PHYSICAL REVIEW B VOLUME 28, NUMBER 10 15 NOVEMBER 1983

Femtosecond excited-state relaxation in polyacetylene

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(Received 8 August 1983)

Excited-state relaxation in polyacetylene has been examined using femtosecond optical pulses. In this Brief Report, we describe the recovery dynamics of an optically induced absorption in the infrared region of the spectrum (1.55 μm) which displays distinctly different recovery dynamics than previously observed at shorter wavelengths.

Recent reports of photoinduced absorption (PA) in polyacetylene have created a great deal of interest and experimental activity.[1-4] In the initial work,[1] PA induced by a 10-ns laser pulse was measured with 10-μs time resolution. In all *trans*-polyacetylene [*trans*-$(\mathrm{CH})_x$], the PA spectrum showed two peaks, at 1.40 and 0.43 eV, with full widths at half maximum of 0.15 and 0.30 eV, respectively.[5] Recently the dynamics of the 1.40-eV absorption peak,[3] and the associated bleaching of the ground-state absorption, were measured with a 0.1-ps resolution.[3,4] Their work showed that the excited-state absorption, previously observed to persist for $\sim 10^{-3}$ s, is formed less than 10^{-13} s after photoexcitation. In the present paper we have extended the spectral range of our measurement to the near-infrared, while maintaining a time resolution of 90 fs. These measurements reveal a distinctly different behavior from previous measurements at higher photon energy.

The experimental apparatus for performing these measurements has been described previously.[6,7] Amplified pulses of 90 fs in duration with a wavelength of 620 nm (2.0 eV) were used to excite a 1000-Å film of *trans*-$(\mathrm{CH})_x$. The sample was kept under vacuum at room temperature. The PA was measured from visible to near-IR wavelengths ($\lambda < 1550$ nm) with 80-fs pulses produced by continuum generation in water. A stepper motor was used to provide a variable path delay between the pumping and probing pulses. The transmission of the probe was measured as a function both of time delay and probe wavelength with a Ge photodiode. The experimental results are plotted in Fig. 1.

Previous measurements have shown that the decay of the PA in the energy range 1.3–2.0 eV can be accurately described by

$$\frac{n(t)}{n(0)} = \mathrm{erf}(\sqrt{\tau/t}) \ , \tag{1}$$

where $n(t)$ is proportional to the PA at time t.[3] The limiting form of this expression, $n(t)/n(0) \sim t^{-1/2}$ is found to fit the observed decay for more than two decades in time, from ~ 0.5 to ~ 100 ps.[3,4] We have previously shown that this form of decay can arise from one-dimensional diffusion-limited recombination.[4] In Fig. 1(a) we show the decay at a probing wavelength of 855 nm (1.5 eV) which illustrates this power-law behavior for $t < 5$ ps. As the wavelength of the probe is increased the decay of the PA becomes distinctly more rapid, as is shown in Figs. 1(b) and 1(c). We find that at $\lambda = 1000$ nm (1.24 eV) and 1550 nm

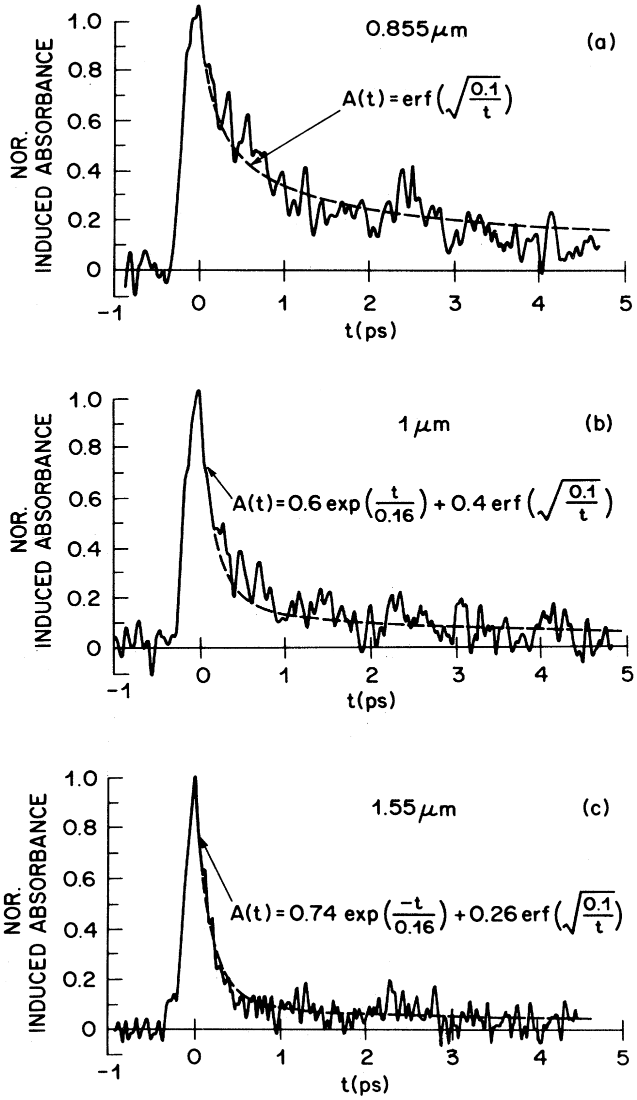

FIG. 1. Decay of photoinduced absorption following pulsed excitation at 0.62 μm for three probing wavelengths. The dashed line shows a fit to the data achieved by calculating the sum of error function and exponential decays.

(0.80 eV) the decay process can no longer be fitted by Eq. (1). The initial decay, $t < 1$ ps, is best described by an exponential with time constant 160 fs. For $t > 1$ ps the persistence of a long tail clearly shows the power-law [Eq. (1)] behavior is still present. The dashed line fits to the data are obtained by calculating a weighted sum of these two functions. From the fitting parameters shown in Fig. 1 it is clear that at shorter wavelengths the power law dominates while at longer wavelengths the decay is more nearly exponential with a single-time constant.

Su and Schrieffer[8] have considered theoretically the dynamic response of a *trans*-$(CH)_x$ chain to the injection of an electron-hole pair. They found that in less than 10^{-13} sec a close pair of kinks develops in the regular pattern of alternating single and double bonds which characterizes the ground-state structure. At a sufficiently long time these kinks propagate away from each other to produce the fully relaxed state of two injected carriers, a pair of solitons. With a one-electron approximation, the energy required to create a pair of isolated solitons is $4\Delta/\pi$ where 2Δ is the semiconductor gap.[9-11] If we associate the threshold for optical absorption of *trans*-$(CH)_x$ at 1.4 eV with this energy, then in our experiment the electron-hole pair must lose ~0.6 eV in order to form the relaxed excited-state configuration. We believe that the 160-fs time constant which we measure is most likely associated with this cooling-off process.

This process should result in spectral shifts in the PA on a sub-picosecond time scale. Associated with each isolated soliton is an electronic level which, in the absence of electron-electron repulsion, lies exactly halfway between the valence and conduction bands.[9,10,12] In the process of forming these two midgap states, a level is split off from the top of the valence band and the bottom of the conduction band. As these (singly occupied) levels move through the band gap the position of the resulting in-gap absorption should shift as well. It is possible that the dynamics we observe in the near IR are connected with this process, although clearly spectral measurements are necessary in order to demonstrate this mechanism.

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