

The Influence of Photoinduced Structural Distortions on Interband Absorption in Polyacetylene

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Abstract. Picosecond pump and probe experiments were carried out on fully oriented trans-polyacetylene. Exciting the sample at 527 nm, photoinduced bleaching and absorption were observed at 527 nm and 1054 nm, respectively. The measurements give an upper limit of 2 ps for the relaxation time of the photogenerated 0.5 eV hot carriers to the band edges. The evaluation of the measured optical processes strongly suggests the conclusion that photoinduced structural distortions of the polyacetylene chain result in observable transient decrease of the interband absorption. This may be ascribed to the reduction of the density of electronic states and to that of the interband transition matrix element of the momentum operator.

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One-dimensional organic semiconductors have demonstrated a wealth of new nonlinear optical processes [1]. In traditional three-dimensional semiconductors the four-fold (or six-fold, etc.) coordination of each atom to its neighbour through covalent bonds leads to a rigid structure. Electronic excitations do not influence this rigid structure significantly, i.e. electronic excitations and excitations of the lattice may be considered as nearly independent elementary excitations of the solid. Consequently, the interaction between radiation and matter can be separated in a well defined way in terms of the interacting particles: a) photon-electron, b) photon-phonon interaction. Whenever the radiation is sufficiently intensive, both types of interaction may result in nonlinear optical

processes, namely a) in redistribution of electrons among excited states (bleaching), b) in various stimulated scattering processes. The situation in one-dimensional (1D) organic semiconductors is quite different, because of the two-fold coordination these systems are more susceptible to structural distortions. In such materials electronic excitations may lead to significant lattice distortions and vice versa, ion displacements may cause considerable change of stationary states of electrons. As a result, the above separation of interaction of radiation with matter does not hold without restrictions. The strong electron-phonon coupling yields a great variety of interesting new nonlinear optical processes in which photon-electron-phonon interaction plays a fundamental role [2–9]. Poly-

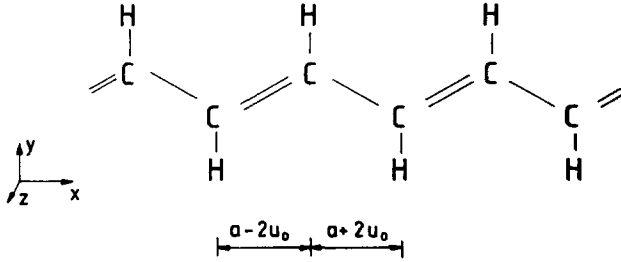


Fig. 1. Trans-(CH)_x. u_0 denotes the amplitude of the Peierls distortion. $2a$ is the length of the elementary cell of the chain (1D solid)

acetylene, (CH)_x, may be considered as the prototype 1D semiconductor. The thermodynamically stable trans-(CH)_x, $E_{\text{gap}} = 1.4$ eV, shown in Fig. 1, was the subject of our investigations. In this work we concentrated our attention on the effect of photogenerated structural distortions on the electronic states in contrast with previous studies, which were focused on lattice deformations arising from photoexcited electron-hole pairs [3–5, 7–9]. Using this kind of generation of structural excitations we searched the influence of these excitations on the interband absorption.

In our experiments we used a Nd³⁺:glass laser system delivering 5 ps optical pulses at 1054 nm (1.18 eV). The excitation pulses for the pump and probe experiments were produced by second-harmonic generation. Time-resolved measurements were performed by exciting the sample at 527 nm (2.35 eV), and monitoring the photoinduced change of the absorption versus time delay with probe pulses at 2.35 eV and 1.18 eV, respectively. We used well-oriented samples of trans-(CH)_x with a nonfibrous morphology obtained by one of us (G.L.) recently [10].

Experimental Details and Results

The Nd³⁺:glass laser system consisting of passively mode-locked oscillator, pulse selector and amplifier stages delivers 5 ps-duration pulses, linearly polarized, at 1.18 eV, 5–10 mJ per pulse, and repetition rate of 0.1 s⁻¹. In order to reduce the scattering of the

measured data originating from unavoidable fluctuations of pulse parameters, we used a recently developed microprocessor-based data acquisition system providing detailed information (duration, energy, peak power) about every single pulse [11]. oo-e type second-harmonic generation produces 3.5 ps duration optical pulses at 2.35 eV with polarization perpendicular to that of the laser pulse. The optical set-up of the experiment can be seen in Fig. 2. A positive lens of 1 m focal length was used to obtain a spot size of about 0.5 mm on the sample. The glass plates and filters were set nearly perpendicularly to the propagation direction of the beam, in order to avoid astigmatism. For technical reasons the optical path length of the pump beam rather than that of the probe beam was changed. Apertures prevented reflections from entering the detectors. The thin ($d = 1$ μm) polymer film was stuck on a copper sample holder inserted into a glass cuvette containing toluol to avoid degradation of the sample in the presence of oxygen. Toluol proved to be fully transparent at the used wavelengths and intensities. The probe beam was carefully adjusted with mirror AM to maintain complete spatial overlap on the sample.

The absorption coefficient at 2.35 eV was strongly different for light polarization perpendicular ($\alpha_{\perp} = 3.7 \times 10^4$ cm⁻¹) and parallel ($\alpha_{\parallel} = 6.7 \times 10^5$ cm⁻¹) to the polymer chains [12]. The relations $\alpha_{\parallel} d \gg 1$, $\alpha_{\perp} d \gtrsim 1$ allow the generation of nonlinearities throughout the whole thickness of the sample only in the latter case. In consequence, we adjusted the polarization of the pump pulse perpendicular to the chain direction to obtain the most intensive nonlinear effect. The same choice was made for the probe pulse at 2.35 eV because of the low transmission of the sample for the other polarization. For the probe pulse at 1.18 eV we preferred the polarization direction parallel to the chains; according to the 1D character of the structural excitations and the associated gap states, greater transition cross section was expected for the parallel than for the orthogonal polarization. Taking these preliminary considerations into account, the experiment was performed with pump pulses of energy of (50 ± 20) μJ (corresponding to an excitation flux of about 10^{16} cm⁻² in

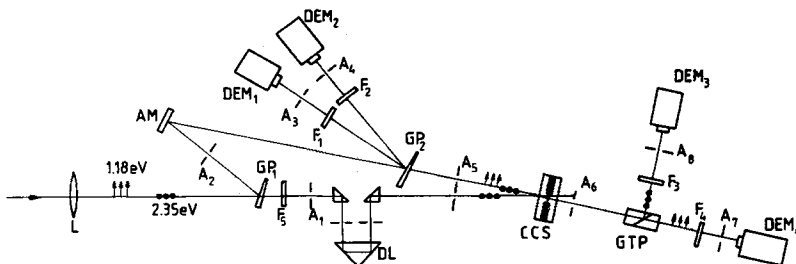


Fig. 2. The experimental set-up (L : $f = 1$ m lens; A_{1-8} : apertures; $GP_{1,2}$: wedged glass plates; DL : delay line; $F_{1,3,5}$: filters at 1.18 eV; $F_{2,4}$: filters at 2.35 eV; AM : aluminium mirror; CCS : cuvette containing the sample; GTP : Glan-Thomson polarizer; DEM_{1-4} : digital energy meters)

our case). The energy of the probe pulses was only about 4% of that of the pump pulses. Detection was carried out with digital energy meters containing silicon photodiodes. The nonlinearity of the detectors was found to be less than 1% over several orders of magnitude. We were interested in the change of transmissions $T_1 = k_1(x_1/x_3)$ at 527 nm and $T_2 = k_2(x_2/x_4)$ at 1054 nm due to photoexcitation, where k_1, k_2 are proportionality factors determined by the transmissions of the cuvette containing toluol, of glass plate GP₂, and of filters F₁, F₂, F₃, F₄. x_1, x_2, x_3, x_4 are the digitized signals of the detectors DEM₁, DEM₂, DEM₃, and DEM₄, respectively.

The measuring procedure was as follows: First, the measurement was performed at a fixed delay position allowing the pump pulse to pass through the sample, and subsequently, without pumping; from the two measurements, the induced relative change of the transmissions $(T_i^P - T_i^0)/T_i^0 f$, $i=1,2$, could be calculated, where T_i^P, T_i^0 are the transmissions with and without pumping, and $f = E_p/50 \mu\text{J}$ is the energy normalization factor (E_p indicates the energy of the actual pump pulse). This procedure was repeated 10 times at each delay position. The averages of the obtained values and their scattering are depicted in Fig. 3a and b. The continuous measurement of T_i^0 during the experiment allowed us to observe any change of the experimental conditions. The initial rapid decay of the photoinduced absorption (PA) and bleaching (PB) takes place within a few picoseconds, which approximately corresponds to the pulse duration. Making a reasonable assumption for the initial time development of PA and PB we used exponential functions for the description of the initial decays ($t < 5$ ps) to obtain characteristic times (τ) for this processes. At longer times, the relaxation of PA and PB seems to rather closely fit a t^{-x} time dependence. The fitting procedure was carried out using a program referred to as MINUIT [13]. We assumed the pulses to have a Gaussian shape. The parameters providing the best fits plotted in Fig. 3b and a were found to be $\tau_A = 1.3 \text{ ps} \pm 0.6 \text{ ps}$, $x_A = 0.41 \pm 0.03$ and $\tau_B = 3.5 \text{ ps} \pm 0.6 \text{ ps}$, $x_B = 0.39 \pm 0.08$ for PA and PB, respectively. Despite the different experimental conditions, the measured curves show reasonable agreement with the results of [6, 7].

Discussion

The measured relative changes of transmission can be approximately expressed as $\Delta T/T = \int_0^d \Delta\alpha(x) dx$, where $\Delta\alpha(x)$ is the corresponding induced spatial change of the absorption coefficient along the beam propagation direction through the sample. We were particularly

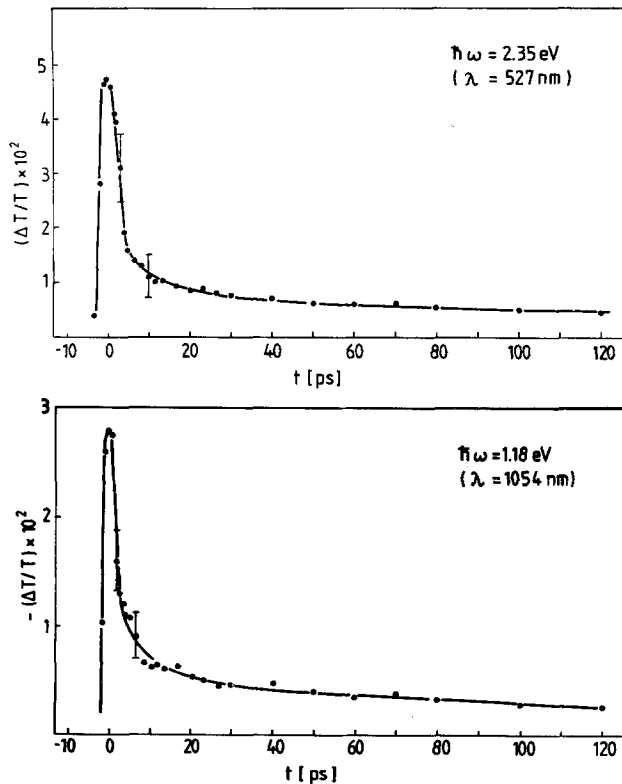


Fig. 3. (a) Time dependence of the photoinduced bleaching at 2.35 eV in trans-(CH)_x at 300 K. (b) Time dependence of the photoinduced absorption at 1.18 eV in trans-(CH)_x at 300 K.

interested in finding the reason for the change of α at 2.35 eV at various times after the excitation of the sample.

The dynamical process following photoexcitation may be described in short as follows. The electronic states connected in the absorption process are symmetrically positioned about the centre of the band gap, as is required by momentum conservation [2]. Accordingly, hot (~ 0.5 eV) electrons and holes are generated due to the high photon energy. Before the excited carriers begin to relax toward the band edges, slight Peierls-type distortion of the lattice is driven by a nearly adiabatic force. During the decay of the hot electrons and holes toward the conduction and valence-band edge, the energy transfer continues in a nonadiabatic way from the electronic manifold to the lattice. As the carriers appear in states near the band edges, the adiabatic channel of relaxation again becomes significant: mobile distortions of the lattice, which are boundaries between two segments (A and B phase) of the chain differing by π in the phase of their Peierls distortion, will be created. Going more into details: if the chain is supposed to be in the A phase [i.e., the x coordinate of the n^{th} site is given by $na + (-1)^n u_0$] before photoexcitation, the generated pairs of phase kinks will confine B segments, in which

the x coordinate of the n^{th} site is given by $na - (-1)^n u_0$ (Fig. 1). This process is associated with simultaneous localization of states split off from the conduction and valence band edges at these phase kinks referred to as topological solitons. Using this terminology, as a final result of the decay of photoexcited hot carriers, soliton-antisoliton pairs are generated from electron-hole pairs [4]. Because of the direct band structure of trans-(CH) $_x$, the relaxation process may also result in photon emission due to direct e-h recombination. However, the quantum efficiency for this process is very small according to the strong electron-phonon coupling [14].

Associated with each soliton is a localized electronic state in the gap, the soliton can be spin- or charge-carrier depending on the occupation of the associated gap state. Hence, the creation of solitons is accompanied with the appearance of new absorption processes below the band gap, which is confirmed by our measurement, as can be seen in Fig. 3b. Comparing the temporal position of the maxima in the curves plotted in Fig. 3a and b we may conclude that the decay of photogenerated hot carriers to the band edges must take place in a time shorter than 2 ps, taking into account the accuracy and the time resolution of our measurement. This result is in agreement with the numerical calculations of Mele, who predicted the time required for the carriers to relax to the band edge to be on the order of 1 ps [4]. The absorption coefficient for transition from the valence to the conduction band (for small intensities) at a fixed polarization is given by

$$\alpha = (4\pi^2 e^2 n / \mu c m^2 \omega) \rho (\hbar\omega/2) |\mathbf{a}_0 \mathbf{p}_{cv}(k)|^2, \quad (1)$$

where n is the density of the π electrons in the sample, μ is the real part of the refractive index, ρ denotes the density of electronic states per spin and per site, \mathbf{a}_0 is the unit polarization vector, e and m are the electron charge and mass, respectively, c is the velocity of light in vacuum, and $\hbar\omega$ is the excitation photon energy. Furthermore, the matrix element of the momentum operator is given by

$$\mathbf{p}_{cv}(k) = -i\hbar \int \psi_k^{c*} \nabla \psi_k^v d^3x, \quad (2)$$

where k is determined by the equation $\hbar\omega = E_c(k) - E_v(k)$; $\psi_k^{c,v}$, $E_{c,v}(k)$ are the one-electron Bloch-states and energies, respectively [15]. Whenever the occupation of valence band states involved in the transition is reduced considerably by strong excitation, α decreases and the expression for α given above does not hold any more. This type of saturation well known in nonlinear optics is detected immediately after photoexcitation. As the hot carriers relax toward band edges, the valence and conduction band states connected in the absorption process will be filled and depleted, respectively; the derived expression for α becomes

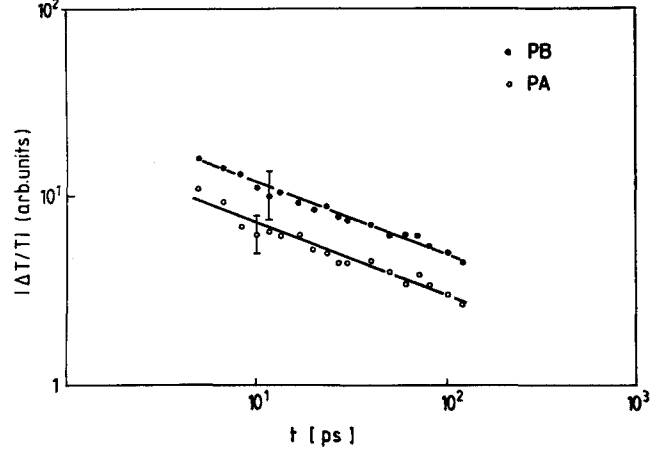


Fig. 4. Photoinduced absorption (PA) and photoinduced bleaching (PB) for times greater than 5 ps

valid again. At these later times, however, a small amount of $\Delta\alpha$ is still remaining. Comparison of PA and PB plotted in Fig. 4, strongly supports the idea that a few picoseconds after photoexcitation the generated solitons are maintaining the small amount of bleaching. From (1) follows, that this reduced absorption may originate from the small reduction of the density of states and from that of the matrix element of the momentum operator. The decrease of the density of electronic states due to the presence of solitons is plausible, since the localized gap states split off from the valence and conduction bands decrease the number of states within the bands [2]. The question arises, whether this interesting nonlinear effect actually contributes to the observed $\Delta\alpha$ to a significant extent.

Using Bloch-functions derived in the tight-binding approximation [2], it can be shown that $\mathbf{p}_{cv}(k)$ depends on the amplitude (increases with the amplitude) but does not depend on the sign (A or B phase) of the Peierls distortion. As a result, $\Delta|\mathbf{p}_{cv}|/|\mathbf{p}_{cv}|$ originating from the presence of solitons is expected to be negative and not to exceed $\Delta\rho/\rho$ considerably.

In our considerations we neglected possible interchain excitation and relaxation processes, which certainly occur with finite probability because of the interchain overlap of atomic $\pi(p_z)$ orbitals. However, interchain overlap of p_z orbitals is significantly smaller than their interchain overlap (the transfer integrals are estimated to be ca. 0.1 eV and 3 eV, respectively) [16, 17], i.e. the interpretation of the experimental results in terms of interchain processes seems to be appropriate.

In summary, we found that photoexcited 0.5 eV hot carriers in fully oriented trans-(CH) $_x$ relax within a time shorter than 2 ps to the band edges and the subsequently created solitons play fundamental role in the remaining bleaching at the excitation wavelength at later times. Theoretical considerations suggest the

conclusion that beside the decrease of the interband transition matrix element of the momentum operator, the reduction of the density of electronic states within the valence and conduction band due to the presence of solitons should also significantly contribute to the reduction of absorption at 2.35 eV remaining after the decay of the photogenerated carriers to the band edges.

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