Photoinduced Infrared Activity in Polyacetylene

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Photoexcitation of *trans* - but not *cis* -polyacetylene, results in the appearance of strongly-ir-active local modes at 1370 and 1260 cm^{-1}. This observation demonstrates that the photogeneration of self-localized charge carriers is unique to the *trans* isomer. In spite of their localization the kinetic mass of these photocarriers is small, $M_c \simeq (1-2.5)m$, a result which is in quantitative agreement with calculations based on single-chain models.

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It has been proposed by Su and Schrieffer[1] that a photogenerated electron-hole pair in *trans*-polyacetylene, $(CH)_x$, is unstable towards the formation of a charged soliton-antisoliton pair. The soliton in $(CH)_x$ denotes a one-dimensional (1D) domain wall which separates the two degenerate ground-state structures of the all *trans* isomer.[2,3] In theory this domain wall can propagate freely along the polymer chain with a remarkably small kinetic mass, $M_s \simeq 5m$, where m is the free-electron mass. However, as Brazovskiĭ[4] and others[5,6] have shown, the soliton in *trans*-$(CH)_x$ is but one of a family of self-localized carriers which play a central role in the photophysics of 1D semiconductors. In a broader class of fully conjugated polymer chains, of which *cis*-$(CH)_x$ is the simplest example, the lower-symmetry structure cannot support an isolated soliton as in *trans*-$(CH)_x$; instead photoexcitation is thought to give rise to a confined soliton-antisoliton pair. Furthermore, different carriers result if a single electron, rather than an electron-hole pair, is added to the chain. Even with photoexcitation this is possible if the photogenerated pair can separate to different chains before the onset of a strong 1D lattice deformation. In this case 1D polarons in both isomers of $(CH)_x$ are envisioned.

Perhaps the best way to detect and characterize these photocarriers is through their optical absorption. As a consequence of their localization they give rise to gap states in both the electron and the phonon level spectrum. The first observation of such states in the gap was made by adding carriers to the chain by doping. In *trans*-$(CH)_x$ dopant-induced carriers give rise to near-midgap optical absorption,[7] and new, strongly IR active, vibrational modes at 900 cm^{-1}, 1260 cm^{-1}, and 1370 cm^{-1}.[8] The parallel study of photoinduced carriers can contribute two crucial pieces of information. First, *cis*- and *trans*-$(CH)_x$ can be compared without the complication of dopant-induced isomerization. Second, the spectrum of carriers which are not strongly pinned to oppositely charged impurities can be obtained. This allows a more direct comparison with theory since the impurity potential is not precisely known.

Recently, the optical absorption due to photogenerated carriers, in the photon energy range 0.5 to 1.6 eV, was reported.[9] In the present work we have extended the transient photoinduced absorption technique to the spectral range of vibrational transitions. In *trans*-$(CH)_x$ we have observed new ir active modes due to the photogeneration of carriers. To our knowledge this is the first observation of this type in a semiconductor. These ir modes are directly correlated with the appearance of an electronic level, also unique to *trans*-$(CH)_x$, whose optical absorption has a peak in the semiconductor gap. From the appearance of ir activity we conclude that photoexcitation of *trans*-, but not *cis*-$(CH)_x$, results in the generation of charge carriers. This confirms the initial proposal based on photoconductivity measurements.[10] The relative oscillator strength of the vibrational and electronic transitions shows that these localized carriers have a small kinetic mass, $M_c \simeq (1-2.5)m$. The vibrational mode frequencies of the photogenerated carriers are the same as dopant-induced carriers except that the peak at 900 cm^{-1} is now absent. This strongly suggests that 900 cm^{-1} is the frequency of the "pinned mode" of dopant-induced carriers. In addition, we found the following properties of photocarriers in *trans*-$(CH)_x$: long lifetime ($>10^{-3}$ sec at low temperatures), thermally activated mobility above 150 K, and a photogeneration quantum efficiency $\sim 10^{-2}$.

In order to measure the transient absorption due to photocarriers an incandescent cw source (glow bar) and monochromator (Jarrell-Ash 16-Y) were used to provide a variable-wavelength probe beam. Electron-hole pairs were photogenerated by the 5145-Å (2.4-eV) line of an Ar^+ laser, chopped at 100 Hz for most measurements. Photoinduced changes in sample absorption were recorded by lock-in detection of the signal from a HgCdTe detector with a low-energy cutoff at 720 cm^{-1}. The *cis*-$(CH)_x$ samples were polymerized[11] at 196 K onto NaCl substrates, and were subjected to less than a few minutes of room-temperature handling. Samples of *trans*-$(CH)_x$ were obtained from the *cis* isomer by a heat treatment of 180 °C for 5 min. The sample thickness was ~1000 Å.

In Fig. 1 the induced absorption $(-\Delta T/T)$ for the two isomers at 10 K is plotted against photon energy. In the *trans* isomer the photoinduced absorption spectrum consists of an asymmetric band peaked at 0.43 eV with full width at half maximum (FWHM) ~0.3 eV, and a much sharper double-peaked feature with maxima at 0.17 eV (1370 cm^{-1}) and 0.156 eV (1260 cm^{-1}) with FWHM ~0.004 eV (30 cm^{-1}). The absorption in *cis*-$(CH)_x$ is smaller by a factor ~15 in this spectral range. The weak absorption near 1360 cm^{-1} is consistent with the unavoidable *trans* content of the nominal *cis*-$(CH)_x$ sample, ~5%. The spectra above 1.0 eV (not shown in Fig. 1) consist of bands centered at 1.36 eV (*trans*) and 1.50 eV (*cis*), and photoinduced bleaching of the interband transition at higher photon energy. These features will be discussed in a subsequent publication.

The transitions at 1370 and 1260 cm^{-1} are due to local vibrational modes which are made ir active by the presence of a photogenerated charge carrier on the polymer chain.[12] From the asymmetric shape of the 0.43-eV absorption we believe that this peak is due to an electronic transition from a state in the gap to the nearest band of continuum levels. These vibrational and electronic transitions arise from the same photogenerated state, as is demonstrated below.

To test for a correlation between the vibrational and electronic transitions, we have measured their magnitudes as a function of chopping frequency and of temperature. In Fig. 2 the induced absorption at 0.43 and 0.17 eV is plotted versus chopping frequency in the range 10 to 3×10^3 Hz. The two features show the same frequency dependence, indicating a common lifetime of about 10^{-3} sec. Figure 3 shows the temperature dependence of the two transitions in the range 10 to 290 K. Again the behavior is the same. Both curves have a knee at ~150 K, indicating a reduction in photocarrier lifetime above this temperature. On the basis of Figs. 2 and 3 it is clear that the two transitions arise from the same center. The steady-state concentration of these centers, n_{ss}, increases with laser intensity as $I_L^{0.5}$ for $I_L < 20$ mW/cm^2. Above this

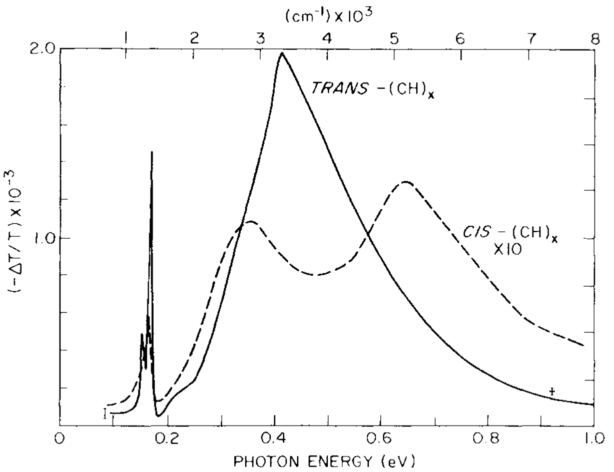

FIG. 1. Photoinduced absorption spectra of *cis*- and *trans*-$(CH)_x$ at 10 K.

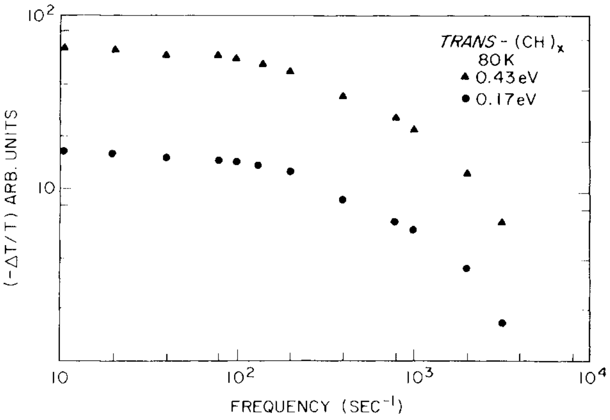

FIG. 2. Comparison of the chopping-frequency dependence of the electronic (0.43-eV) and vibrational (0.17-eV) transitions.

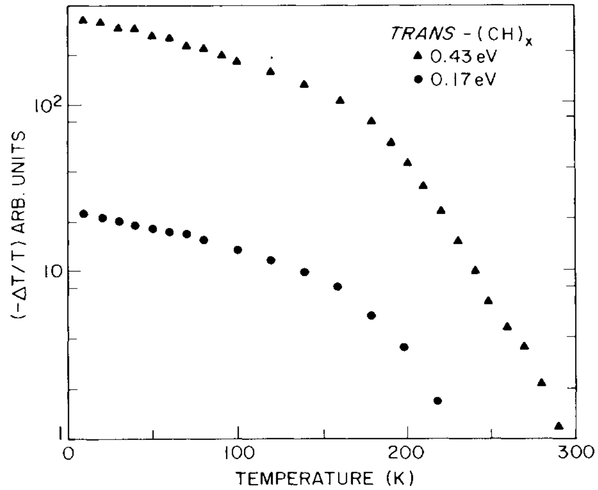

FIG. 3. Comparison of temperature dependence of electronic (0.43-eV) and vibrational (0.17-eV) transitions.

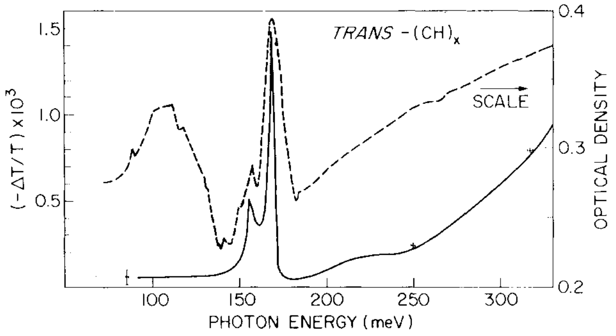

FIG. 4. Expanded plot of spectrum of Fig. 1 (solid line) compared with spectrum of dopant-induced (AsF_5) (Ref. 14) carriers.

power level n_{ss} increases even more slowly with I_L. The magnitude of n_{ss} may be estimated if we assume that the integrated absorption cross section is the same for dopant and photoinduced carriers. Using the cross section obtained from electrochemical doping measurements[13] we find that a maximum of $\sim 4\times10^{17}$ cm^{-3} photocarriers can be generated by cw excitation. With the relation $\langle n_{ss}\rangle = y\alpha_L I_L \tau$, where α_L is the absorption coefficient of $(CH)_x$ at 5145 Å and y is the quantum efficiency, we estimate $y \sim 10^{-2}$.

The spectrum of local modes due to photocarriers in *trans*-$(CH)_x$ is similar to that of dopant-induced carriers. In Fig. 4 we compare, on an expanded energy scale, the dopant- (AsF_5) (Ref. 14) and photoinduced ir activity. The most striking aspect of these spectra is that the vibrational and electronic transitions can be displayed on the same scale, i.e., their oscillator strengths are comparable. Since the integrated absorption strength of a charge is inversely proportional to its effective mass, typical ir oscillator strengths for local impurity modes are smaller than those for electronic transitions by a factor $\sim 10^3$.[15] It is obvious from comparing the vibrational to electronic absorption strengths in Fig. 4 that in *trans*-$(CH)_x$ the defect is anomalously light.

There has been considerable progress in understanding the origin of this anomalous behavior, primarily due to the work of Mele and Rice,[12] and Horovitz.[16] It is now generally agreed that the large ir absorption requires coupling of the localized vibrational modes to the oscillator strength of the self-trapped electron. In the adiabatic limit the antisymmetric modes of the defect cause the electronic charge distribution to move back and forth across the center of symmetry. A small motion of the C atoms, of order the difference between single and double bond lengths u_0, results in displacement of the defect by its length, ξ_0. This reduces the defect mass, compared to the mass of a C atom, by a factor $u_0^2/\xi_0 a \sim 10^{-4}$.

The charged defect gives ir activity to the modes of the ground-state structure that are coupled to the π electrons, at a frequency shifted down into the gaps of the phonon bands. One of these modes should appear at $\omega = 0$, reflecting the translational invariance of the perfect $(CH)_x$ chain. The presence of a static defect or impurity on the chain breaks this translational invariance and restores the $\omega = 0$ mode to finite frequency. This is the "pinned mode." On the basis of this argument, Horovitz[16] identified the lowest-energy (900-cm^{-1}) absorption in doped $(CH)_x$ as the mode due to the binding of the dopant-induced carrier to the dopant ion. This assignment is supported by comparison of the two spectra seen in Fig. 4. Here the 900-cm^{-1} peak is absent from the photoinduced spectrum, reflecting the fact that the photocarrier is not bound to an oppositely charged impurity.

Horovitz's calculation can be used to determine the photocarrier mass directly. For the integrated absorption strength of the 1370-cm^{-1} mode he finds that $\Sigma_{ph} = A(\rho/M_c)e^2$,[16,17] where ρ is the linear density of defects. The factor A is between 0.2 and 0.4, depending on the frequency of the pinned mode of the photogenerated defect, which must be in the range $0 < \omega_p < 720$ cm^{-1}. The integrated electronic absorption for the soliton defect is given by $\Sigma_{el} = 2.8(\rho/m^*)e^2$,[7] where m^* is the effective band mass. Equating this result for Σ_{el}/Σ_{ph} with our experimental value of 90, we obtain $M_c/m^* \cong 5-12.5$, or $M_c/m \cong 1-2.5$.

To summarize, excitation of *trans*-$(CH)_x$ results in self-localized photocarriers whose small kinetic mass is in quantitative agreement with 1D models. Although several predictions of current models have been confirmed, the question of whether these carriers are solitons or 1D polarons has proved elusive. Given the uncertainty in the $(CH)_x$ parameters, our experimental determination of the photocarrier mass is consistent with the prediction for the soliton ($M_s/m^* \cong 18$) and the polaron ($M_p/m^* \cong 3.6$). Furthermore, within a continuum description of these carriers, their local mode frequencies are the same.[16] Unambiguous proof of soliton photogeneration requires the demonstration that charged photocarriers in *trans*-$(CH)_x$ do not carry spin. Recent measurements[18] of light-induced spin resonance in *trans*-$(CH)_x$ place an upper limit of $\sim 10^{16}$ cm^{-3} spins under excitation conditions which generate $\sim 4 \times 10^{17}$ cm^{-3} charge carriers. This supports the assignment of these carriers as spinless charged solitons. However, our observation that the threshold for optical absorption by these carriers is ~ 0.5 eV below the midgap position predicted for solitons poses a fundamental problem. In our view reconciling this with the soliton picture requires a $U_{eff} \sim \Delta$. This points toward the importance of correlation effects in attempting to understand excitations in $(CH)_x$.

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