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PHOTOGENERATED GAP STATES IN POLYACETYLENE

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Résumé -Nous avons mesuré le spectre optique d'absorption d'états d'origine optique dans le gap du polyacétylène $(CH)_x$. La charge de ces excitations est déterminée à partir de comparaisons avec les spectres d'électroabsorption. Des états neutres (semblables à des excitons) sont observés pour les deux isomères de $(CH)_x$. De plus, dans le cas du trans $(CH)_x$, on peut observer un porteur d'origine optique avec une absorption située profondément dans le gap.

Abstract - We have measured the optical absorption spectrum of photogenerated gap states in polyacetylene, $(CH)_x$. From a comparison with electroabsorption spectra the charge state of the excitations is determined. In both isomers of $(CH)_x$ locally neutral (exciton-like) states are observed. In addition a charged photocarrier, with optical absorption deep in the gap, is seen in trans-$(CH)_x$ only.

There has recently been a great deal of interest in the nature of photoexcitations in polyacetylene, $(CH)_x$. This is largely due to the prediction by Su and Schrieffer[1] of a new type of photocarrier unique to *trans*-$(CH)_x$, the charged soliton. However, the soliton is but one of a variety of self-localized states which are predicted to play a central role in the photophysics of 1D semiconductors. In *cis*-$(CH)_x$, for 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.[2] Furthermore, different types of carriers result if a single electron, rather than an electron-hole pair, is added to a 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.[1-4]

Perhaps the best way to detect and characterize these photoexcitations is through their optical absorption. The scheme of our experiments is the following: we photoexcite with above band-gap ($h\nu > 2\Delta$) light, and then probe the optical absorption of the sample in a broad range from IR to visible. Essentially we obtain difference spectra, i.e., the difference in the optical absorption of $(CH)_x$ when it contains a non-equilibrium carrier concentration, and that in the equilibrium ground state. For photoexcitation we have used a variety of sources, CW (Ar^+) laser,[5] pulsed (10 ns) dye laser,[6] and a mode-locked dye laser which produces pulses of $\sim$ 0.1 psec duration.[7] In general a loss of sensitivity and spectral range occurs at the expense of increased time resolution. To give an overview of the

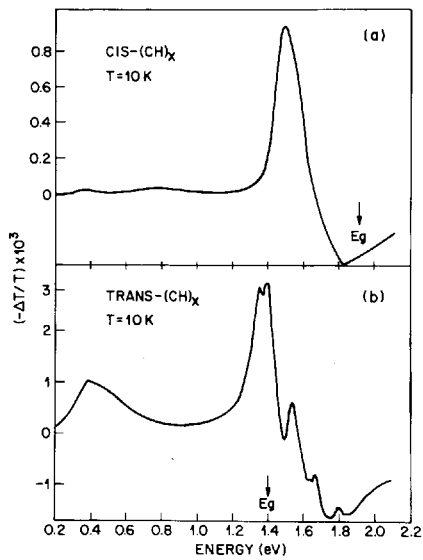

Fig. 1 Comparison of spectrum of photogenerated gap states in the two isomers of $(CH)_x$.

photoinduced absorption (PA) spectrum, results obtained with Ar^+ excitation (20 mW/cm^2 at 5145Å) are shown in Fig. 1. The two panels show the PA for both *cis* and *trans*-$(CH)_x$ held at 10K. The arrows indicate the approximate position of the band edge. The spectrum of *cis*-$(CH)_x$ is clearly the simpler of the two, containing a single peak at 1.5 eV. Above 1.65 eV the spectrum changes sign, indicating photoinduced bleaching of the interband transition. The spectrum of *trans*-$(CH)_x$, on the other hand, appears to be more complicated. At $\sim$ 1.40 eV there is a peak which is similar to the feature in *cis*-$(CH)_x$ in both width and position relative to the bandgap. However, superposed on this peak is a series of oscillations at regular intervals of 0.11 eV (890 cm^{-1}). Finally, there is an additional peak in *trans*-$(CH)_x$ at 0.45 eV which is not evident in the *cis* isomer.

We begin by discussing the features in the *trans*-$(CH)_x$ which occur near the band edge. The fine structure in the spectrum is similar to effects seen in modulation spectroscopy of semiconductors, both organic and inorganic.[8] In modulation spectroscopy the spectrum of $\frac{\partial \alpha}{\partial X}$, where X is an external perturbation, is measured. These spectra pick out density of states features otherwise buried in the absorption edge. To test whether a perturbation of the absorption edge is relevant to the PA spectra in *trans*-$(CH)_x$, we performed both thermoabsorption (TA) and electroabsorption (EA) measurements on both isomers. The results will be described in full in a subsequent publication, for the present we will discuss the aspects which are important to the PA spectra.

The technique for measuring TA and EA is straightforward. The experimental arrangement is almost the same as for PA, except that either a thin-film heater or electric field takes the place of the chopped laser in producing a change in sample absorption. The (TA) spectrum, $\frac{\partial \alpha}{\partial T}$ vs photon energy ϵ, was found to reproduce quite accurately $\frac{\partial \alpha}{\partial \epsilon}$, as expected. The derivative spectrum differs from the PA shown in Fig. 1 in shape and in sign. This demonstrates that the PA features do not result from a laser-induced rigid shift of the absorption edge. The EA spectrum, $\frac{\partial \alpha}{\partial \epsilon}$, looks considerably different from the TA spectrum. In Fig. 2, the EA effect in both isomers is shown with solid lines. The dashed lines indicate the optical absorption in the same spectral region. The spectra were recorded at 150K, with a field modulation of $2.5 \times 10^4 V - cm^{-1}$. We find that the shape of the EA spectrum corresponds closely to $\frac{\partial^2 \alpha}{\partial \epsilon^2}$ versus ϵ, and that the magnitude of $\frac{\partial \alpha}{\partial F}$ is proportional to $|F|^2$. The periodic oscillations result from structure in the edge due to multiphonon emission processes, which is enhanced in the second derivative. Although there is a great deal of information about the fundamental absorption process in $(CH)_x$ in these spectra, we are concerned now mainly with understanding their relation to the PA spectra from Fig. 1.

This relationship is made clear in Fig. 3 where several different spectra are shown together for comparison. The three curves shown in solid lines are PA spectra recorded at different pump laser intensities, 2 mW - cm^{-2}, 20 mW - cm^{-2}, and 200 mW - cm^{-2}. The dashed-line spectrum shows the EA effect in *trans*-$(CH)_x$ measured at the same temperature.

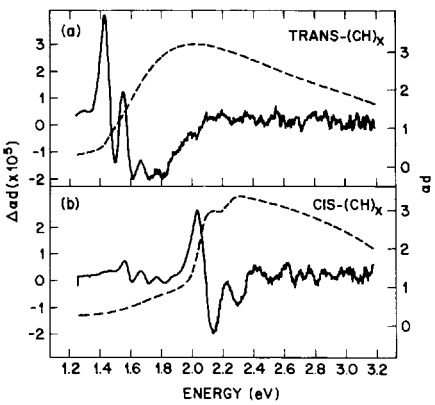

Fig. 2 Absorption (dashed line) and electroabsorption (solid line) spectra for *cis* and *trans*-$(CH)_x$.

It is clear that the PA in this spectral region has two components: an absorption peak at 1.38 eV, and fine structure due to electric-field induced modulation of the absorption edge. The appearance of the EA structure in the PA spectrum of *trans*-$(CH)_x$ indicates that the photoexcitation creates strong electric fields in the material. We believe that these fields arise from photoexcited carriers which are able to move apart after they are generated.

The appearance of EA structure in the PA spectrum turns out to be very useful in identifying the charge state of the photogenerated gap states in $(CH)_x$. From measurements in which sample temperature and laser intensity are varied we know that the low energy absorption in *trans*-$(CH)_x$ is directly correlated with the appearance of the EA structure.[5] This correlation indicates that the absorption at 0.43 eV in *trans*-$(CH)_x$ is due to a charge carrier. Furthermore, the absorption peaks at 1.38 eV in *trans*- and 1.55 eV in *cis*-$(CH)_x$ arise from states which are overall neutral, since they are not correlated with the appearance of EA.

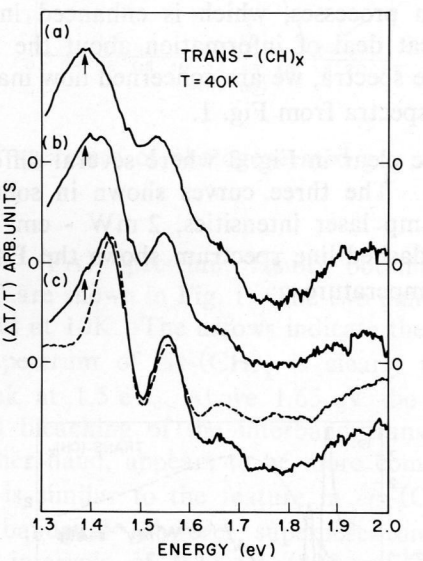

Fig. 3 PA spectra for three different laser intensities compared with EA spectrum.

There are several observations which can be made by examining Fig. 3. First, the features in the EA spectra clearly account for the oscillatory fine structure in the PA data. Second, there is an additional peak in the PA spectra at 1.39 eV, which is not seen in EA. This peak can be easily distinguished from the EA structure by varying the intensity of the pump beam. It increases faster with intensity than the EA features, giving rise to a double peak structure at 20 mW – cm^{-2}, and dominating the spectrum at 200 mW – cm^{-2}.

Additional support for this charge assignment is presented in another contribution to these proceedings.[9] Evidence that these gap states are intrinsic, i.e., not associated with defects or impurities has been presented previously.[6,7] At this point it is useful to compare the spectra we obtain with the predictions of current models. According to these models, a photogenerated electron-hole pair in the *trans* isomer can give rise to a pair of isolated solitons. Associated with each is a midgap level.[10–12] In *cis*-$(CH)_x$, the solitons are thought to be confined after photogeneration because of the lower symmetry of the C backbone.[2] In this case the levels are split by their interaction to produce bonding and antibonding levels displaced from the gap center. In comparing our observations with these ideas, the 0.43 eV peak immediately suggests the charged soliton, which is unique to the *trans* isomer. The higher energy peaks are consistent with a close pair of solitons which has energy levels near the conduction and valence band edges. However, several difficulties with this straightforward interpretation present themselves: first, the 0.43 peak is not at the gap center, but at least 0.2-0.3 eV below; second, the neutral soliton pair in *trans*-$(CH)_x$ should dissociate on a sup-picosecond time scale; and third, the pair ought to have two strong transitions in the gap rather than one.[13]

We suggest that the explanation for these observations requires going beyond 1-electron models for the self-localized gap states. In particular, an isolated charged soliton, being doubly occupied, should have a smaller binding energy than the neutral midgap level. In the case of the 1.38 eV peak, the Coulomb attraction could be sufficient to bind the kink pair in *trans*-$(CH)_x$ at sufficiently low temperature. A firm identification of these excitations must, however, await a determination of their spin/charge relation in addition to their absorption spectrum and lifetime.

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