sample is located; $\alpha(\omega)$ of the cis segments, on the other hand, peaks at 2.3 eV. (ii) The HE band increases from 1.47 eV at 10K to 1.55 eV at 250K, consistent with similar increase in the trans HE band (and oscillations) and with the increase of the trans phonon frequencies with the temperature.[14] The cis oscillations (from 2 to 2.4 eV) and its phonon frequencies do not shift when the temperature increases.[15] (iii) The HE band at 1.47 eV is higher than the HE band in trans (1.39 eV) by 80 meV. This is consistent with a parallel increase in the energy gap and phonon frequencies of trans chains in cis-rich sample.[15] Since the trans twofold degeneracy is lifted in the trans segments surrounded by the cis chains,[16] (due to CDW interaction from neighboring chains or due to short chains effects), the photoexcited ss pair cannot separate. It is not surprising therefore that they form bound ss pairs. In this case the HE band is associated with the ss pair optical transitions. The similarity between the HE PA bands in 80% cis and in the trans sample supports therefore the bound ss assignment for the latter.

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