Charged-Soliton Dynamics in *trans*-Polyacetylene

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Picosecond time-resolved absorption studies of the midgap absorption associated with photogenerated charged solitons in *trans*-polyacetylene are reported. Both direct photogeneration of charged-soliton pairs and neutral- to charged-soliton conversion are observed. The former are created by intrachain absorption and decay on a subpicosecond time scale. The latter are formed following interchain photoexcitation and are the dominant population of charged solitons at times greater than 20 ps.

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trans-polyacetylene [$(CH)_x$] is unusual because of its degenerate ground-state configurations which result from different phases of bond alternation between single and double bonds (see Fig. 1). The transition regions between domains of these configurations are thought to be mobile and solitonlike in nature,[1] having analogs in many other branches of physics.[2] A great deal of excitement was sparked by Su and Schrieffer's proposal[3] that topological solitons are the primary photoexcitations of the quasi-one-dimensional *trans*-polyacetylene lattice. Indeed, much evidence points to the existence of photogenerated charged solitons,[4] including the observation of a midgap photoinduced absorption[5,6] corresponding to the prediction of the Su-Schrieffer-Heeger model. These midgap absorptions are correlated with the photoconductivity of *trans*-$(CH)_x$, a fact which has been taken to indicate that charged solitons play a role in the photoconductivity.[1,7-11] However, the nature and formation mechanism of these lattice deformations remain mysterious. In particular, whether the origin of the solitons is intrinsic or extrinsic has remained a point of controversy.[11,12] In the present Letter we report picosecond dynamical studies which resolve this issue and present a reasonably complete picture of the dynamics following above-band-gap photoexcitation of *trans*-$(CH)_x$.

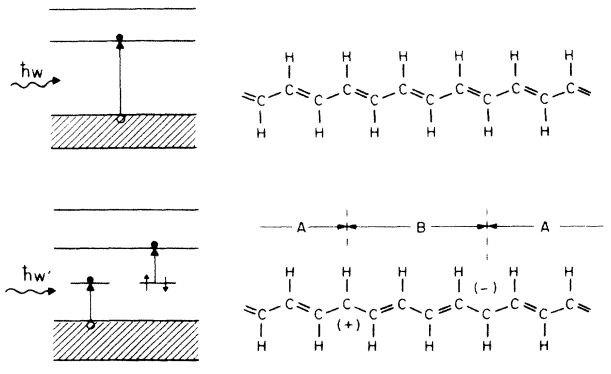

FIG. 1. Schematic of direct photogeneration of charged solitons and midgap absorption in *trans*-$(CH)_x$. *A* and *B* denote the distinct but degenerate domains.

Several picosecond measurements of near-band-edge photoinduced absorption[13,14] and photoinduced interband bleaching[15] have been done, but the results are difficult to interpret in terms of soliton generation and decay since they probe dynamics associated with other excitations. In fact, the dynamics of charged solitons has not been monitored directly on time scales shorter than 10 μs.[4] Here we present picosecond time-resolved measurements of the *photoinduced midgap absorption associated with charged solitons* as shown schematically in Fig. 1. Our measurements clearly show that charged solitons arise from *both intrinsic and extrinsic* mechanisms. We observe the directly photogenerated charged-soliton pairs resulting from the rapid lattice deformation described by Su and Schrieffer.[3] In addition, we identify charged solitons which result from conversion of neutral to charged solitons[12] and survive to long times. Our experiments are consistent with relaxation dynamics along the lines proposed by Kivelson and Wu.[16]

Two types of thin *trans*-$(CH)_x$ films on sapphire are used as samples. The first have been thermally isomerized from the *cis* form synthesized by the technique of Shirakawa, Ito, and Ikeda.[17] The second type are synthesized directly as *trans*-$(CH)_x$[18] and differ principally in their concentration of neutral soliton defects which is 3-4 times smaller. The samples are mounted in a closed-cycle cryostat capable of cooling to 25 K.

A synchronously pumped dye laser having 3-4-ps pulses at 2.1 eV is amplified at 10-Hz repetition rate and used as the excitation source. Part of the beam is used to generate a white-light continuum which is difference-frequency mixed with residual 2.1-eV radiation in $LiIO_3$. This results in picosecond infrared pulses[19] of picojoule energies tunable from 2.5 to 5.5 μm by angle tuning of

the nonlinear crystal. The infrared pulses are overlapped with the visible and are used to map out its dynamics. The cryostat ordinarily has birefringent sapphire windows so that the pump and probe beams are essentially unpolarized. A fraction of the incident probe beam is diverted to a cooled InSb reference detector and the transmitted infrared is measured by a separate InSb detector. These signals are relayed to a dividing boxcar integrator which computes normalized probe transmission and this is averaged by a laboratory computer.

Figure 2 illustrates the time-resolved midgap absorption with a 2.8-μm (0.45-eV) probe and incident pump fluence of about 2×10^{15} photons/cm^2. In the curve of Fig. 2(a), taken at $\sim$25 K ambient temperature, there are two prominent features. We find that this unusual dynamics is caused by superposition of two separate photoinduced absorptions having different origins. Initially, there is an absorption which decays rapidly and we ascribe it to directly photogenerated charged solitons. Following this, and persisting for several hundred picoseconds, is an absorption due to charged solitons formed via neutral- to charged-soliton conversion. The remainder of this paper is devoted to support of these assignments and to elucidation of the formation mechanism and quantification of the dynamics of these species.

We first turn our attention to the initial peak. Figure 3 presents the spectrum of the midgap absorption when the pump and probe are temporally overlapped. A comparison with the long-time (>10-μs) photoinduced absorption[4a,20] (dashed line) indicates that the spectra are essentially the same. This identifies the picosecond species to be charged solitons similar to those seen at longer times. The lack of spectral shift or broadening suggests that these rapidly cool to the lattice temperature.

The pump fluence dependence of the photoinduced absorption at zero delay has been measured and is linear at low fluence.[21] These data provide an estimate of the charged-soliton lifetimes from their steady-state concentration during the pulse. The probe absorbance A is given by $2\Phi N\sigma(\tau_s/t_p)$, where N is the number of photons absorbed per unit area, σ is the charged-soliton cross section, Φ is the quantum yield of soliton-antisoliton pairs, τ_s is the charged-soliton lifetime, and t_p is the pulse duration. We have assumed that soliton lifetime $\tau_s \ll t_p$ so that τ_s/t_p approximates the steady-state fraction which remain excited at a given time during the excitation pulse. The cross section is determined from optoelectrochemical doping measurements[22] to be $\sigma=4\times10^{-16}$ cm^2. This gives $\Phi(\tau_s/t_p)\sim0.05$, or a charged-soliton lifetime of about 0.25 ps on the assumption of unity quantum yield. Lower quantum yields would mean longer lifetimes and, from the upper bound of the pulse duration, a minimum quantum yield of $\sim$0.1 for directly photogenerated charged solitons can be inferred. The slight asymmetry in the early absorption peaks of Fig. 2 is because some absorption from these directly photogenerated solitons is observable at 10–15-ps delay. The decay would be limited by the experimental resolution if it were exponential with $\tau_s\sim0.25$ ps, and we therefore conclude that the decay is of the form of a power law in nature like those observed for band-edge photoinduced absorption[13] and for photoinduced interband bleaching.[15]

A fused-silica window was placed on the cryostat to permit meaningful polarization measurements of the transient absorbance to be made. At zero delay, linear

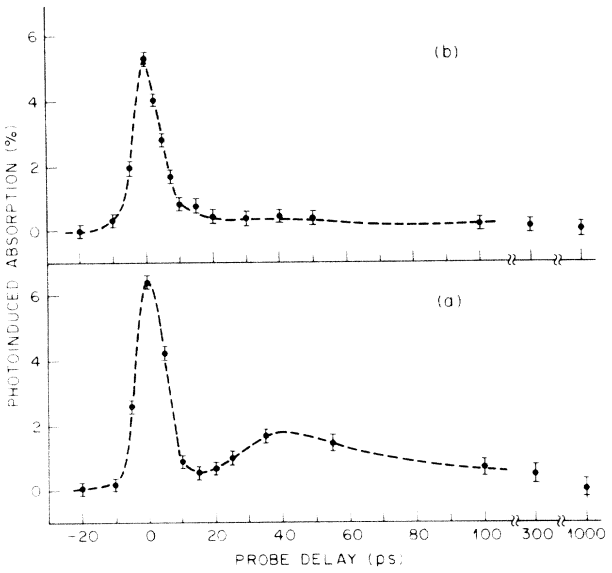

FIG. 2. Transient midgap absorption of *trans*-$(CH)_x$ films. (a) 25 K and (b) 300 K ambient temperature. Pump fluence is approximately 2×10^{15}/cm^2. Dashed lines are to guide the eye.

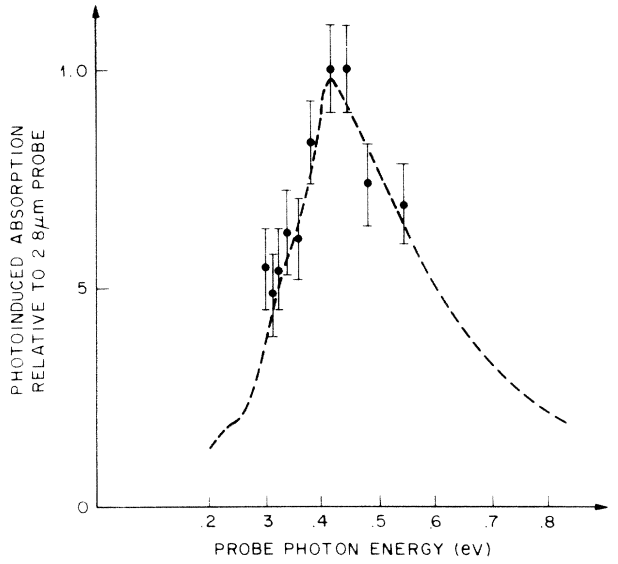

FIG. 3. Spectrum of photoinduced midgap absorption at zero pump-probe delay. Pump fluence is approximately 4×10^{15}/cm^2. Dashed line is the microsecond-delay charged-soliton spectrum from Ref. 4.

probe polarization parallel to the pump was absorbed 1.8 ± 0.2 times as strongly as was perpendicular probe polarization. For an isotropic distribution of chain directions in the sample, one expects transient absorbance for parallel pump and probe polarizations to be three times that for perpendicular polarizations [$A(\parallel)/A(\perp)=3$]. The discrepancy between this and the measured ratio is anomalous since, for soliton lifetimes of $\sim 10^{-3}$ s, we do not expect to see depolarization due to soliton motion.[15] It seems equally implausible, however, to hypothesize absorption moments significantly deviating from the chain direction to explain this discrepancy.

We turn to a discussion of the transient absorption at times > 20 ps after photoexcitation. The increase of absorption observed after 20 ps in Fig. 2(a) illustrates that the transients seen at long times have a different origin, and are not merely escaped charged solitons which have been directly photogenerated. It is observed that this absorption near 30–50 ps is greatly suppressed in the *trans*-$(CH)_x$ synthesized by a non-Shirakawa method[18] where fewer unpaired spins (neutral solitons) are observed in ESR measurements. The absorption for $\tau < 20$ ps is, however, unaffected. One way these observations can be accounted for is by our ascribing this absorption to charged solitons formed by trapping of photogenerated charge by neutral solitons. This model has been suggested by Orenstein *et al.*[12] and, more recently, by Bleier, Leising, and Roth[10] to explain features of the photoconductivity of oriented *trans*-$(CH)_x$. In their models, a small fraction of the photoexcited electrons and holes ($\gtrsim 0.01$) are formed on separate chains. These single electrons and holes do not form charged-soliton pairs that can annihilate.[12] Instead, they diffuse as polarons until they decay or find neutral solitons and are trapped. The observed delayed absorption is due to the polaron diffusion time.

Strong confirmation of this picture comes from the measured polarization ratio at 50-ps delay of $A(\parallel)/A(\perp)=0.4 \pm 0.3$. The probe absorption is principally perpendicular to the pump polarization because creation of electron and hole on separate chains requires fields orthogonal to the chain (soliton dipole) direction. This is consistent with measurements on stretch-oriented *trans*-$(CH)_x$ which exhibit higher fast photoconductivity,[10] dc photoconductivity, and long-time midgap absorption[23] with pump polarization perpendicular to the stretch direction. The polarization ratio indicates that the origin of the absorption at $\gtrsim 20$ ps in Fig. 2(b) (300 K) is also due to neutral- to charged-soliton conversion. Clearly, the ambient temperature affects the formation time and/or generation efficiency of these solitons. Simple heat-flow calculations indicate that rapid cooling on the time scale of tens of picoseconds allows the substrate ambient temperature to manifest itself.[21] The difference between 25- and 300-K dynamics may result from a decrease in polaron mobility with temperature.[24]

The amplitude of absorption at 50 ps delay and the known cross section for isolated charged solitons[20] put their quantum yield at about 0.01 to 0.05, consistent with estimates of interchain absorption probability given by Orenstein *et al.*[12] This yield, of course, decays by 1 or 2 orders of magnitude at later times (microseconds). Saturation of the signal at 30–50 ps occurs at absorptions of 1%–2%, approximately what one expects for conversion of all the neutral solitons to isolated charged solitons. Even so, there may be alternative pictures for the generation mechanism of the long-lived solitons such as interaction of pairs of like charged polarons on the same chain.[25] This pathway would be intrinsic and might be suppressed for some other reason in the low-spin *trans*-$(CH)_x$ samples.

The direct study of charged-soliton dynamics complements transient band-edge absorption[13] and bleaching[15] experiments. A picture which we believe to be consistent with the results of all of these experiments is close to that of Kivelson and Wu.[16] The initial absorption is principally ($> 90\%$) in the intrachain component. The midgap absorption of charged solitons (0.45 eV), band-edge absorption (1.4 eV), and bleaching of the ground state (2 eV) all decay on similar subpicosecond time scales with power-law decays. This fact, along with the large transient absorption strengths at both midgap and band edge which demand quantum yields of order unity, suggests that these two absorptions are likely to represent different species in a single decay channel. A reasonable hypothesis is that charged-soliton pairs are directly photogenerated within 10^{-13} s and then decay to neutral-soliton pairs (which absorb at 1.4 eV)[26] in several hundred femtoseconds.[27] The neutrals in turn decay very rapidly to phonons so that the apparent decay observed is actually the rate-limiting decay of the charged-soliton precursor. Under this hypothesis, no neutral-soliton rise time is resolved in the experiments of Shank *et al.*[13] because their short lifetime means that a steady-state concentration is reached quickly. Further work is in progress to test the ramifications of this hypothesis.

In summary, we have directly observed photogeneration of intrinsic charged solitons in *trans*-$(CH)_x$ and obtained information about their absorption spectrum and decay dynamics on a picosecond time scale. These can be distinguished from charged solitons which are formed at later times by neutral- to charged-soliton conversion and are apparently responsible for $(CH)_x$ photoconductivity at times greater than 20 ps after photoexcitation.

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