Photoexcitations in *trans*-(CH)$_x$: A Fourier-Transform Infrared Study

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Photoinduced absorption spectra of *trans*-(CH)$_x$ and -(CD)$_x$ between 15 and 8000 cm^{-1} are presented. The data demonstrate that the photoexcitations result in charged solitons which are pinned. The isotope shifts observed in *trans*-(CD)$_x$ provide new information about the internal modes of the excitation. Saturation of the signal at low levels is discussed in terms of a photoassisted decay channel.

Recent interest in polyacetylene has focused on the topological domain-wall excitations, often referred to as solitons, which connect the two degenerate ground states of opposite bond alternation. It was shown that charge transfer (via doping) should occur through the formation of charged solitons. The presence of a soliton locally distorts the lattice and introduces an electronic state at the center of the band gap.[1-4] Spectroscopic studies of lightly doped *trans*-(CH)$_x$ have identified both the "midgap" electronic transition that arises upon doping[5,6] and the associated infrared active modes[7-9] introduced by the local lattice distortion.

Su and Schrieffer[10] demonstrated that a photogenerated electron-hole pair would decay into a pair of solitons in a time comparable to an optical phonon period, 10^{-13} sec. As predicted, photoinduced excitations have been observed[11-13] and their dynamics[14,15] have been studied.

We present here photoinduced (PI) spectra for *trans*-(CH)$_x$ and -(CD)$_x$ in the energy range from 15 to 8000 cm^{-1} (0.0018 to 1.0 eV). The PI infrared signatures were studied as a function of temperature and laser power for pure and lightly doped *trans*-(CH)$_x$ samples. Comparison of the PI features and those introduced by doping show that they are associated with the same charged state. We find that the isotope shift in the infrared active modes (both PI and doping induced) differs from previous results, and that, contrary to the current understanding, the PI solitons are pinned. The number of PI solitons saturates[13] at extremely low levels (10^{17}–10^{18} cm^{-3}). The origin of this saturation is discussed.

The experiments utilized an IBM Instruments Fourier-transform infrared interferometer modified to allow a laser beam to be incident on the sample while accumulating ir spectra. The thin-film *trans*-(CH)$_x$ sample (≈ 0.5 μm) was polymerized on a KI substrate and placed on the cold

finger of an Air Products Helitran allowing control of the sample temperature between room temperature and 10 K. In the region of the sample probed by the infrared beam, photoexcitations were created with a cw argon-ion laser ($\hbar\omega = 2.4$ eV). Interferograms with the laser either on or off the sample were alternatively collected every 10 secs. The data were signal averaged until the signal-to-noise ratio was a few parts in 10^5. The ratio of the transformed spectra [(laser on)/(laser off)] yields directly the changes in the transmission ($\Delta T/T$) of the sample due to the photoexcitations created by the laser.

In Fig. 1 we present the PI absorption spectra of *trans*-(CH)$_x$ from 15 to 8000 cm^{-1}. There are three main features which appear at 3870, 1370, and 500 cm^{-1} (0.48, 0.17, and 0.06 eV, respectively). As shown in the inset, the peak at 3870 cm^{-1} has an asymmetric line shape similar to that predicted[5] for the transition between the gap
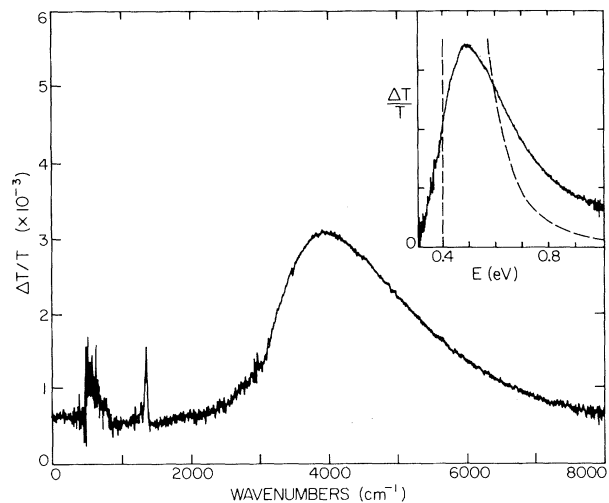

FIG. 1. Photoinduced absorption spectra of *trans*-(CH)$_x$ at 10 K. Inset: the midgap transition compared with the theoretical line shape (Ref. 5).

state and the valence (or the conduction) band. The mid-ir region shows two sharp lines at 1370 and 1250 cm^{-1}, both of which appear at the same energies as the corresponding modes induced by doping.[7-9] Finally, a well defined absorption is evident at about 500 cm^{-1}. By comparison with the infrared spectra of chemically doped samples,[7-9] we assign this mode to the pinned translational mode of the soliton.[14,15]

In Fig. 2 we show the PI spectra for $(CD)_x$ from 700 to 2500 cm^{-1}. The mid-infrared absorption at 1370 cm^{-1} in $trans$-$(CH)_x$ is shifted to 1045 cm^{-1} in $trans$-$(CD)_x$. The 1045-cm^{-1} absorption is broader than that at 1370 cm^{-1} and has an asymmetric line shape. Although the spectra suggest a double peak, data with a resolution of 2 cm^{-1} failed to resolve it. The near-infrared transition in $(CD)_x$ is identical to that shown in Fig. 1 for $trans$-$(CH)_x$ but shifted down to 400 cm^{-1} (0.05 eV).

Figure 3 shows the strength of the PI peaks at 3870, 1370, and 500 cm^{-1} (0.48, 0.17, and 0.06 eV) as a function of the laser intensity (I). The three peaks show a similar dependence upon laser intensity, increasing as $\sqrt{I}$ at low powers and saturating above $I \simeq 50$ mW/cm^2. By comparing the strength of the absorption at 1370 cm^{-1} and midgap to previous data[6-9] on doped $trans$-$(CH)_x$, we estimate that the saturation occurs at a soli-
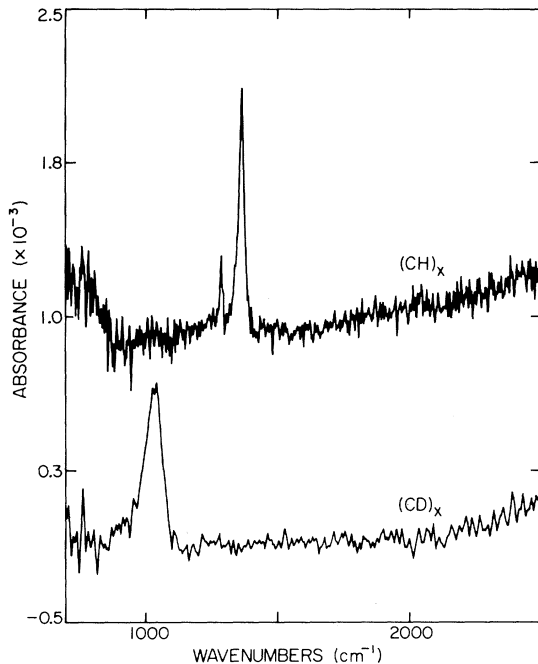
ton density equivalent to a concentration of 10^{17}–10^{18} cm^{-3}. This behavior is only slightly affected by impurities; spectra obtained with use of a sample doped to 0.1% I_3^- showed the same saturation curve. The PI features are insensitive to temperatures below approximately 150 K, but decrease sharply at higher temperatures.[13]

The general features of $\Delta T/T$ in photoexcited and doped $(CH)_x$ are similar, implying that they have a common origin. However, the previously reported "midgap" absorption for the doped system peaks at about 0.7 eV while the PI absorption occurs at about 0.5 eV. To check this apparent discrepancy we measured the doping-induced absorption on the same sample after dilute doping ($\approx 0.1\%$) with iodine. Although we found that the broad doping-induced transition peaked at 0.65 eV at room temperature, the peak shifts to about 0.55 eV at 10 K close to the observed value in the PI spectra. The "midgap" absorption for doped samples is broader[5,6] and only slightly asymmetric, implying a distribution of frequencies. The fact that the midgap transition is present in the photoinduced spectra at an equivalent concentration of excitations $\le 10^{-5}$ indicates that it does not arise from a zero crossing in ϵ_1 due to free carriers as proposed by Glick.[16] Moreover, a direct and careful check of the region from 15 to 100 cm^{-1} failed to show any free-carrier contribution.

FIG. 2. Mid-infrared absorption spectra of $trans$-$(CH)_x$ and $trans$-$(CD)_x$ at 10 K.
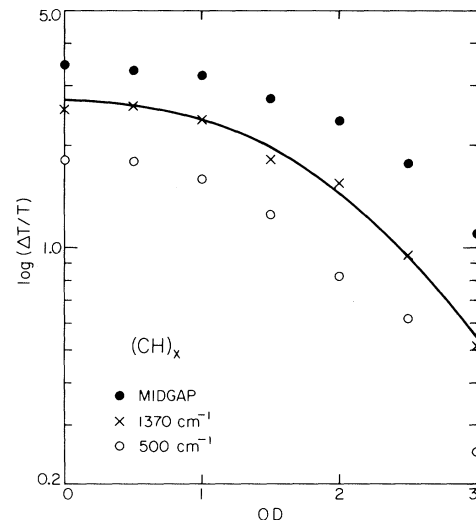

FIG. 3. Intensity of the 0.48-eV (solid circles), 0.17-eV (crosses), and 0.06-eV (open circles) transitions vs the optical density (OD) of neutral-density filters used to attenuate the laser. The solid curve represents a fit to the data using Eq. (1).

Since the characteristic signatures observed in the photoexcited and doped $trans$-$(CH)_x$ are in one-to-one correspondence, the same charged excitation is responsible in both cases. The absence of PI spin resonance[17] implies that both arise from spinless charged solitons.

The effect of the Coulomb interaction on the soliton electronic energies has been investigated.[18] With an on-site interaction U, the energy of the doubly occupied gap state is shifted off the gap center by $\Delta E = U/2\xi$, where 2ξ is the width of the soliton. Therefore, the measured shift of 0.2 eV implies $U = 3$ eV.

In the current theory of soliton-induced infrared activity[19,20] there are three local modes that become ir active as a result of the coupling to the charge of the soliton. One of these modes [900 cm^{-1} in $(CH)_x$] corresponds to the binding of the charged domain wall to the donor or acceptor impurity. Horowitz[20] argued that this pinned mode should go to zero frequency in the absence of an impurity potential. The recently reported PI study of Vardeny, Orenstein, and Baker,[13] covering frequencies greater than 720 cm^{-1}, appeared to support this picture. Our results demonstrate, however, that even the photogenerated solitons are in fact pinned. The origin of this unexpected pinning is not presently understood. However, the pinning frequency in $trans$-$(CD)_x$ is below that of $(CH)_x$ by about 100 cm^{-1}, suggesting that the pinning mechanism is intrinsic.

The PI absorption of $trans$-$(CD)_x$ (Fig. 2) shows a single infrared mode at 1045 cm^{-1} with a width of 75 cm^{-1}. The slight asymmetry and excess width [compared with 31 cm^{-1} for the 1370-cm^{-1} line in $(CH)_x$] could be associated with two unresolvable lines. Previous calculations[8] on $(CD)_x$ predicted two lines but at the somewhat higher frequencies of 1160 and 1270 cm^{-1}. Doping with I_3^- (~3%) gave a peak[9] at 1090 cm^{-1} indicating that photoexcitation and doping result in the same charged state. Earlier results[8] using a freestanding film doped with AsF$_5$ showed a broad (300 cm^{-1} width) mode centered at 1120 cm^{-1}. The narrower absorption line that we obtained after doping may result from the use of a thinner, and therefore, more uniformly doped $(CD)_x$ film.

In attempts to understand the strong saturation at such low excitation densities, we have considered a simple phenomenological rate equation of the form

$$\frac{dN}{dt} = \Phi\epsilon - \frac{\eta}{d}\frac{N^2}{\tau} - \Phi N\sigma, \qquad (1)$$

where ϵ is the quantum efficiency, N the number of excitations per unit area in a sample of thickness d, Φ the laser photon flux, η the volume per excitation, and τ the relaxation time. The first term describes the photogeneration process, and the second term represents the standard bimolecular decay of the excitations through recombination. These two terms yield a steady-state density that grows as $\sqrt{I}$ without saturation. The insensitivity to sample purity of the bimolecular decay and saturation effects is especially important. This behavior is to be contrasted with electron and hole recombination in conventional semiconductors where impurities induce monomolecular decay through trapping, etc. Apparently the photoexcitations in $trans$-$(CH)_x$ must decay in pairs, consistent with the topological nature of the soliton. The last term in Eq. (1) represents a photoinduced mode of decay; for example, a photon absorbed from the midgap state would convert a charged soliton into a neutral one, leading to new and possibly more rapid channels of decay. The cross section for such a decay mode should be comparable to the midgap transition.

The solid curve in Fig. 3 is a fit of Eq. (1) to the data with a saturation density of 5×10^{17} cm^{-3} in the 0.5-μm film, $N_s = 2.5\times 10^{13}$. The relevant parameters are $\sigma = 4\times 10^{-16}$ and $\eta/\tau = 2\times 10^{-16}$. The quantum efficiency value ($\epsilon = 0.01$) was inferred from the time-resolved studies.[12] The resulting cross section is in agreement with that of the midgap transition. Taking η, the volume per particle, to be 10^{-22}/cm^3, as would be obtained by assuming the width of the excitation to be fifteen carbon atoms on a (CH) chain, one obtains $\tau = 5\times 10^{-7}$ sec. Note, however, that the transient response is determined in the bimolecular decay by the quantity $\tau_{eff}^{-1} = N_s\eta/\tau d$. Using the values given above, we find $\tau_{eff}\sim 10^{-2}$ sec in good agreement with the measured value.[13,21]

In summary, photoexcitations in $trans$-$(CH)_x$ and -$(CD)_x$ result in charged solitons. Contrary to previous suggestions, the photogenerated solitons are pinned. The PI $trans$-$(CD)_x$ spectra provide needed detailed information on the local phonon modes of the excitations. Finally, the unusual saturation effects that appear at low excitation intensity may be understood in terms of the opening of an efficient photon-assisted decay channel.

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