

Optically induced soliton excitations in soluble polyacetylene

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Neutral-type soliton excitations were observed in films of soluble trans-polyacetylene in the temperature range 100–300 K by the method of photoinduced spectroscopy. The relationship between the structural defects of polyacetylene and the soliton states is discussed.

Polyacetylene $(\text{CH})_x$ is a quasi-one-dimensional semiconductor with a system of conjugate bonds. The dynamics of delocalized π electrons in polyacetylene (PA) is almost one-dimensional. This circumstance, together with the degenerate electronic ground state of the trans-isomer of polyacetylene, account for the existence of self-trapped electronic excitations—solitons.¹ In an interband optical absorption the induced electron-hole pair binds into a soliton state in a time on the order of $2 \cdot 10^{-13}$ sec. The soliton excitations are believed to be responsible for the extremely high optical nonlinearities of polyacetylene: The nonresonant third-order nonlinear susceptibility $\chi^{(3)}$ reaches $\sim 10^{-8}$ cgs units.³

The soliton states are observed in the photoinduced absorption (PIA) spectra in the form of bands below the fundamental absorption edge. It was shown experimentally in crystalline PA that two PIA bands correspond to the soliton states: a low-frequency band at ~ 0.4 – 0.7 eV and a high-frequency band at ~ 1.4 – 1.5 eV (Ref. 4). The low-frequency band is associated with charged solitons and the high-frequency band can be induced by both neutral and charged solitons. The physics of soliton excitations in polyacetylene is far from being completely understood. One of the main reasons for the lack of complete understanding is, evidently, that the properties of soliton excitations basically depend on the content of different types of defects, on the morphology, and on the method used in obtaining polyacetylene.

In the present letter we report the results of an experimental study of films of the so-called soluble form of PA, in which 150 to 300-Å globules of PA are introduced into a polymer matrix (PA*). High- and low-frequency PIA bands were recently observed in the soluble form of PA prepared by the method of Ref. 5. We will show that both PIA bands are induced exclusively by charged solitons.⁶ In the PA* which we investigated the properties of the soliton excitations differ significantly from those of the soliton excitations observed previously in different types of crystalline and soluble PA. Photoexcitation in PA*, for example, generates mainly neutral solitons, while generation of predominantly charged solitons was observed previously; furthermore, neutral soliton states have been recorded for the first time at room temperature.

We investigated films of soluble PA*. The films were prepared by the method of Ref. 7. The PA concentration in the polyvinyl butyral matrix was 3–5% and the

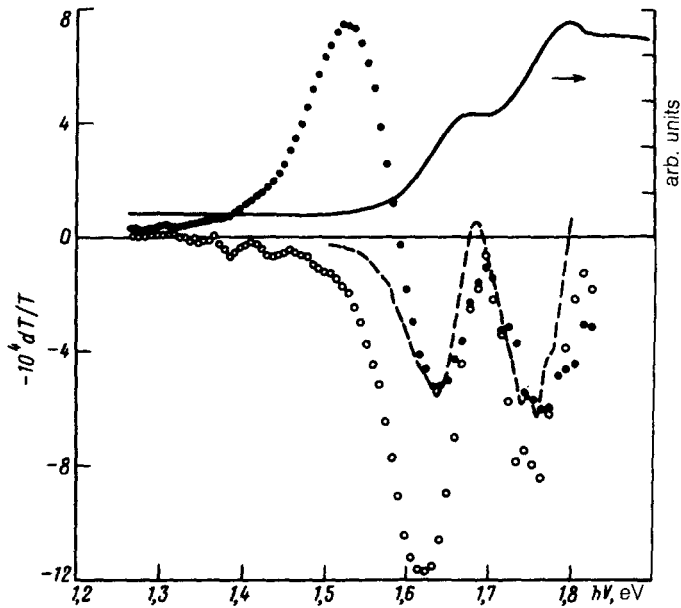


FIG. 1. Photoinduced absorption spectra ($-dT/T$) for in-phase $(dT/T)_A$ (●) and the square-law $(dT/T)_B$ (○) channels of the synchronous detector, the absorption spectrum (solid curve), and the derivative of the absorption spectrum (dashed curve). The temperature of the sample was 100 K, the pump intensity was 300 mW/cm^2 , and the pump modulation frequency was $f=83 \text{ Hz}$. The signal from the quadrature channel of the synchronous detector is phase shifted by $\pi/2$ with respect to the pump.

optical density of the film was ~ 1 . The experiments were performed on polyacetylene films which were allowed to stand, after preparation, for one year and were thermally isomerized into the trans-form at 473 K. A $6\text{-}\mu\text{m}$ -thick PA* film was inserted between two sapphire substrates and placed in an evacuated nitrogen cryostat whose temperature could be regulated from 100 to 300 K. The PIA spectra were measured by the standard method⁸ with deep-band excitation with He-Ne laser radiation ($h\nu=1.96 \text{ eV}$) with intensity up to 400 mW/cm^2 . The PIA and absorption spectra of PA* were recorded with the help of a monochromator, illuminated by a halogen incandescent lamp. The signal from a silicon photodetector was measured with a synchronized quadrature detector with mechanical modulation of the pump beam in the frequency range $10\text{-}10^2 \text{ Hz}$.

We observed in the PIA spectra of PA*, just as for previously studied types of polyacetylene, at 1.52 eV and in-phase with the pump an absorption band below the fundamental absorption edge (Fig. 1). In addition, antireflection peaks are induced at 1.62 and 1.75 eV. The signals corresponding to these peaks are shifted in-phase with respect to the pump by approximately $\pi/4$ (Fig. 1). We investigated the intensities of three photoinduced bands (with maxima at 1.52, 1.62, and 1.75 eV at 100 K) as a function of the temperature of the sample (Fig. 2), the modulation frequency (Fig. 3), and the pump intensity. It was established that the intensities of all bands increase

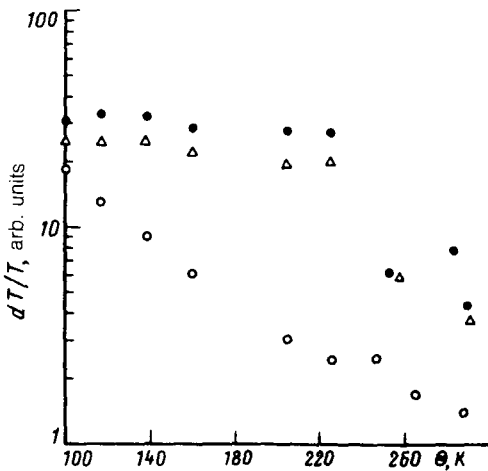


FIG. 2. Intensities of the PIA-band maxima as a function of the temperature of the sample with pump modulation frequency $f=83$ Hz. The intensities of the PIA bands are defined as follows: 1.52 eV (\circ)— $dT/T=|(dT/T)_A|$; 1.62 (\bullet) and 1.75 (Δ) eV— $dT/T=((dT/T)_A^2+(dT/T)_B^2)^{1/2}$.

linearly with the excitation intensity in the entire range studied, 20–400 mW/cm². The intensities of the 1.62 and 1.75-eV bands do not depend on the temperature in the range 100–220 K and they decrease as $1/f$ with increasing pump modulation frequency. The plots of the intensities of the 1.52-eV absorption band as functions of the excitation conditions are substantially different. First, the band intensities decrease monotonically by an order of magnitude as the temperature is raised from 100 to 300 K. Second, the intensity of the indicated band is virtually independent of the pump modulation frequency in the entire experimental frequency range 15–750 Hz (Fig. 3).

It follows from the observed features of the PIA spectra that the antireflection peaks at 1.62 and 1.75 eV are induced by laser heating of the PA* film over a time $1/(2f)$, where f is the pump interruption frequency. In order to separate the thermally induced contribution to the PIA spectrum, we employed PA* samples on a glass

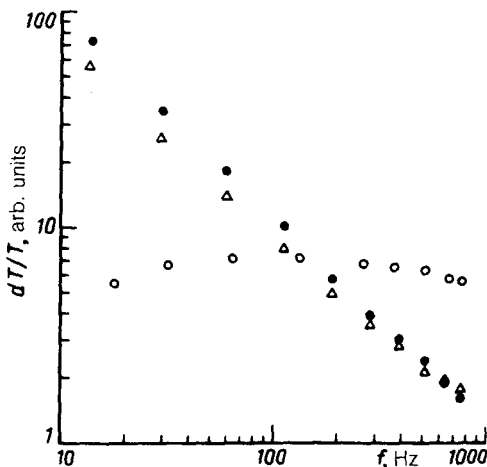


FIG. 3. PIA band intensities as a function of the pump modulation frequency at sample temperature of 100 K. The notation is the same as in Fig. 2.

substrate. This procedure increased by more than a factor of 5 the intensities of the thermally induced 1.62 and 1.75-eV bands. This corresponds to absence of thermal contact between the PA* film and the substrate at pump modulation frequencies above 20 Hz. Here the temperature of the PA* film is estimated to increase by ~ 2 K over a time $1/(2f) = 25$ msec. This increase gives rise to a shift of the absorption edge of PA*. This shift corresponds in magnitude and sign to the observed PIA signals. The position of the indicated band correlates with the maxima of the derivative of the absorption spectrum (Fig. 1); this correlation also follows from the temperature dependence of the position of the fundamental absorption edge. It should be noted that thermally induced peaks were not observed previously under similar experimental conditions in other types of polyacetylene; i.e., the temperature dependence of the absorption at the absorption edge is much stronger for our PA*. The intensity of the 1.52-eV absorption band remained unchanged when the sapphire substrate was replaced with a glass substrate. This result indicates that this band is of nonthermal origin. It was shown previously in different modifications of PA that this PIA band can be induced by neutral and charged solitons. In the latter case, the charged soliton states induce an absorption band at the edge of the conduction band by the electro-absorption mechanism.⁴ It was established⁶ in the recently investigated soluble form of PA that the high-frequency band is induced exclusively by charged solitons; neutral soliton states were not observed.

One of the most important features of the PIA spectra, which were not observed in any of the known types of polyacetylene, is that there is no low-frequency absorption band associated with a charged soliton. In other types of polyacetylene at temperatures above 80 K this band was always stronger than the neutral-soliton band.^{9,10} We tried to record the PIA signal in the spectrum below 1 eV by using a germanium photodetector. Here no photoinduced signal was observed within $dT/T = 3 \times 10^{-5}$, under the conditions corresponding to Fig. 1. Photoexcitation in our samples of PA* thus generates predominantly neutral soliton states.

Comparing the PIA spectra of PA prepared by different methods,^{4,5,10} we can assume that charged solitons are formed on defects of different types. In addition, our PA* is the most perfect of the known polyacetylene samples. It is distinguished by the following features: a) sharp edge of the absorption spectrum with a fine structure (Fig. 1), b) no strong PIA band of a charged soliton, c) neutral soliton excitations in the PA* are at least an order of magnitude stronger than previously observed in the best types of crystalline PA,¹⁰ and d) the soliton excitations depend much less on the temperature of the sample and can be easily recorded at room temperature (Fig. 2).

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