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Optical Absorption in Polyacetylene: A Direct Measurement Using Photothermal Deflection Spectroscopy

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We present direct measurements of the optical absorption in undoped and ammonia-treated polyacetylene utilizing the technique of photothermal deflection spectroscopy. Our spectra show an Urbach-type edge and a broad, NH_3-sensitive sub-band-gap absorption. Quantitative comparisons of absorption and spin-resonance results do not show the predicted midgap absorption from neutral solitons.

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Measurements of the optical properties of polyacetylene have provided much of the experimental basis for current theories of its electronic structure.[1] The strength of the optical absorption and the shape of the spectrum in the visible–near-IR range have been analyzed in terms of a one-dimensional direct band-gap semiconductor.[2] Doping-induced sub-band-gap absorption[3] has been attributed to electronic transitions involving bond-alternation kinks (solitons).[4–6] Doping also leads to dramatic increases in electrical conductivity.[7] Spin-density determinations[8] indicate that the doping-induced charge carriers are nonmagnetic consistent with a soliton picture.

As a result of its complicated fibrillar morphology, polyacetylene is a very complex optical medium. Typically, absorption spectra have been inferred from transmission measurements on ~1000-Å films. We have found using integrating sphere techniques over the energy range 0.7–2.0 eV that such films *diffusely* scatter several percent of the incident light. Transmission measurements cannot distinguish between scattering and absorption. Therefore, absorption constants lower than 10^4 cm^{-1} inferred from transmission measurements are inaccurate, even when corrected for specular reflectivity.

In this paper, we present a direct measurement of the room-temperature optical absorption for undoped and ammonia-compensated films of both *cis*- and *trans*-$(CH)_x$ using photothermal deflection spectroscopy (PDS).[9] These spectra provide the first measurement of the true absorption edge of $(CH)_x$. What is revealed is an exponential edge reminiscent of Urbach edges found in disordered semiconductors.[10] The quantitative comparison of the below-gap absorption in as-grown and NH_3-compensated films with spin-resonance data clearly demonstrates that neutral solitons do not absorb near midgap.

Photothermal deflection spectroscopy measures the heating of the sample caused by the absorption of light. The sample heating caused by a monochromatic pump beam is transferred to a transparent fluid in which the sample is immersed (in our case, CCl_4). The thermal modulation of the refractive index of the fluid results in a deflection of a probe beam (a He-Ne laser) tangential to the sample. The deflection of the probe is proportional to the absorption in the sample of the pump beam and is monitored by a position-sensitive diode detector. PDS is sensitive only to those photons actually absorbed by the sample and, unlike uncorrected transmission measurements, will not record the scattering of a photon as an absorption event. The Exxon spectrometer is sensitive to absorptions as small as 10^{-4}.

We obtained absorption spectra on films ranging in thickness from 0.1 to 4 μm. The thicknesses of the 1–4-μm films were measured using both an optical microscope and a mechanical profilometer. The thickness of the 0.1-μm film was inferred from the relative magnitude of its absorption. Spectra for both the *cis* and *trans* isomeric forms of $(CH)_x$ were obtained. The *cis* films were removed from the CCl_4 subsequent to measurement and thermally isomerized under vacuum prior to reinsertion in the CCl_4 as *trans*. Total air exposure was only a few seconds. Ammonia compensation of the $(CH)_x$ films was performed *in situ* by bubbling NH_3 through the CCl_4. It should also be noted that immersion of the $(CH)_x$ in the spectroscopic grade

CCl_4 had no measurable effect on dc conductivity or spin density.

In Fig. 1 are displayed the PDS absorption spectra for *trans*-$(CH)_x$ samples of different thicknesses. Also shown is the effect of NH_3 compensation on these samples. Figure 2 presents data for a sample of intermediate thickness and displays the result of the *cis-trans* thermal isomerization. All uncompensated samples display two common features: an exponential absorption edge above 1.1 eV and a relatively featureless absorption band in the range 0.7–1.1 eV. (We extended these measurements to 0.5 eV on one 0.1-μm sample. The data indicated that any peak associated with the below-gap absorption occurs below 0.5 eV). The strength of the absorption along the exponential edge scaled roughly with sample thickness as one would expect for a homogeneous medium. However, the low-energy absorption was relatively thickness independent, varying in the range 0.05–0.1 absorption at 0.7 eV for samples whose thicknesses differed by more than an order of magnitude. If the below-gap absorption is associated with impurities in the film, then the data suggest that the number of impurities is independent of film thickness. Since the amount of catalyst employed in the preparation of films of different thickness did not vary, residual catalyst is a likely source of these impurities. Figures 1 and 2 show that the effect of NH_3 treatment of the samples was to eliminate the low-energy absorption and extend the exponential edge. The sub-band-gap absorption could be restored to its initial level by brief exposure of the film to air and subsequently recompensated by further NH_3 treatment.

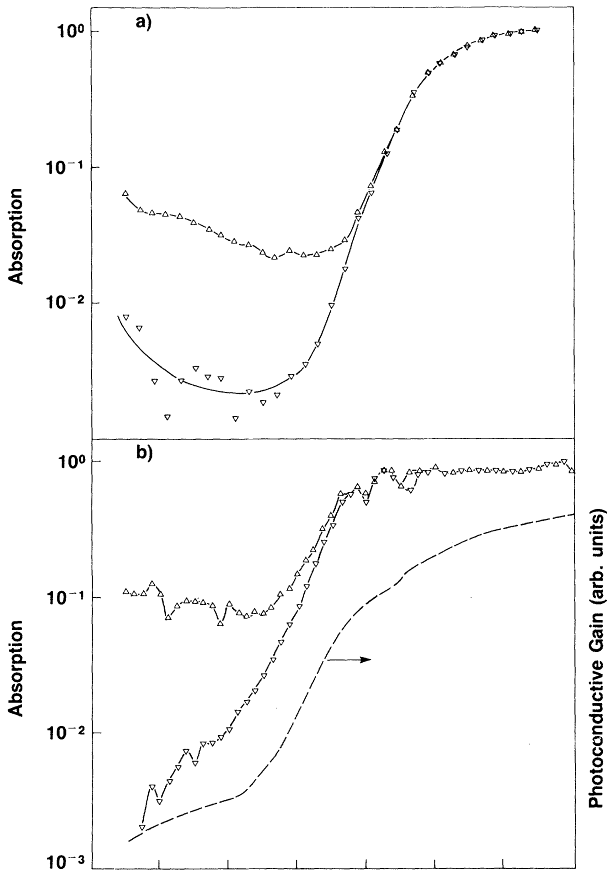

FIG. 1. PDS absorption spectra of (a) 0.1-μm-thick *trans*-$(CH)_x$: triangles, as grown; inverted triangles, ammonia compensated, and (b) 4.0-μm-thick *trans*-$(CH)_x$: triangles; as grown; inverted triangles, ammonia compensated. Dashed line, photoconductivity (Ref. 16).

Within the widely used model Hamiltonian,[4–6] which treats polyacetylene in terms of a coupled electron-lattice system, solitons are a primary excitation of the polymer chain. Quantitative calculations[3] of the absorption cross sections for the soliton midgap state have been carried out and described in terms of the occupancy of single-particle electronic states. Four possible optical transitions involving charged ($S^{\pm}$) and neutral (S^0) solitons and valence-band (e_v) and conduction-

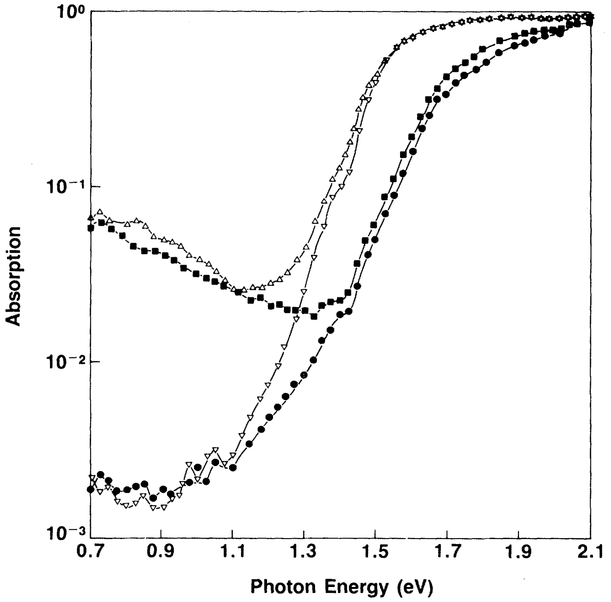

FIG. 2. PDS absorption spectra, 0.5-μm-thick film: squares, *cis*-$(CH)_x$ as grown; circles, *cis*-$(CH)_x$ ammonia compensated; triangles, *trans*-$(CH)_x$ uncompensated; inverted triangles, *trans*-$(CH)_x$ ammonia compensated.

band (e_c) electrons exist:

$$h\nu + S^0 + e_v \rightarrow S^-, \tag{1}$$

$$h\nu + S^0 \rightarrow S^+ + e_c, \tag{2}$$

$$h\nu + S^+ + e_v \rightarrow S^0, \tag{3}$$

$$h\nu + S^- \rightarrow S^0 + e_c. \tag{4}$$

In the absence of Coulomb interactions, the optical absorption peak associated with each of these transitions should occur at midgap, 0.7 eV.

The PDS absorption spectra presented in this paper are inconsistent with a model which ignores Coulomb interactions. Spin-resonance measurements performed on the NH_3-compensated *trans* sample used for the PDS measurement [Fig. 1(b)] yielded a spin density of 0.03%. NH_3 treatment leaves the density of spins (neutral solitons) unaltered,[8] lowering the electrical conductivity by compensating charged centers (S^+). Absorptions due to transitions 1 and 2 should remain unattenuated, but are not observed. In Fig. 3, the discrepancy between the absorption data and the simple soliton model is quantified. Shown is the spectral dependence of the absorption constant for NH_3-compensated $(CH)_x$ obtained from a composite of two PDS spectra. Also shown is the theoretical absorption[3] due to transitions 1 and 2 for the film of Fig. 1(b), assuming that its measured spin density is due to neutral solitons and that Coulomb correlations are absent. The theoretical divergence at half the gap has been rounded to the width of the photoinduced absorption[11] peak while conserving total oscillator strength. The measured absorption near midgap is two orders of magnitude smaller than that theoretically predicted. The unavoidable conclusion of this analysis is that, while charged solitons may contribute to the midgap absorption, neutrals do not.

The effect of Coulomb interactions on these transitions has been considered theoretically through several approaches.[12-14] These models predict that the S^0 absorption peaks at higher energies. Our results (Fig. 3) show that this peak must be higher than 1.3 eV, indicating that Coulomb correlations play an important role in determining the electronic structure of $(CH)_x$. Similar effects may be used to explain the presence of a photoinduced absorption at 0.5 eV.[11]

The exponential absorption edge of $(CH)_x$ revealed by NH_3 compensation in our PDS spectra is a feature common to semiconductors. Although the absorption edge of $(CH)_x$ is only approximately exponential in character (Fig. 3), if the data are fitted to the traditional Urbach form[15] $\alpha = \alpha_0 \times \exp(E/E_0)$ for $1.1 < \epsilon < 1.5$ eV, the slope that is obtained is $E_0 \sim 70$ meV. This is a value comparable to that obtained for disordered semiconductors.[10] Comparison of the photoconductive edge to absorption derived from transmission data[16] apparently indicated a red shift of the photoconductive threshold which was attributed to direct photogeneration of charged (S^+,S^-) soliton pairs. Comparison of the photoconductivity spectrum (Ref. 16) to the PDS absorption spectrum [Fig. 2(b)] for films of comparable thickness, in fact, reveals no such shift between the two edges. Such a comparison should be made carefully, however, as the photoconductive spectrum depends on factors other than absorption such as branching ratios into channels not producing mobile carriers or energy-dependent recombination kinetics (geminate recombination).

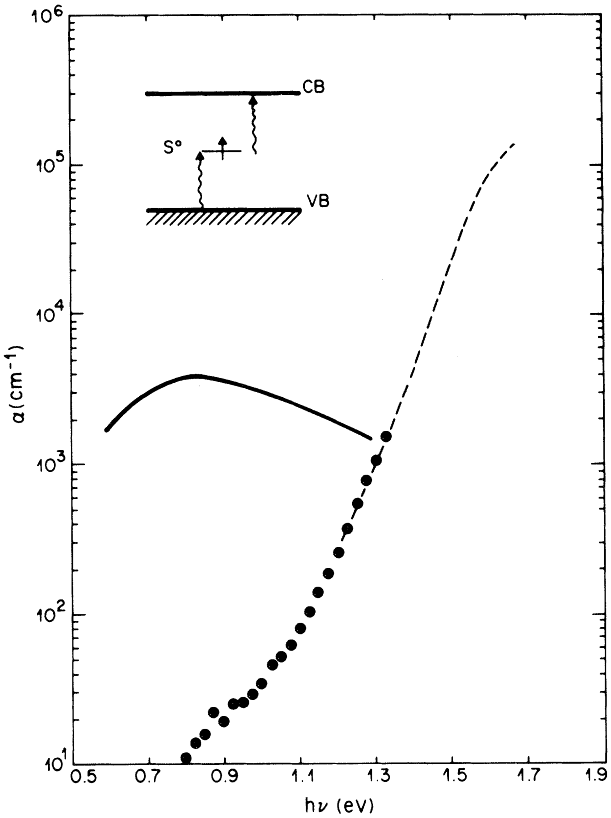

FIG. 3. Absorption edge of NH_3-compensated *trans*-$(CH)_x$ (composite: 4-μm sample, circles; 0.1-μm sample, dashed line); solid line, theoretical S^0 absorption with no Coulomb correlation.

What the comparsion in Fig. 1(b) does suggest is that the absorption processes represented by the

PDS data are related to the production of at least one mobile carrier. The comparison shown provides no clear indication of the nature of these carriers. Several possibilities exist. The room-temperature absorption edge displayed in Fig. 3 may indeed contain contributions from photogenerated soliton pairs[16, 17]; however, transitions to and from disorder-induced band tails cannot be discounted.[18] Although $(CH)_x$ does not have short-range crystalline order,[19] its complicated morphology along with thermally induced fluctuations are surely pertinent to the optical properties of the polymer. A further contribution to the absorption edge in *trans*-$(CH)_x$ may originate from soliton transitions shifted from midgap by strong correlation effects.

To summarize, our measurements have provided the first determination of the true absorption in undoped and compensated $(CH)_x$ in the low-absorption, sub-band-gap energy range. Revealed are an Urbach-type absorption edge of slope 70 meV and a broad, NH_3-sensitive, midgap absorption. Quantitative comparisons made with spin-density measurements clearly demonstrate that in *trans*-$(CH)_x$, optical absorption by neutral solitons does not occur at energies near midgap.

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