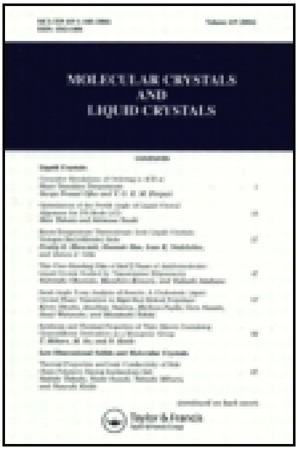

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Band Edge and Neutral Soliton Absorption in Polyacetylene: The Role of Coulomb Correlation

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BAND EDGE AND NEUTRAL SOLITON ABSORPTION IN POLYACETYLENE: THE ROLE OF COULOMB CORRELATION

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Abstract. The technique of Photothermal Deflection Spectroscopy (PDS) has provided the clearest measurement of the absorption edge in polyacetylene. Compensated *trans*-$(CH)_x$ has an Urbach edge which covers orders of magnitude change in absorption in the range 0.9-1.7 eV. Parallel measurements of PDS and spin resonance on compensated *trans*-$(CH)_x$ fails to reveal the predicted neutral soliton (S^o) absorption near midgap. The S^o absorption has been measured in a Photoinduced Absorption (PA) experiment in which the PA spectrum is dominated by a change in the number of S^o centers. These results provide new insight into such fundamental issues as the importance of Coulomb correlations and the role of disorder in polyacetylene.

Polyacetylene is the prototype conducting polymer because of the simplicity of its molecular structure [1]. Its uniquely simple electronic structure has been a model for theoretical studies of 1-*d* semiconductors. However, due to its complicated fibrillar morphology, such important issues as the exact size and the origin of its optical gap have so far remained unresolved. Of particular importance are the role of Coulomb correlation and disorder in determining the electronic structure of such a simple model structure. In this article we review the results of our recent absorption and photoinduced absorption (PA) measurements that have enabled us to address experimentally these two issues.

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 thin shiny films which have been polymerized directly on glass substrates. We have found using integrating sphere techniques, that such apparently specular films diffusely scatter several percent of the incident light in the energy range 0.7-2.0 eV [2]. Therefore, absorption constants lower than 10^4 cm^{-1} inferred from transmission measurements are inaccurate, unless they have been measured by a direct method.

The absorption below the band-edge of *trans*-$(CH)_x$ has been measured directly by Photothermal Deflection Spectroscopy (PDS), a calorimetric technique suitable for the measurement of weak absorptions in thin films [3]. The PDS spectra reveal an exponential Urbach-type edge which extends over orders of magnitude in absorption, and a broad NH_3-sensitive sub-band gap absorption [2]. Analysis of the Urbach edge in terms of a disordered 1-*d* semiconductor [4] yields a value of 1.9 eV for the intrinsic 1-*d* band gap in polyacetylene. Quantitative comparison of absorption and concurrent spin-resonance results show that the predicted "midgap" absorption peak of neutral solitons (S^o) is shifted under the tail of the band edge. The absorption peak of the S^o centers has been detected at 1.4 eV in a recent PA measurement [5]. The relatively large shift of S^o absorption from midgap provides a direct measure of the Coulomb correlation in polyacetylene [6].

In Fig. 1 we show the PDS absorption spectra from *trans*-$(CH)_x$ before and after compensation with NH_3. The true absorption of uncompensated films displays two common features; an intrinsic exponential edge and a relatively featureless broad band which is sensitive to NH_3 compensation. The intrinsic Urbach-like absorption edge is prominently exposed after compensation. The striking result is the absence of an absorption band near midgap which would correspond to the relatively abundant S^o defects. Joint measurements of the number of S^o centers by magnetic resonance and PDS on a 4μ thick film confirms the absence of S^o absorption in the midgap region [2]. The shaded area in Fig. 1 represents the expected size of the S^o absorption peak in the compensated sample. The magnitude of the absorption band of a soliton has been estimated from optoelectrochemical studies [7]. These results indicate the S^o absorption peak is displaced to an energy higher than 1.3 eV.

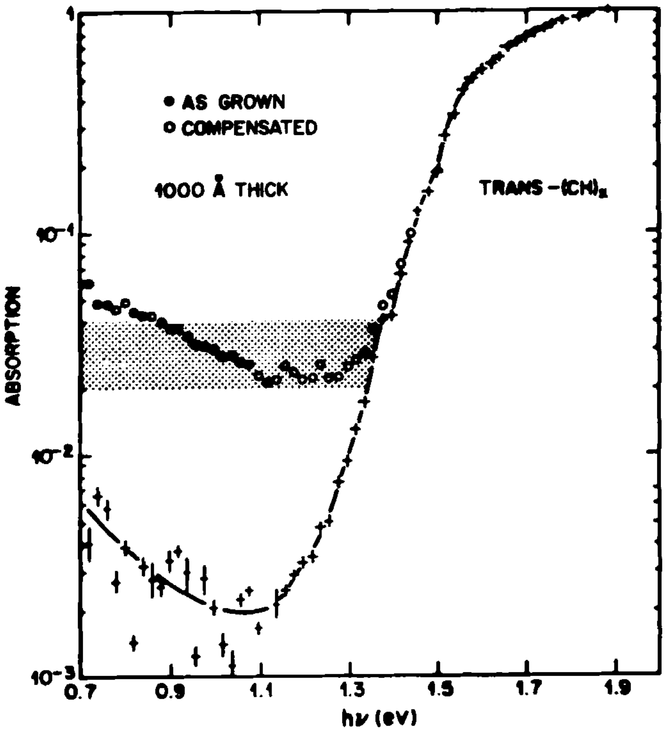

Figure 1. The absorption spectra of trans-$(CH)_x$ before and after compensation with NH_3. The shaded area is the expected size of the S^0 absorption peak.

In the inset to Fig. 2, we show the effect of dilute doping with iodine on the absorption spectrum of *trans*-$(CH)_x$. The level of doping at the lightly doped stage is within a factor of two of the adventitious doping level in as-grown films. The absorption spectra after each compensation step are displayed in Fig. 2. These results indicate that chemical doping followed by compensation broadens the intrinsic band edge. We note that the uniform broadening of the band edge between stage I and II is caused by a very low doping level, comparable to the doping level in an as-grown film.

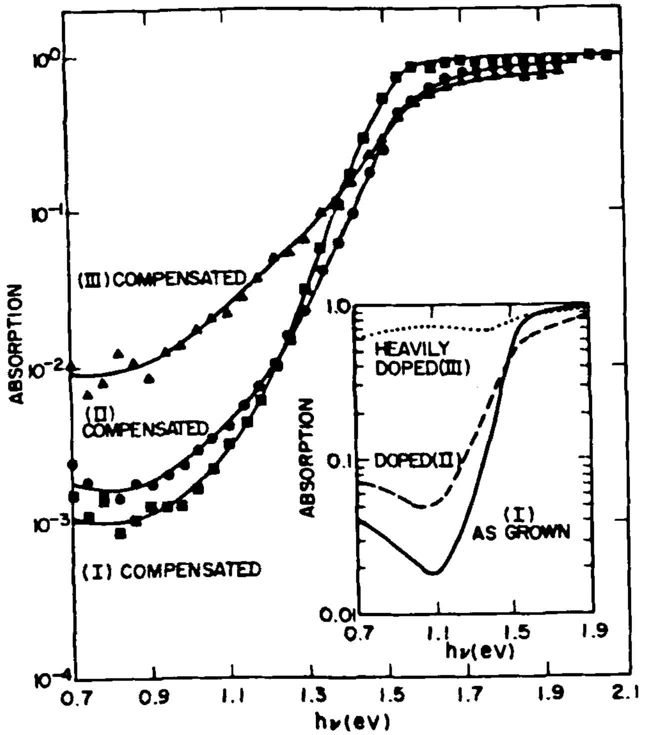

Figure 2. The absorption spectra showing the effects of compensating a trans-$(CH)_x$ film at three levels of doping. The inset shows the absorption spectra before compensation.

Comparison of the PDS spectra from compensated films of different thickness [2] shows that the intrinsic Urbach-edge extends over the energy range 0.9-1.7 eV. This observation indicates the broad band-edge is not solely due to a distribution of chain lengths in *trans*-$(CH)_x$ [8]. Since the decrease in the size of the 1-*d* gap with increasing chain length saturates at a limiting value of about 1.5 eV, such a distribution can smear the divergence in the 1-*d* joint density of states only on the high energy side of this limiting value. Alternative explanations of the broad band edge in *trans*-$(CH)_x$ have considered smearing of 1-*d* band edge by 3-*d* coupling [9] or by fast relaxation into configurations involving soliton-antisoliton pairs [10].

Despite the fit to the absorption data these interpretations ignore the possible inhomogeneous effects which can be caused by the obviously disordered morphology of polyacetylene. As discussed below, an alternative model based on the inherent disorder found in polyacetylene is equally successful in explaining the Urbach edge.

The presence of an Urbach edge over such a large energy range has commonly been attributed to random fluctuations in the electronic energies near the band edge. The origin of these fluctuations lies in a distribution of site energies caused by a random dynamic or static potential. In the latter case, such a potential is due to the presence of impurities or defects. The X-ray reflection spectra from both sides of free standing films shows a higher degree of disorder in the shiny side which is polymerized in contact with the glass wall of the reactor [11]. Thin polyacetylene films are thus expected to be highly disordered because they correspond to the shiny side of the film. Furthermore, the results of Fig. 2 indicate that doping-compensation at a level comparable to the unintentional level of doping in the as-grown film further broadens the absorption edge. More experiments are necessary to elucidate the microscopic nature of disorder in polyacetylene samples because of the complex chemistry of doping and compensation. Nonetheless, these observations suggest that disorder is important and its contribution to the broadening of the band edge should be considered. Since polyacetylene has an anisotropic band structure [12], we shall attempt to analysis the Urbach edge in terms of the theory of disorder in a 1-*d* semiconductor.

If the electronic wave functions were localized at individual sites, the joint density of states and the absorption coefficient (α) would scale as; $\ln\alpha \sim -(h\nu-2\Delta)^2$, where 2Δ is the intrinsic gap. In this expression the effect of the random potential is approximated by a Gaussian broadening of the site energies. Due to the spread of the wavefunction over several sites, whose number scales with the dimensionality *d*, the broadening in the electronic energies is renormalized to give

$$\ln\alpha \sim -(h\nu-2\Delta)^{(2-\frac{d}{2})}$$

This expression is valid in the transitional region close to the intrinsic gap where the states are neither extended nor strongly localized [4]. These theoretical calculations show that near the intrinsic band edge of a disordered 1-*d* semiconductor, the absorption coefficient varies as

$$\ln\alpha \sim -(h\nu - 2\Delta)^{\frac{3}{2}} \tag{1}$$

The spectral dependence of α derived from the PDS spectrum of the compensated samples fits the dependence shown in Eqn. (1) over a relatively large energy range of 1.3-1.8 eV. Thus, assuming the Urbach-edge in *trans*-$(CH)_x$ is from disorder, the intrinsic 1-*d* gap, which is the single parameter of this fit, has a value of $2\Delta = 1.9 \pm 0.1$ eV.

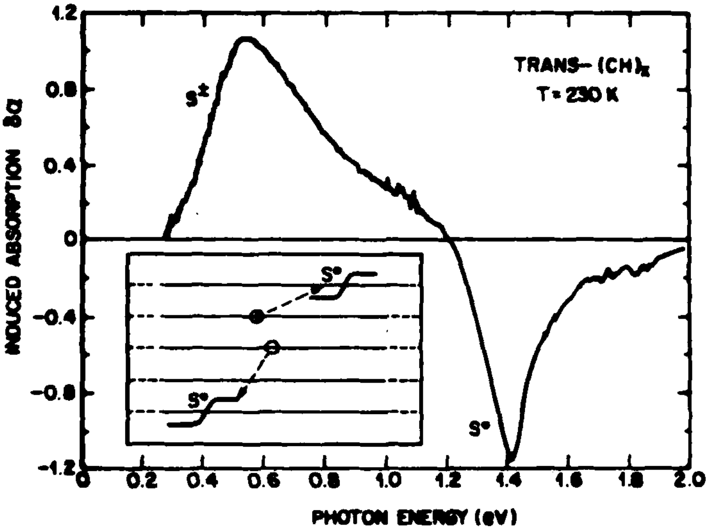

Figure 3. The Photoinduced Absorption result associated with the observed process shown in the inset.

Due to the presence of the Urbach edge, an exact determination of the position of the S^o absorption is not possible from the PDS spectrum. The S^o absorption has been measured in transient absorption measurements in which the PA spectrum is dominated by a change in the number of the S^o centers [5]. In the inset to Fig. 3 we have summarized the conclusion of an extensive set of photoinduced experiments which are reviewed separately [5]. Joint measurements of the charge and spin of the photoinduced states in *trans*-$(CH)_x$ identifies the conversion of S^o to $S^{\pm}$ as the dominant process at long times ($t \sim 1$ ms). The emerging picture from these results is that most absorbed photons generate photoexcited states which decay nonradiatively to the ground state. A small but detectable fraction of photons generate free electrons and holes which are trapped in two separate S^o centers. The net result is an increase in the number of $S^{\pm}$ at the expense of S^o centers. This is clearly seen in the PA spectrum shown in Fig. 3. The oscillator strength of S^o absorption is shifted to that of $S^{\pm}$ absorption at 0.5 eV [13]. The sharp dip in the PA spectrum at 1.4 eV is thus a direct measure of the S^o absorption peak. The large shift of about 0.9 eV in the energy of the absorption peak of the neutral compared to the charged solitons is direct evidence for the importance of Coulomb correlations in polyacetylene [6].

The absorption peaks of S^o and $S^{\pm}$ correspond to optical transitions which leave the localized state of the soliton defect in an opposite-charge state; *i.e.*,

$$S^o + h\nu_o \rightarrow S^{\pm} + \binom{e}{h} \tag{2}$$

$$S^{\pm} + h\nu_{\pm} \rightarrow S^o + \binom{h}{e} \tag{3}$$

where $h\nu_o$ and $h\nu_{\pm}$ are the energies of S^o and $S^{\pm}$ absorption peaks, respectively. The difference in the rest mass of $S^{\pm}$ compared with S^o is then half the shift in their absorption peaks; *i.e.*, about 0.5 eV. We note that this difference is primarily due to localization of two electrons (or holes) in a soliton localized state, and hence can be used as an experimental parameter to estimate the magnitude of the effective Coulomb correlations, U_{eff}. There are, however, two relatively small corrections which are expected to contribute in opposite directions to $h\nu_o$ in Eqn. (2). First is the attractive interaction between the $S^{\pm}$ and $\binom{e}{h}$. This correction tends to increase the inferred magnitude of $h\nu_o$ and the strength of U_{eff}. Second is the smaller size of a charged compared to a neutral soliton. Since the optical transitions occur adiabatically, the higher energy of an unrelaxed $S^{\pm}$ in the Eqn. (2) tends to decrease the magnitude of $h\nu_o$ and U_{eff}.

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