

**Femtosecond Dynamics of Photogenerated Solitons and Polarons in *trans*-Polyacetylene**

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Intrachain and interchain excitations are clearly identified by polarized time-resolved absorption studies of photoinduced midgap bands in well-aligned *trans*-polyacetylene. We report spectroscopic evidence of the lattice deformation during intrachain photogeneration of charged soliton pairs, and see these pairs recombine geminately in  $< 2$  ps. For incident polarization perpendicular to the chain direction, our data also show that interchain electron-hole pair excitation occurs with fairly high quantum yield and leads to polaron formation.

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The structural simplicity of *trans*-polyacetylene has made this material a model system for the study of electron-phonon coupling and carrier dynamics in quasi-one-dimensional semiconductors.<sup>1</sup> In addition, the broken-symmetry degenerate ground states in *trans*-polyacetylene lead to some novel predictions for both the nature of the charge carriers in this material, and their photoexcitation and transport mechanisms. For example, theoretical studies by Su and Schrieffer of the lattice dynamics after electron-hole (e-h) pair creation predict the formation of self-localized charge carriers, with energy levels deep in the semiconducting gap.<sup>2</sup> These were predicted to take the form of oppositely charged soliton pairs in the case of intrachain photoexcitation, where e-h formation occurs on a single chain, or conversely polarons in the case of interchain photoexcitation where the e-h pair is formed on neighboring chains.<sup>2-4</sup> More recently, however, theoretical work by Vogl and Campbell<sup>5</sup> and by Jacobs, Macready, Szeto, and Maki<sup>6</sup> has brought into question the stability of polarons in polyacetylene. In this Letter, we report subpicosecond time-resolved absorption experiments on well-aligned *trans*-polyacetylene which address the controversy surrounding interchain excitation directly.

Our previous picosecond time-resolved measurements of absorption due to photogenerated gap states in *trans*-polyacetylene verified the existence of directly photogenerated ("Su-Schrieffer") charged solitons.<sup>7</sup> As these measurements were performed on unoriented samples, the intrinsic anisotropies predicted for the photoexcitation process were not experimentally accessible. However, recent advances in the synthesis of polyacetylene have allowed the preparation of samples with well-oriented polymer chains,<sup>8,9</sup> and this allows for polarization-dependent studies of interchain and intrachain photoexcitation.<sup>10,11</sup> In this material, we observe equilibration of Su-Schrieffer charged soliton pairs on the femtosecond time scale and show that they recombine geminately in

about 1 ps. Saturation of the absorption is due to volume filling by these solitons and provides a quantitative understanding of the resonant third-order susceptibility  $\chi^{(3)}(\omega, \omega, -\omega, -\omega)$ .<sup>12</sup> We measure a large quantum yield for directly generated charged soliton pairs even when exciting with light polarized perpendicular to the chain direction. In this configuration, we also see photoinduced subgap absorption which persists for  $> 1$  ns and ascribe this signal to polaron absorption.

The experiments were performed on 5- $\mu\text{m}$ -thick films of stretch-oriented Durham-route polyacetylene.<sup>8</sup> The stretch ratio of these films is 12, and x-ray measurements on similar samples show that chain alignment is good to better than  $\pm 3$  FWHM.<sup>13</sup> Polarized Fourier-transform infrared measurements verify this to be the case over the entire sample and indicate that contributions from misaligned regions are negligible. The polyacetylene samples were sandwiched between thin  $\text{CaF}_2$  plates and mounted in a cryostat with  $\text{CaF}_2$  windows. As we have noted previously, pulsed laser heating can raise the sample temperature as much as 100 K.

The optical system<sup>14</sup> provides intense pump pulses at  $\sim 575$  nm and synchronized tunable midinfrared pulses (2.5–5.5  $\mu\text{m}$ ). The instrumental resolution (pump-probe cross correlation) is measured independently<sup>12</sup> to be  $\lesssim 0.5$  ps. The sample is sufficiently thick that, except for reflection, 575-nm light of either polarization is completely absorbed. Note, however, that about half of the incident light is reflected for parallel polarization.<sup>10</sup> The probe is always polarized parallel to the chain direction, and the pump and probe are overlapped on the sample with variable delay.

Figure 1 plots the photoinduced absorption at 0.43 eV versus pump-probe delay. The induced absorption in the parallel case is due to directly photogenerated (Su-Schrieffer) solitons as we have shown previously.<sup>7</sup> The charged soliton decay dynamics are essentially the same as in Shirakawa polyacetylene,<sup>15</sup> consisting of rapid

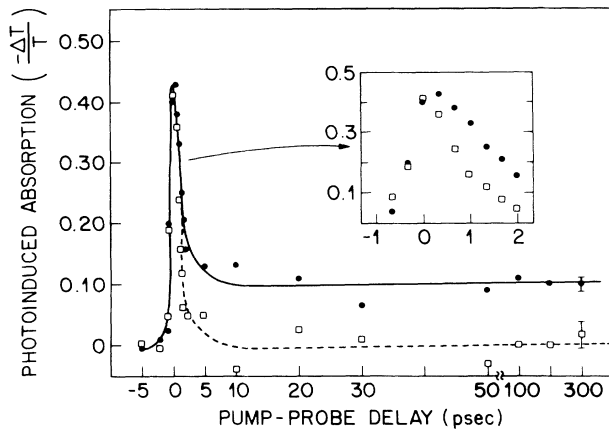


FIG. 1. Change in normalized transmission at 0.45 eV due to a 575-nm pump vs pump-probe delay. The open squares correspond to pump polarization parallel to chain direction and the solid circles are for pump perpendicular to the chains. Inset: An expanded view of the data at short delays. Zero delay is chosen arbitrarily as the signal maximum in parallel case.

1–2-ps decay. This is not surprising since these are intrachain excitations and the long-range morphology should not be very important for such a short-lived excitation. Note, however, that the dynamics are very different for perpendicular pump. There is a short-lived component which is very similar (see inset), but there is a sizable tail with at least a 300-ps lifetime.

We first consider the fast response and postpone discussion of the tail. Figure 2 illustrates the photoinduced absorption spectra at very short delays. In the parallel case, we note the dramatic evolution on a subpicosecond time scale. We choose zero delay arbitrarily to correspond to the time of maximum photoinduced absorption signal at 0.45 eV for parallel pumping. This time corresponds to the probe slightly following the pump pulse. At delays greater than this the spectrum remains fairly stable and is characteristic of charged solitons.<sup>15,16</sup> Figure 2 also shows that the spectra in the case of perpendicular excitation are strikingly similar. Because of this and the apparently identical decay dynamics of the fast components in each case, we associate the short-lived transient in the perpendicular case with Su-Schrieffer charged solitons as well. Thus, light polarized perpendicular to the chains also creates primarily intrachain excitations with substantial quantum yield, as predicted by Baeriswyl and Maki.<sup>17</sup>

We find the rapid evolution of the spectrum to be a very exciting result since it corresponds to observing the lattice dress the initially created electron and hole. The first spectra appear to be substantially redder and decrease toward the blue. Qualitatively, this is what one expects for free-carrier absorption evolving to that of a lattice stabilized quasiparticle. Bishop *et al.*<sup>3</sup> have calculated the dynamics of levels moving into the gap and predicted them to reach midgap in  $\sim 150$  fs. While the

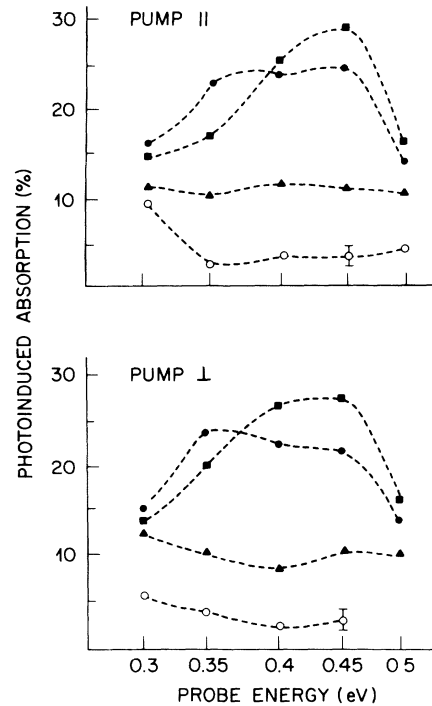


FIG. 2. Evolution of the photoinduced absorption spectra for perpendicular and parallel pump polarization. Time delays are as follows: open circles,  $-0.75$  ps; triangles,  $-0.5$  ps; solid circles,  $-0.25$  ps; squares, 0 ps.

results of Fig. 2 are complicated by our 0.5-ps instrumental resolution, they suggest that the equilibrium time for charged solitons is somewhat longer, perhaps as much as 0.5 ps. Since our pump energy of 2 eV leads to electron-hole pair creation about 0.6 eV above the band gap, carrier thermalization effects may also be responsible for some of the spectral evolution. A comparison of our spectra with appropriate theoretical work may put better constraints on the parameters typically used (e.g., electron-phonon coupling) in lattice-dynamics simulations and we hope that these data will stimulate such calculations.<sup>2,3</sup>

We now turn to an analysis of the long-lived photoinduced absorption following perpendicularly polarized photoexcitation. By comparison with the parallel case, we conclude that the long-lived component is associated with interchain electron-hole pair creation which presumably leads to polarons.<sup>2</sup> The solid circles in Fig. 3 show the spectrum in the tail absorption ( $+10$  ps) of the perpendicular pump case. The transient spectrum is nearly independent of delay from 5 to 100 ps. Provided for comparison in the figure is the rescaled spectrum for millisecond photoinduced absorption (solid line) of Durham polyacetylene.<sup>16</sup> In all of our experiments, we have found substantially more absorption in the red than in the millisecond case. To quantify this, we have measured ratios of photoinduced absorption (PA)  $PA(0.30 \text{ eV})/PA(0.45 \text{ eV})$  and  $PA(0.35 \text{ eV})/PA(0.45 \text{ eV})$  at

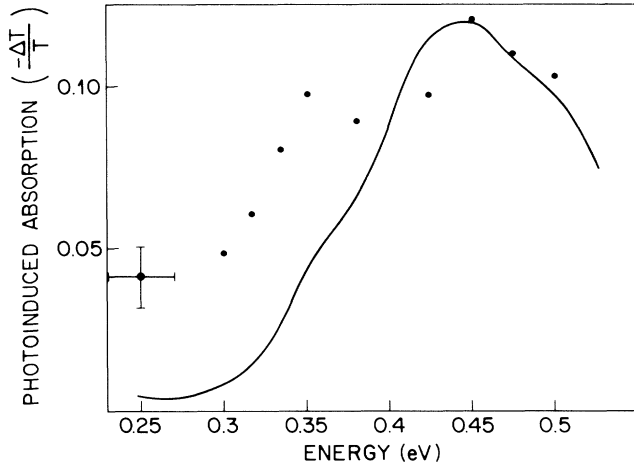


FIG. 3. Photoinduced absorption spectrum at 10-ps delay with perpendicular polarized pump (solid circles). For comparison, the millisecond spectrum from Ref. 16 is rescaled to the same value at 0.45 eV.

+1-ps delay carefully for both perpendicular and parallel pump. At 1-ps delay, 1.4 times more absorption is observed at 0.3 eV in the perpendicular case than for parallel excitation, and at 0.35 eV there is 2.0 times as much PA for perpendicular excitation. The assignment of the long-lived component to a distinct species is also consistent with the fact that the maximum absorption in the perpendicular case is observed at slightly longer delay (see the inset of Fig. 1). We can understand this if we decompose the perpendicular dynamics into the sum of the soliton dynamics and a long-lived polaron component which accumulates during the pump pulse and has the effect of delaying the maximum.

Consequently, we assign the long-lived absorption for perpendicular pumping to polarons, and we believe this to be the first unambiguous direct evidence for photogenerated polarons in *trans*-polyacetylene. A transition energy of about 0.35 eV is about 0.1 eV higher than predicted by theory,<sup>4</sup> but the theory does not include Coulomb correlation. Previous workers have also attributed a near band-edge absorption ( $\sim 1.4$  eV) to polarons<sup>18</sup> but this assignment is complicated by other phenomena including neutral soliton pair absorption,<sup>19</sup> breather absorption,<sup>20</sup> band-gap renormalization, and heating effects. Since the stretch ratio of the polyacetylene in those experiments was only 2.3:1, it was difficult to use polarization discrimination to isolate a possible polaron contribution.

One possibility that must be considered is that some solitons escape in the perpendicular case where the absorption depth is large because their density is lower. This is unlikely since we observe no intensity dependence to the soliton lifetime, a result consistent with the parallel and fast perpendicular components decays being the same (cf. Fig. 1) even though solitons are at least an or-

der of magnitude more dense with the parallel pump. Also, we have never observed induced absorption at  $\geq 5$ -ps delay in the parallel pump case. The residual absorption remaining at 5 ps compared to that at 0-ps delay puts a limit of  $< 0.05$  on the soliton escape probability. This small fraction could still be responsible for the nearly isotropic fast photoconductivity<sup>11</sup> while the inter-chain contribution dominates the slow anisotropic photoconductivity.<sup>10</sup>

Previous experiments in Shirakawa (unoriented) *trans*-(CH)<sub>x</sub> suggested that polarons trapped or annihilated on about a 50-ps time scale to form secondary charged solitons.<sup>12</sup> In the present paper, we have suggested that polarons persist for at least 300 ps. There are several reasons why this might be the case and we mention them below, although further work will be necessary to differentiate between them. The most obvious is again due to the much longer (25 $\times$ ) absorption depth in the oriented material. This leads to a lower volume density of polarons in the oriented Durham (CH)<sub>x</sub> and the annihilation reactions<sup>21</sup>  $2P^\pm \rightarrow 2S^\pm$  are much slower. Alternatively, the number and nature of neutral solitons in the Durham material is known to be different<sup>22</sup> and this could make polaron trapping processes  $P^\pm + S \rightarrow S^\pm$  unimportant. We also observe no temperature dependence to the size of the tail in Fig. 1 in marked contrast to the increase at low temperatures in secondary soliton yield on millisecond time scales.<sup>10,22</sup> This is consistent with the view that the temperature dependence reflects thermal effects on transport processes and not on the initial photogeneration of carriers. Indeed, the millisecond PA at various temperatures appear to extrapolate to a common value at short times.<sup>23</sup> Further work is in progress to fully characterize the differences in decay dynamics and temperature dependences for Durham and Shirakawa samples.

Figure 4 presents the intensity dependence at zero delay for parallel and perpendicular excitation. At low intensity, the quantum yield is near unity based on the slope and the measured doping soliton absorption cross section.<sup>12,24</sup> This slope corresponds to a resonant third-order susceptibility  $\chi^{(3)}(-\omega, \omega, \omega, -\omega)$  of about  $10^{-7}$  esu. The saturation in the parallel case is consistent with volume filling by charged soliton pairs and geminate recombination. Since the light continues to be absorbed by the sample even at intensities where saturation sets in, there must be creation of electrons and holes which cannot fully evolve into charged soliton pairs. Thus, at high intensities, the quantum yield for soliton pair formation falls dramatically.

The volume-filling picture is consistent with the diminished saturation for perpendicular pump where the absorption depth is 20 times greater. By comparing parallel and perpendicular soliton absorption at low intensity (see Fig. 4), we estimate the quantum yield for charged soliton pairs with perpendicular photoexcitation to be  $0.6 \pm 0.3$ , consistent with the calculated value of Baer-

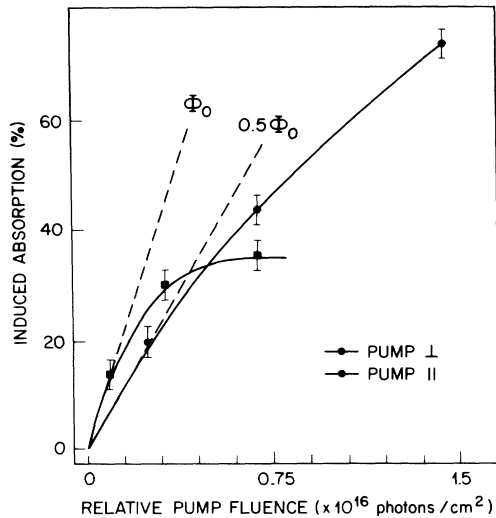


FIG. 4. The pump-intensity dependence of the photoinduced probe absorption at 0.45 eV. The solid lines are merely to guide the eye.

iswyl and Maki.<sup>17</sup> We presume that the yield for polarons, then, is about 0.4. The alignment of our samples is sufficiently high that the uncertainty quoted above resides entirely in our measurement of the slopes in Fig. 4 and has no contribution due to chain misalignment.

<sup>1</sup>A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W.-P. Su, *Rev. Mod. Phys.* **60**, 781 (1988).

<sup>2</sup>W. P. Su and J. R. Schrieffer, *Proc. Natl. Acad. Sci. U.S.A.* **77**, 5626 (1980).

<sup>3</sup>A. R. Bishop, D. K. Campbell, P. S. Lohmdahl, B. Horowitz, and S. R. Phillpot, *Phys. Rev. Lett.* **52**, 671 (1984).

<sup>4</sup>K. Fesser, A. R. Bishop, and D. K. Campbell, *Phys. Rev. B*

**27**, 4804 (1983).

<sup>5</sup>P. Vogl and D. K. Campbell, *Phys. Rev. Lett.* **62**, 2012 (1989).

<sup>6</sup>A. E. Jacobs, W. G. Macready, K. Y. Szeto, and K. Maki, *Phys. Rev. B* **41**, 3647 (1990).

<sup>7</sup>L. Rothberg, T. M. Jedju, S. Etemad, and G. L. Baker, *Phys. Rev. Lett.* **57**, 3229 (1986).

<sup>8</sup>P. D. Townsend, C. M. Pereira, D. D. C. Bradley, M. E. Horton, and R. H. Friend, *J. Phys. C* **18**, L283 (1985).

<sup>9</sup>D. White and D. C. Bott, *Polym. Commun.* **25**, 98 (1984).

<sup>10</sup>P. D. Townsend and R. H. Friend, *Synth. Met.* **17**, 361 (1987).

<sup>11</sup>H. Bleier, S. Roth, Y. Q. Shen, D. Shafer-Siebert, and G. Leising, *Phys. Rev. B* **38**, 6031 (1988).

<sup>12</sup>L. Rothberg, T. M. Jedju, S. Etemad, and G. L. Baker, *Phys. Rev. B* **36**, 7529 (1987).

<sup>13</sup>M. M. Sokolowski, E. A. Marseglia, and R. H. Friend, *Polymer* **27**, 1714 (1986).

<sup>14</sup>T. M. Jedju and L. Rothberg, *Appl. Opt.* **27**, 615 (1988).

<sup>15</sup>L. Rothberg, T. M. Jedju, S. Etemad, and G. L. Baker, *IEEE J. Quantum. Electron.* **24**, 311 (1988).

<sup>16</sup>R. H. Friend, H. E. Schaffer, A. J. Heeger, and D. C. Bott, *J. Phys. C* **20**, 6013 (1987).

<sup>17</sup>D. Baeriswyl and K. Maki, *Phys. Rev. B* **38**, 8135 (1988).

<sup>18</sup>M. Yoshizawa, T. Kobayashi, K. Akagi, and H. Shirakawa, *Phys. Rev. B* **37**, 10301 (1988).

<sup>19</sup>C. V. Shank, R. Yen, J. Orenstein, and G. L. Baker, *Phys. Rev. B* **28**, 6095 (1983).

<sup>20</sup>B. Horovitz, A. R. Bishop, and S. R. Phillpot, *Phys. Rev. Lett.* **60**, 2210 (1988).

<sup>21</sup>F. Moraes, Y. W. Park, and A. J. Heeger, *Synth. Met.* **13**, 113 (1986).

<sup>22</sup>P. D. Townsend and R. H. Friend, *Phys. Rev. B* **40**, 3112 (1989).

<sup>23</sup>Z. Vardeny and E. Ehrenfreund, in *Proceedings of the Conference on Transport and Relaxation Processes in Random Materials Gaithersburg, Maryland, 1986*, edited by J. Klafter, R. J. Rubin, and M. F. Shlesinger (World Scientific, Singapore, 1986), p. 21.

<sup>24</sup>A. Feldblum, J. H. Kaufman, S. Etemad, A. J. Heeger, T. C. Chung, and A. G. MacDiarmid, *Phys. Rev. B* **26**, 815 (1982).