Dephasing Dynamics of the Vibronic States of Epitaxial Polydiacetylene Films

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The dynamics of polydiacetylene (pDCH) vibronic states has been measured with photon echoes and pump probe techniques using femtosecond optical pulses. The excitonic dephasing (52 fs) is shown to be dominated by interactions between excitons and the vibration modes of the polymer chain. The importance of the C=C double bonds compared to the C≡C triple bonds shows up both in the dephasing and early population dynamics. These results suggest that just after excitation the polydiacetylene backbone undertakes a transient structural change with a butatrieniclike distribution of the electronic states.

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Polydiacetylenes (PDA) have interesting physicochemical properties due to their high degree of polymerization in the solid state [1]. In particular, the important delocalization of the π electronic orbitals along the PDA chains leads to high nonlinear optical susceptibilities with ultrafast response times in the visible spectrum [2]. Previous experiments [3–7], performed on the femtosecond time scale, have revealed many interesting aspects of the electronic states relaxation of different PDA systems. The exciton lifetime of polytoluene sulfonate (pTS) has been measured to be of the order of 2 ps [3,4], while its dephasing time was shorter than the 300 fs pulse duration [3]. A detailed dynamical study of the resonantly and virtually excited excitons has shown the importance of phonon-mediated exciton-exciton interactions in this system [5,6]. Yoshizawa *et al.* [7] made an extensive study of PDA-3BCMU and 4BCMU where an ultrafast excitonic decay of the order of 100 fs is attributed to the formation of self-trapped excitons. On these same systems, four-wave mixing measurements performed with an incoherent nanosecond laser have shown wavelength dependent dephasing times attributed to different chain length distribution [8]. Huxley *et al.* [9] also reported the existence of band gap states due to exciton-vibration coupling which are responsible for the 95 fs exciton decay time in pTS. These papers have stressed the importance of exciton-phonon interactions in the decay process of exciton population.

To our knowledge, no clear-cut experiment studying the influence of these interactions on the phase relaxation of the excitoniclike vibronic states has been done. Previous femtosecond photon echo measurements, performed with dye molecules in solution [10], have shown the important role played by the molecule system modes on the electronic dephasing. In conjugated polymers, one expects that it is the different backbone carbon-carbon bondings that dominate during the dephasing. It is the aim of the present Letter to study such effects in a highly oriented PDA system.

We report the first experimental investigation of the time evolution of the vibronic spectrum of epitaxial poly[1,6–di(n–carbazolyl)–2,4 hexadiyne] (pDCH) films excited with 10 fs optical pulses. A transverse excitonic relaxation time T_2 of 52 ± 5 fs as well as 23 fs period quantum beats associated with the C=C vibration mode have been determined by photon echo experiments. In addition, differential transmission measurements reveal a significant delay (>50 fs) between the double ($X_{C=C}$) and triple ($X_{C\equiv C}$) bond coupled excitons. These results clearly establish the predominant role of a double bonding character of the PDA backbone during the early dynamics. They are interpreted as a change from the initial acetylenic to a transient butatrieniclike configuration followed by a return to the stable acetylenic configuration in the excited state.

The highly oriented pDCH films are grown by epitaxy on a potassium acid phtalate crystalline substrate [11]. They are characterized by a large degree of polymerization (>98%) and present a uniaxial orientation of the polymer chains. Their low temperature (2 K) absorption and reflectance spectra are similar to the ones observed in single crystals [12,13]. This indicates high crystallographic quality films as characterized earlier [11]. Figure 1 shows the absorbance spectra at room temperature of a 120 nm thick film for light polarization parallel and perpendicular to the chain. The dichroic ratio is of the order of 20 at the excitonic resonance for photon energy $E_x = 1.919$ eV. The two sidebands at 2.08 and 2.15 eV are due to the optically coupled vibronic states corresponding to the C=C and C≡C bonds of the pDCH chain. The optical pulses are obtained from 60 fs CPM (colliding-pulse mode-locked laser) pulses at 620 nm which are amplified with a 5 kHz repetition rate copper vapor laser and compressed to 10 fs with the fiber-grating-prism compression technique [14]. Two types of

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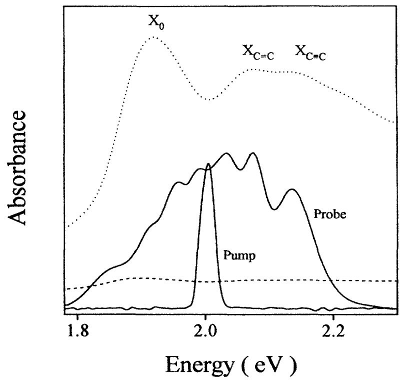

FIG. 1. Absorbance spectra of pDCH for light polarization parallel (dotted line) and perpendicular (dashed line) to the chain. Full lines: 60 fs pump and 10 fs probe pulse spectra.

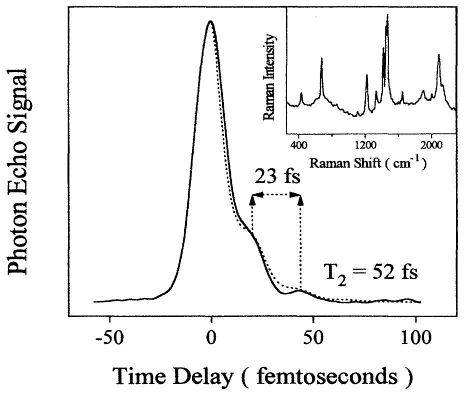

FIG. 2. Photon echo decay obtained with 10 fs pulses (full line) and corresponding fit (dotted line). The inset displays the Raman spectrum of pDCH.

measurements have been performed at room temperature. Self-diffracted photon echoes generated by the sample excited by two 10 fs pulses with wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ are measured in the direction $2\mathbf{k}_1 - \mathbf{k}_2$ as a function of delay τ between the two pulses. This type of measurement allows one to probe the dephasing dynamics of the vibronic states. The second type of experiment consisted of differential transmission measurements made with 60 fs pump and 10 fs probe pulses. In this case, the transmission changes induced by the pump pulse are recorded as a function of delay τ for different spectral regions of the probe pulse selected with a monochromator after the sample. The temporal detection is performed by using stepper motors and a standard lock-in technique. A careful spectrotemporal characterization of the pulses was made in order to eliminate any spurious effect due to the pulse itself. The solid curves in Fig. 1 represent the probe and pump pulse spectra. The chirp characterization was made by cross correlation in a potassium dihydrogen phosphate (KDP) crystal of the amplified uncompressed pulse with different spectral portions of the 10 fs pulse. The temporal position of the signal maxima coincide within ±5 fs over the entire pulse spectrum indicating chirp-free pulses.

We first studied the dephasing dynamics of the excitonic resonance. In Fig. 2, we have plotted the amplitude of a typical photon echo signal $S_{2\mathbf{k}_1-\mathbf{k}_2}(\tau)$, obtained with an energy of 400 pJ/pulse (approximate power density: 5 GW cm^{-2}). In addition to an overall asymmetric decay, oscillations with a period $T = 23$ fs are observed. These oscillations correspond to quantum beats between the excitonic state and a vibronic state with excess energy $E_{\mathrm{C=C}} = h/T$ of 180 meV relative to the excitonic resonance. This type of behavior is well established in time-resolved quantum beat spectroscopy and was observed in molecular or semiconductor systems [10,15]. The value 180 meV obtained here corresponds to the energy of the C=C double bond mode of the pDCH chain. This was confirmed by measuring the Raman spectrum of the sample under cw excitation with a helium-neon laser at 632.8 nm. The inset in Fig. 2 displays this spectrum with the group of phonon modes near 1450 cm^{-1}. The quantum beats of Fig. 2 suggest that most of the dephasing is related to the double bonding character of the pDCH backbone via $X \rightleftarrows \mathrm{C{=}C}$ phonon interactions. No efficient coupling between the exciton and the triple bond mode shows up in the first tens of femtoseconds during which the dephasing process takes place. The corresponding 16 fs beat period, associated with the 2090 cm^{-1} C≡C stretching mode in the Raman spectrum, should be observed with our 10 fs pulse.

To investigate further the mechanism related to the preceding observations, we studied its effect on the vibronic populations with pump-probe measurements. Figure 3(a) shows a three-dimensional plot of differential transmission spectra $\Delta T/T$ for different delays between the probe and pump pulses. These spectra reveal many details of the energy relaxation in pDCH, including hole burning at the pump wavelength, exciton bleaching, and excited state formation which we shall not discuss here. The most important feature is the observation of a delay between the induced transmission at energies $E_x + E_{\mathrm{C=C}}$ and $E_x + E_{\mathrm{C\equiv C}}$. In order to better show this delay, we have resolved temporally three spectral regions (2 nm wide) of the probe pulse with a 4 fs step. The three temporal variations, corresponding to energies E_x (exciton), $E_x + E_{\mathrm{C=C}}$ (double bond replica), and $E_x + E_{\mathrm{C\equiv C}}$ (triple bond replica), are displayed in Fig. 3(b). The interesting point for our purpose is the 50 fs delay which is observed between the two phonon sidebands. This again indicates that the C=C mode couples more efficiently to the exciton during the first 50 fs. The population saturation for $\hbar\omega \geq E_x E_{\mathrm{C\equiv C}}$ occurs later. In Fig. 3(c) the up-converted signal from the cross correlation between the probe and pump pulses is plotted for the same three spectral regions as in Fig. 3(b). The absence of delay in Fig. 3(c) rules out any experimental artifact in Fig. 3(b)

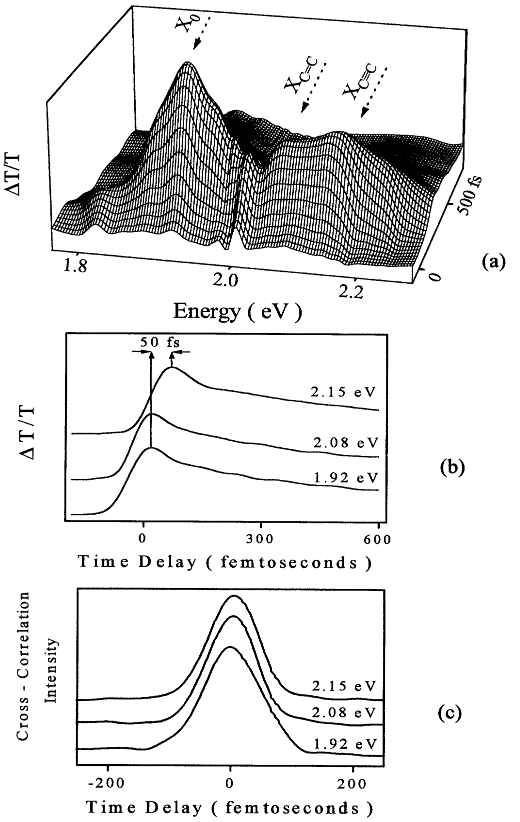

FIG. 3. Population dynamics obtained with 60 and 10 fs probe pulses. (a) Differential transmission spectra for delays between -100 and $+800$ fs. (b) Detailed dynamics for photon energies 1.92, 2.08, and 2.15 eV corresponding to X_0, $X_{C=C}$, and $X_{C\equiv C}$ bonds. (c) Up-converted signals from the cross correlation between the pump pulse and different spectral slices of the probe pulse.

due to pulse chirping effects. We now discuss the different mechanisms involved in the results of Figs. 2 and 3.

The dephasing dynamics observed in Fig. 2 can be modeled using the optical Bloch equations (OBE) of a three-level system (ground state and two excited vibronic states) interacting with an ultrashort pulse. Assuming that the two excited states, corresponding to the free and C=C coupled excitons, have the same dephasing time T_2, we obtain the following photon echo decay behavior:

$$S_{2\mathbf{k}_1-\mathbf{k}_2}(\tau) \sim [1 + \alpha \cos(\tau E_{C=C}/\hbar)]^2 \exp(-4\tau/T_2)\,, \quad (1)$$

where α corresponds to the ratio of the dipole moments for the transitions from the ground state to the two excited states. Equation (1) is derived by solving the OBE to third order in time ($\chi^{(3)}$ nonlinear process) and assuming δ-function pulses as well as infinite inhomogeneous broadening of the electronic states. Similar models [16] used with different degrees of sophistication allowed us to explain successfully the dynamics of systems like molecules in solution or exciton-photon interactions in semiconductors. As can be seen in Fig. 2 (dotted curve) the main features of the photon echo decay are reproduced with this simple model, using the parameters $T_2 = 52$ fs, $E_{C=C}/\hbar = 0.273$ rad fs^{-1}, and $\alpha = 0.11$. In the model, we assume that no triple bonding is necessary during the first 50 fs. This is consistent with the pump probe measurements which show a delayed bleaching at energies $\hbar\omega \geq E_x + E_{C\equiv C}$.

To account for the observed dephasing and population dynamics, we propose a mechanism which involves a transient transformation of the pDCH backbone (Fig. 4). Initially, the pDCH chain conformation corresponds to its well established acetylenic configuration with alternative single, double, and triple bonds both in the ground and excited states [12]. Under excitation with the ultrashort pulse, the electronic density is redistributed along the chain, leading to a butatrieniclike structure where double bonds are predominant. Intuitively, this corresponds to the most equiprobable electronic distribution along the backbone in a time scale where nuclei movement has not yet taken place. In the next step, during which the dephasing process takes place, an energy transfer occurs along the chain via the system mode. During this process of coherence loss, which lasts ~50 fs, quantum beats associated with the C=C modes are observed. Later on, a return to the acetylenic configuration may occur with the creation of self-trapped excitons (STE) along the chain (symbolized by the star in Fig. 4) within 120 fs. This thermalization process of STE is followed by tunneling to the fundamental state and triplet creation which occur

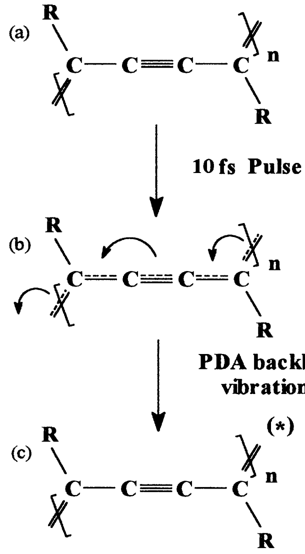

FIG. 4. Proposed mechanism for the electronic delocalization and backbone vibrations leading to the loss of phase memory in pDCH. (a) Acytelenic, (b) butatrienic, and (c) self-trapped electronic configurations.

within, respectively, ~600 fs and >5 ps, in agreement with previous observations [7,9].

It is important to insist on the transient character of the mechanism proposed in Fig. 4. It is well admitted that, for pDCH, the stable static configuration is the acetylenic one [12]. Our dynamical results do not contradict this fact since the C≡C triple bond is shown to play an important role in the dynamics for time delays larger than ~50 fs. It is only during the very first relaxation step, which is crucial for polarization dephasing, that the butatrieniclike structure is believed to dominate. We would like to point out that the mechanism of Fig. 4 does not necessarily occur on the entire PDA chain since PDA excitons have a charge transfer character [17] with a spatial extent of a few repetitive units of the polymer. Let us notice that the above results do not offer unique information on the exciton-phonon interaction. Valuable information can also be obtained with time-resolved Raman scattering which allows spectral selection of the exciton dynamics as reported for instance by Bosma *et al.* [18]. The full advantage of these experiments, however, lies in the frequency tuning of the pump which may be achieved at the expense of a lower temporal resolution.

In conclusion, we have reported dephasing and energy relaxation measurements of the excitonic vibronic states in epitaxial pDCH films using ultrashort optical pulses. The observed dynamics shows that, during the first 50 fs, during which the electronic dephasing occurs, the exciton strongly couples to the C=C double bond vibration mode of the PDA chain. These results are interpreted as the first observation of a transient butatrieniclike electronic distribution along the PDA backbone [19]. These experiments, as well as further studies of this type in different conjugated systems, should lead to a better understanding and modeling of the electronic delocalization dynamics in polymers.

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[19] During the publication process, new experimental results, obtained by time-resolved Raman scattering with 300 fs resolution, have been reported by M. Yoshizawa, Y. Hattori, and T. Kobayashi [Phys. Rev. B **49**, 13 259 (1994)]. To interpret these results, the authors suggest a geometrical relaxation of the chain from an acetylenic to a butatrienic structure due to the formation of self-trapped excitons. In contrast, our results, which also show a transient butatrienic configuration, clearly establish a further return to an acetylenic configuration in the excited state which we attribute to the STE creation process.