

High-Pressure Effects on Ultrafast-Relaxation Kinetics of Excitons in Polydiacetylene 4BCMU

B. C. Hess,^{(1),(2)} G. S. Kanner,⁽²⁾ Z. V. Vardeny,⁽²⁾ and G. L. Baker⁽³⁾

⁽¹⁾*Physics Department, California State University, Fresno, California 93740*

⁽²⁾*Physics Department, University of Utah, Salt Lake City, Utah 84112*

⁽³⁾*Bell Communication Research, Red Bank, New Jersey 07701*

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Ultrafast-relaxation kinetics of the singlet excitons in polydiacetylene 4BCMU was measured at hydrostatic pressures up to 80 kbar, using the pump-probe photoinduced-absorption technique with 70-fs resolution at 2 eV and 5 ps in the spectral range 1.2–2.2 eV. The 100-fs decay component survives at high pressures, but the slow component evolves from a 1.5-ps exponential decay at atmospheric pressure to a much slower stretched-exponential decay at high pressures with a complete recovery in the ns time range. Results suggest that the fast decay component is a 1D relaxation process, whereas the slow component is due to exciton recombination which requires a subsequent 3D distortion of the polymer chain.

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π -conjugated polymers continue to attract substantial interest because of their quasi-1D excitations¹ and associated large optical nonlinearities and fast recovery times.² Polydiacetylenes (PDA) are particularly attractive because they can be formed as both single crystals and processible solutions and films which have promise for optical nonlinear devices.³ Optical nonlinearities have been shown^{4–6} to be due to the optical Stark effect and phase-space filling of singlet excitons with remarkably short lifetimes. Several time-resolved studies, however, have identified longer-lived components due to defect states⁷ and triplet excitons.^{8,9} In this work we study the dynamics of the singlet excitons. Two stages in the singlet exciton recovery have been identified by femtosecond photoinduced-absorption techniques^{5,9,10} in several polydiacetylenes: PTS, 15-8 3BCMU, and 4BCMU; (1) an initial ultrafast process of about 100 fs,¹⁰ insensitive to temperature, associated with the onset of a rather featureless subgap absorption;⁵ (2) a second process with time constant ranging from^{5,7} 1 to 3 ps with slower times at low temperatures.^{7,9} The first stage is believed^{5,10} to be associated with exciton self-trapping which may assist the subsequent recombination process in the second stage. However, the few existing experiments are insufficient to precisely determine the excited-state dynamics and to distinguish between the various proposed models.^{9,10}

In this paper we use the photoinduced absorption (PA) pump-probe technique, with 70-fs (and 5-ps) time resolution at hydrostatic pressures up to 80 kbar, to study the singlet exciton dynamics in PDA 4BCMU. We show that high pressure does not affect the fast decay component, but dramatically increases the exciton lifetime by affecting the dynamics of the slow component, without substantial change in the PA spectrum itself. The slow decay kinetics, however, changes from a 1.5-ps exponential decay at ambient pressure to a much slower stretched-exponential (or power-law) decay at high pressures, distributed over several decades in time.

This indicates that high pressure inhibits the 3D distortions of the excited chains needed for the fast recombination. The stretched-exponential decay kinetics is explained by exciton diffusion along the chain to reach recombination centers which are probably in the form of 3D defects.

PDA-4BCMU films were deposited on 12- μ m Mylar by spin casting (sample 1) and from a cooled toluene solution (sample 2). Because the conditions for preparing sample 2 are nearer to equilibrium, sample 2 is more ordered than sample 1. Pieces were cut to fit in a gasketed Piermarini-Block diamond-anvil cell.¹¹ Deoxygenated water was chosen as the quasihydrostatic medium. The pressure was measured by the ruby-luminescence method;¹¹ the inhomogeneity in pressure was less than $\sim 5\%$ up to 70 kbar. Two laser systems were used to measure the exciton dynamics: a dispersion-compensated colliding pulse passively mode-locked (CPM) ring dye laser with 70-fs time resolution at 2 eV and two synchronously pumped dye lasers sync-pumped system which covered the spectral range from 1.2 to 2.15 eV with 5-ps resolution. We used the pump-probe PA technique; the longest delay time was 3 ns. An amplitude-modulated (at 4 MHz) pump beam and a delayed probe beam were focused through the diamond anvils to a ~ 30 - μ m spot on the sample. Changes ΔT in the probe transmission T were measured as a function of the probe delay using a Si detector, a preamplifier tuned to 4 MHz, and a high-frequency lock-in amplifier. The ~ 2 mm-thick diamonds had no noticeable group-velocity dispersion effects on the 70-fs pulses. The photon density was kept below 2×10^{13} cm⁻² to avoid sample damage and saturation effects.⁹ To measure the absorption spectra, a 100- μ m pinhole at the exit of a $\frac{1}{4}$ -m monochromator was illuminated by a tungsten lamp and imaged on the sample.

In Fig. 1 we show the singlet exciton PA decays for pump and probe beams at 2 eV with CPM laser for pressures up to 70 kbar. When both pump and probe are at 2 eV the PA is negative (i.e., photobleaching).^{4,5,10} The

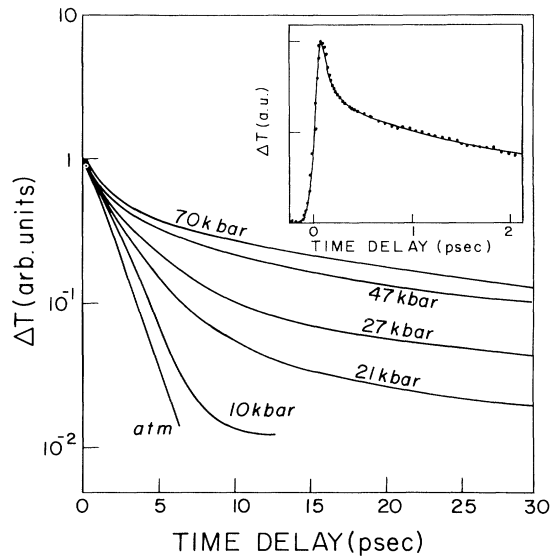


FIG. 1. Transient PA (slow component) of the singlet excitons in PDA-4BCMU (sample 1) at 2 eV for several hydrostatic pressures, normalized at 300-fs delay and plotted on a semi-logarithmic scale. Inset: The ultrafast decay component at 40 kbar on a linear scale; the solid line is a fit involving a 100-fs exponential decay and a slow component.

line marked "atm" is the 1.5-ps exponential decay at ambient pressures, a result identical to that reported for PDA-3BCMU.⁵ At pressures as low as 21 kbar, the decay becomes much slower and is clearly nonexponential. In fact, at 40 kbar some PA response is still detectable up to 3 ns, our maximum probe delay. The inset of Fig. 1 displays the PA response at 40 kbar up to 2 ps. The solid line is a fit to the experimental decay that convolutes the pulse autocorrelation with a 100-fs exponential decay and a slower component. The femtosecond ultrafast decay at 40 kbar is the same as at ambient pressure (not shown in Fig. 1) measured by us and others.^{5,10} We therefore conclude that high pressure does not affect the first-stage relaxation, but must inhibit the relaxation of the second stage, which is also temperature dependent.⁷

As shown in Fig. 2(b), the absorption band in PDA redshifts (E_g decreases) with increasing pressure¹² as determined from extrapolation of the band edge (an example is seen in Fig. 3). Up to about 35 kbar we measure a redshift of ~ 10 meV/kbar; however, saturation sets in at about 40 kbar. Similarly, the increase in the slow component decay time as measured by $\tau_{0.1}$ (90% decay) also saturates at about 40 kbar as shown in Fig. 2(a). Since the pressure-induced redshift in many solid-state polymers is probably associated with 3D van der Waals-type interaction¹² and/or 3D conformational changes,¹³ the similarity between $\tau_{0.1}$ and E_g dependences with pressure seen in Fig. 2 indicates that the slow component is probably also associated with a 3D

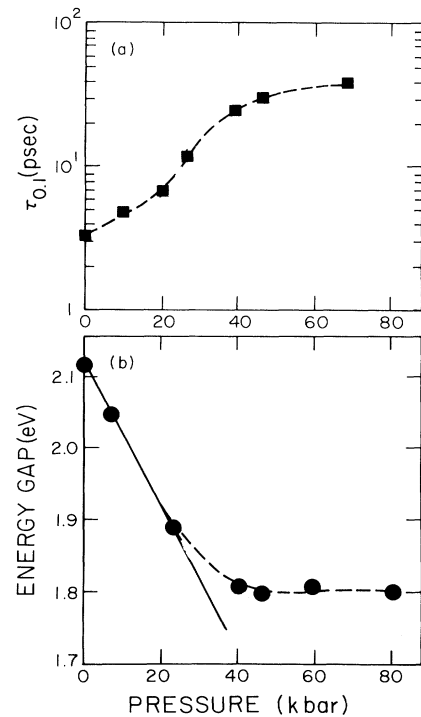


FIG. 2. Effect of high pressure on exciton dynamics and the energy gap for sample 1. (a) Time for PA to decay to 10% ($\tau_{0.1}$) vs pressure. (b) Extrapolated band edge vs pressure. The straight line is a linear redshift reported in Ref. 9.

effect, which saturates at high pressures.

To be sure that the slower dynamics is not due simply to the shift of the absorption band relative to the CPM laser line, we used the sync-pumped laser system to study the PA decay at atmospheric pressure with pump and probe energies up to 2.2 eV. The 200-meV shift of the sync-pumped laser line relative to the CPM laser line is equivalent to the redshift of the absorption band at 20 kbar (Fig. 2). We found that the 1.5-ps exponential decay is the same at 2 and 2.2 eV. This clearly shows that the increase in the exciton lifetime with pressure seen in Figs. 1 and 2 is a true pressure effect.

To determine the nature of the photoexcitations at high pressures, we measured the PA spectra at ambient and high pressures using two sync-pumped lasers with 5-ps cross correlation, where the pump photon energy was fixed at 2.14 eV. Figures 3(a) and 3(b) show the PA spectrum for zero time delay at atmospheric pressure and at 40 kbar, respectively. The PA spectrum at 40 kbar is essentially identical to that at ambient pressure, except for the redshift of the band with pressure and a slight broadening of the absorption edge. This shows that at high pressures the PA is still due to self-trapped 1D singlet excitons⁵⁻¹⁰ and that the slow decay of the PA reflects an increase in the 1D exciton lifetime with pressure, rather than the presence of new long-lived pho-

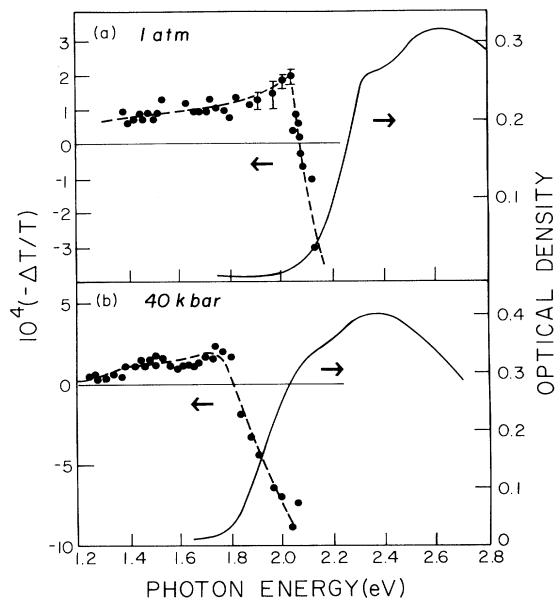


FIG. 3. Spectra of exciton absorption and PA at zero time delay (5-ps time resolution) excited at 2.14 eV (a) at atmospheric pressure and (b) at 40 kbar.

to excitations such as polarons, interchain excitons, or intrachain triplet excitons. Further evidence against involvement of triplet excitons at high pressures is that the long decay times are still too fast compared to triplet exciton lifetimes ($\sim 10^{-5}$ s) in PDA.⁸

We consider 1D and 3D processes in the exciton recovery and the possible effects of pressure on each. A 1D process maintains the planar, rodlike conformation of the ground state, but induces changes in the bond order of the carbon atoms along the backbone of the polymer chain. Our experimental evidence, which includes redshifts of the exciton absorption spectrum (Figs. 2 and 3) and the PA band (Fig. 3) as well as extensive studies of resonant Raman scattering at high pressures,¹⁴ shows that the 1D properties of the polymer are only slightly affected by pressure. We conclude therefore that the first stage of the exciton recovery is a 1D process, but the second stage, which is so susceptible to pressure, is not. Pressure, on the other hand, has a significant influence on the 3D structure of π -conjugated polymers in general,¹³ and PDA in particular.^{12,13} The reason is that higher pressures favor forms with lower specific volumes (i.e., planar, rodlike chains). In PDA-4BCMU solution, for example, application of high pressures causes a transition from coil-like chains to rodlike chains.^{12,13} The 3D kinks or twistings, that are very sensitive to pressure, are the excited-state deformations suggested by Greene *et al.*⁹ to explain the fast picosecond exciton recovery in PDA at ambient pressure. We suggest that the application of pressure makes the 3D distortions more costly in energy and hence inhibits the fast decay in the second

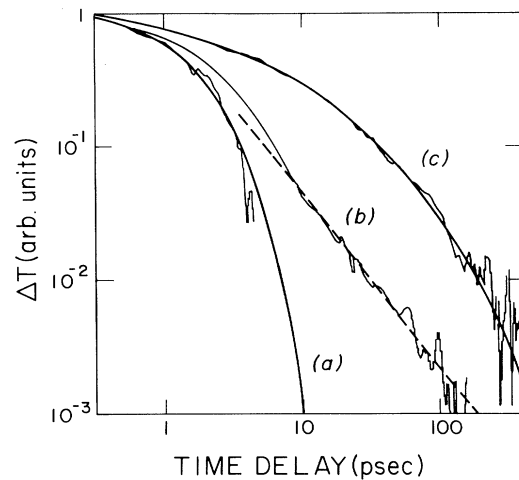


FIG. 4. The slow component of the PA decay at 2 eV. Curve *a*, exponential decay at atmospheric pressure. Curve *b*, power-law decay at 21 kbar. Curve *c* stretched-exponential decay at 40 kbar.

stage. However, 3D defects are still present in the film at high pressures, acting as recombination centers. To recombine within the nanosecond time domain, excitons probably migrate to reach these centers and this may explain the slow decay kinetics at high pressures.

Figure 4 shows in more detail the decay kinetics at high pressures. At atmospheric pressure (Fig. 4, curve *a*) it is a 1.5-ps exponential decay (as in Fig. 1). At 10 kbar, the decay is nearly exponential up to about 7 ps when a slower decay takes over (Fig. 1). The decay kinetics develops into a power-law decay $t^{-\alpha}$ at intermediate pressures (21 kbar, Fig. 4, curve *b*), with $\alpha \approx 1.1$; significantly larger than the $\alpha = \frac{1}{2}$ observed in many polymers.¹⁵ At higher pressures, the two samples (1 and 2) have similar overall decays. The exponent α decreases slightly in sample 1, whereas in the more ordered sample 2, the decay changes form (Fig. 4, curve *c*) into a stretched exponential $\exp[-(t/\tau)^\beta]$ with $\beta \sim 0.4$ and $\tau \approx 1.6$ ps; it changes very little between 40 and 80 kbar. The stretched-exponential decay can be readily explained by considering exciton diffusion along the chain towards recombination centers with density c per unit cell ($c \ll 1$). In this case, the exciton density $N(t)$ is given by

$$N(t) = N(0)(1 - c)^{n(t)} \approx N(0)e^{-cn(t)}, \quad (1)$$

where $N(0)$ is the initial exciton density and $n(t)$ is the number of sites visited by the exciton within the time t . For a simple 1D diffusion process¹⁶ $n(t) = (2.5\vartheta_0 t)^{1/2}$, where ϑ_0 is the attempt frequency for hopping. From Eq. (1) we obtain $N(t) = N(0)\exp[-(t/\tau)^\beta]$, where $\tau = (2.5\vartheta_0 c^2)^{-1}$ and $\beta = 0.5$, in good agreement with the experiment. We expect a ϑ_0 of about 10^{13} s⁻¹, which is of the order observed for the hopping frequency of soli-

ton defects¹⁷ and photoexcitations¹⁵ in polyacetylene. Then the measured $\tau = 1.6$ ps gives $c \approx 0.1$ per unit cell. Since this is greater than the concentration of chain ends ($c \approx 5 \times 10^{-4}$ from our molecular-weight measurements),¹⁴ other kinds of 3D defects must be also operative.

In summary, we have observed dramatic effects of pressure on singlet exciton recombination in polydiacetylene, but essentially no effect on the initial ultrafast relaxation. Our results strongly suggest that the initial ~ 100 -fs relaxation is a 1D process and the slower non-radiative recombination requires subsequent 3D distortions of the excited chain.

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