Excitation of a Breather Mode of Bound Soliton Pairs in *Trans*-Polyacetylene by Sub-Five-Femtosecond Optical Pulses

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(Received 23 January 2002; published 19 June 2002)

Trans-polyacetylene with a degenerate ground state has a nonlinear excitation of soliton after photoexcitation, due to the electron-phonon coupling. The excess energy of an excited electron-hole pair over a soliton pair creation induces a *breather* oscillation characterized by collective stretching vibration of the carbon-carbon bonds. A time-frequency analysis of pump probe signal shows that instantaneous frequencies of stretching modes are modulated for ~50 fs after excitation and the modulation period is 44 ± 3 fs consistent with the theoretical expectation, clearly verifying the breather.

DOI: 10.1103/PhysRevLett.89.027401 PACS numbers: 78.47.+p, 78.66.Qn, 82.35.Ej

Polyacetylene (PA) is the simplest π-conjugate polymer that consists of a CH chain and is a prototype of quasi-one-dimensional electronic system. *Trans*-polyacetylene (t-PA) has especially attracted a lot of interest because of soliton formation, which originates from its twofold degeneracy of ground states [1]. The soliton is related to anomalous (10^{13}-fold) increase in conductivity by chemical doping [2], but the primary dynamics of the soliton has not yet been experimentally observed. According to the simulation performed using the SSH (Su-Schrieffer-Heeger) Hamiltonian [3], a photogenerated electron-hole (e-h) pair evolves into a soliton-antisoliton ($S\overline{S}$) pair within 100 fs following photoexcitation because of the barrier-free relaxation in the one-dimensional system. It has been also theoretically predicted [4–10] that within this initial time the soliton pair is spatially localized to form a dynamic bound state called a breather. The excess energy of a photogenerated e-h pair over a soliton pair induces the collective carbon-carbon oscillation, namely the breather mode, due to electron-phonon coupling.

In spite of many theoretical predictions, no clear experimental observation of the dynamics of a soliton pair and the creation of the breather has emerged so far. Shank *et al.* determined the formation time of a soliton pair in t-PA to be shorter than 150 fs from the time-resolved photoinduced absorption measurement [11]. Previously we determined the formation time of solitons in several substituted polyacetylenes is about 90 fs [12]. Infrared pump-probe experiment was also performed to study the charged soliton pair in the spectral range of 2.5–5.5 μm [13]. However, these papers [11–13] referred only to the formation time and decay dynamics of solitons with no description of the breather state in t-PA partly because of the insufficient time resolutions of the experiments. Very recently, the breather excitons are suggested to be the primary photoexcitations in conjugated polymer from the similarity of the decay dynamics between cis-polyacetylene and a polydiacetylene with nondegenerate ground states [14]. However, no direct evidence was presented in the paper either due to the limited time resolution. In this Letter, we could for the first time time-resolve the primary dynamics of solitons, that is, conversion process from the breather to separated solitons in *trans*-polyacetylene.

In our pump-probe experiment both the pump and probe pulses are derived from a noncolinear optical parametric amplifier (NOPA) system [15,16] developed previously in our group. The visible pulse at the repetition rate of 1 kHz is shorter than 5 fs in duration and covers the spectral range of 520–760 nm, within which it carries a constant spectral phase. Samples of polyacetylene were fabricated by polymerizing acetylene on a new renium catalyst in a highly viscous solution of polyvinyl butyral (PVB) [17]. This method allows preparing soluble compositions containing nanoparticles of polyacetylene in PVB solution. in contrast with the conventional method of polyacetylene synthesis [18], these nanoparticles (15–30 nm in diam) have only a negligibly low concentration of conformational and chemical defects [17]. They are extremely stable and exhibit a number of unique optical properties such as large Raman cross section, thermochromism, and a transparent band in the optical spectrum in the near-infrared field [17]. The resistance of these films to the aerobic atmosphere and their small thickness make them ideal samples for sub-5 fs spectroscopy. First of all, they avoid the necessity to precompensate the dispersive pulse broadening in the wall of a glass cell, which is a very difficult task for the experiments using the ultrashort pulses with such a large bandwidth. Second, the change of the pulse duration inside a 2 μm film is negligible even for sub-5 fs pulses.

Figure 1(a) depicts the normalized transmittance change ($-\Delta T/T$) of a *trans*-isomer sample plotted as a function of the delay time between the pump (pulse energy ~20 nJ, beam spot size ~0.1 mm) and probe (~2 nJ, ~0.1 mm) pulses at several probe wavelengths, selected by a monochromator behind the sample. The pump-probe signals probed at 740 and 750 nm are negative while those probed at wavelengths shorter than 720 nm are positive. The positive signals in this spectral range can be explained

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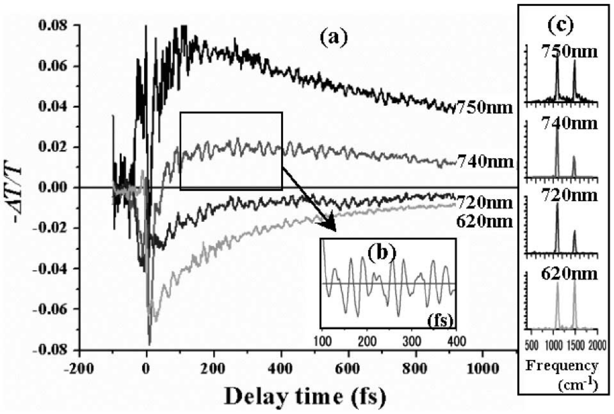

FIG. 1. (a) Time dependence of pump-probe signals probed at several wavelengths. (b) Periodically oscillating components of the pump-probe signals probed at 740 nm extracted by applying a bandpass filter. (c) Power spectra of Fourier transform of the oscillating components of pump-probe signals integrated over the whole range of pump-probe measured delays. Two peaks at 1080 ± 7 and 1470 ± 7 cm^{-1} are identified as the stretching modes of single and double bonds of carbon atoms, respectively, from the results of the stationary resonant Raman scattering [16].

by photoinduced absorption [11] and the negative $-\Delta T/T$ are attributed to the ground-state depletion and gain induced by stimulated emission. Photoinduced absorption signals have finite rise time and peaks at about 100 fs after excitation while the negative signals damp exponentially. In addition, all the signals exhibit periodically oscillating features as shown in Fig. 1(b), which is due to molecular vibrations. The oscillating components are extracted from the pump-probe kinetics by removing slowly varying components using a high-pass filter with a cutoff frequency of 280 cm^{-1}. Fourier power spectra that were obtained over the whole pump-probe positive delay range are shown in Fig. 1(c). They are composed of two peaks located at t_1:1080 ± 7 and t_2:1470 ± 7 cm^{-1}. These are close to the observed frequencies by stationary resonance Raman scattering, which are attributed to the stretching modes of single and double carbon-carbon bonds, respectively, of carbon atoms [19]. All of the Fourier components found in the kinetics at 10 probe wavelengths are the same within the experimental error.

Because the breather can exist only in a photogenerated state that is adiabatically connected to an electronic excited state, analysis to the data pump-probe kinetics at 740 and 750 nm, i.e., the data taken in the region of induced absorption are to be made. The oscillations in these traces clearly reflect the wave-packet motion in the excited state, because the overall positive sign of the corresponding kinetics suggests a negligible contribution of the ground state. This wavelength region is located at the edge of the stationary absorption spectrum and is far from resonance. Additionally, frequency spectra of the oscillations, obtained from the traces at 740 and 750 nm, exhibit several features that are not present at shorter wavelengths (*vide infra*).

The time evolution of the amplitude of each vibrational mode was studied by a spectrogram analysis [20,21]. We processed the pump-probe traces by applying the following Gaussian window function with a HWHM $\Delta t = 96$ fs: $W(t - t_d) = \exp[-(\ln 2)(t - t_d)^2/(2\Delta t)^2]$. A time-frequency contour map (Fig. 2) is produced by sweeping the delay time t_d of the peak of the Gaussian window function and by performing a Fourier transformation. This two-dimensional plot shows the time evolution of the frequency distribution of molecular vibrational modes. In Fig. 2(a), t_1 and t_2 correspond to the stretching modes of the single and double bonds, respectively, appearing as the two distinct peaks in Fig. 1(c). In addition to these two modes, several broader bond features (t_1', t_1'', t_2', and t_2'') appear in the spectrogram. These vibrational modes cannot be found in Fig. 1(c) or in the stationary resonant Raman scattering spectrum [19] because of their short lifetimes [notice that short-time Fourier transform is performed with a gate-peak t_d being swept in Fig. 2, while in Fig. 1(c) it is performed over the whole time range of probe delay]. Moreover, the spectrogram shows an initial increase in the amplitudes of the t_1 and t_2 modes, which peak at 120 and 180 fs, respectively. These values are close to the relaxation time of short-life components (t_1', t_1'', t_2', and t_2''). We will discuss how these features are related to the formation of breather in the next paragraph. It should be pointed out that in the spectrograms obtained from the traces probed at the wavelengths below 720 nm, the short-lived modes could not be clearly observed as a result of superposition with the signal contributed from the ground-state vibrations. The pump pulses can excite not only the wave packet of the excited-state vibrations but the ground-state wave packet by the impulsive Raman mechanism, and the latter vibrations definitely do not contribute to the breather mode. If the ground-state vibrations are probed with a shorter-wavelength probe pulse, it is superimposed on the signal due to the wave-packet motion in the excited state. It is very interesting to distinguish these vibrations by exciting only the ground-state or the excited-state vibrations selectively using chirped pulse [22], but in this Letter this ambiguity can be avoided by analyzing only the induced absorption signals.

As pointed out above, a soliton pair forms a dynamic bound state that is immediately generated upon photoexcitation of t-PA and this state can be regarded as a breather that exists only during the initial periods of relaxation. The formation of the breather is accompanied by the oscillatory change in the bond length and can be detected in the pump-probe experiment as modulation of the instantaneous vibrational frequencies as a result of the mode coupling between the carbon-carbon stretching modes and the breather mode. The modulation periods were predicted to be 40–50 fs by Heeger *et al.* [3], 38 fs by Bishop *et al.* [4,5], and 33 fs by Sasai *et al.* [6]. These figures are somewhat longer than that of the optical phonon, i.e., the vibrational period of the two stretching modes

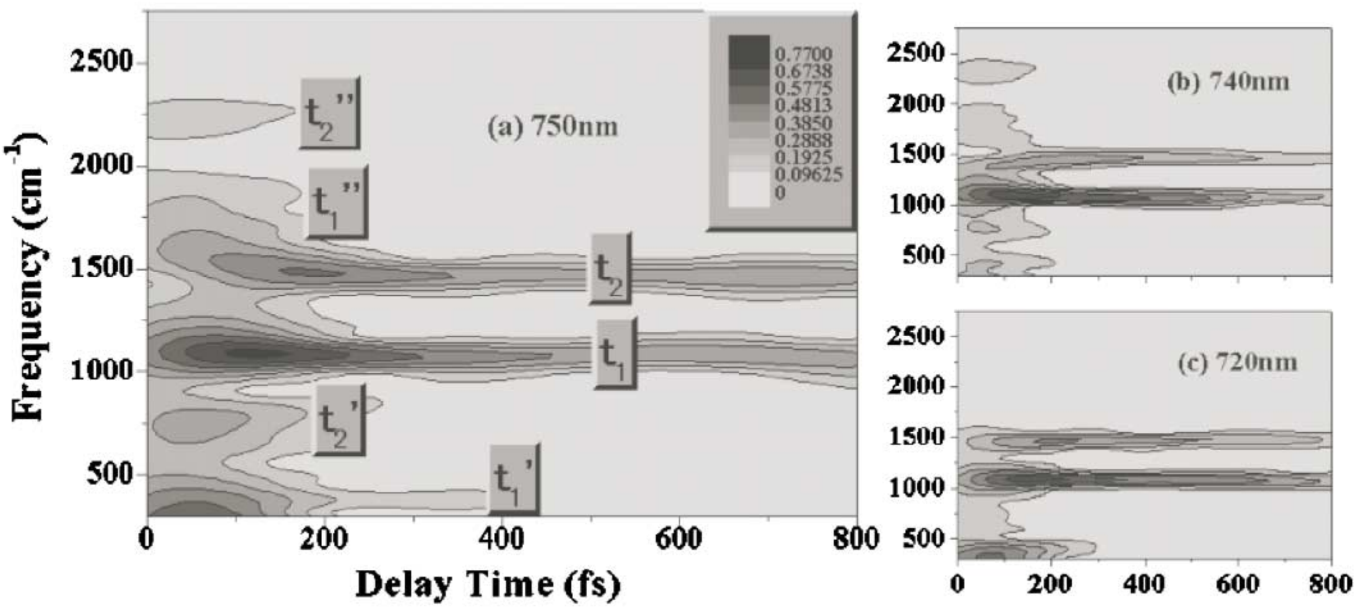

FIG. 2. Spectrogram of periodically oscillating components of pump-probe signals probed at (a) 750 nm, (b) 740 nm, and (c) 720 nm, which are calculated using a Gaussian window function with a HWHM $\Delta t = 96$ fs. t_1, and t_2 denote the stretching modes of single and double bonds that appear in Fig. 1(c), respectively. Short-lived satellite bands (t_1', t_1'', t_2', and t_2'' associated with t_1 and t_2 modes, respectively) indicate the modulation induced by the breather state.

(1080 and 1470 cm^{-1}, corresponding to oscillation periods of ~31 and ~23 fs, respectively). In addition, it was shown that the lifetime of the breather is very short and it decays into two single solitons in less than 100 fs. Based on these theoretical predictions, listed above, the time trace [Fig. 3(a)] and the frequency distribution of the vibrational frequencies [Fig. 3(b)] of the simulation signal with a modulation period of 44 fs and a modulation duration time of 50 fs are shown. Fourier power spectrum [Fig. 3(c)] and the spectrogram [Fig. 3(d) calculated using the simulation signal reproduce all the characteristic features of the Fourier power spectra and the spectrogram computed from the experimental pump-probe traces. In the Fourier power spectra, modulation cannot be detected because of its short duration time. In the analysis of the spectrogram, any modulation with the characteristic period shorter than the time width of the window function (HWHM of 96 fs) does not appear clearly, which results in the absence of fast modulation in Fig. 3(b). The evidence of the modulation appears in the spectrogram indirectly in the shape of satellite bands t_1', t_1'', t_2', and t_2'' on both sides of the main vibrational modes t_1 and t_2, respectively. This result suggests that the unidentified short-lifetime modes visible in Fig. 2(a) can be explained by the modulation of the vibration modes caused by the mode coupling. The period of the modulation is determined to be 44 ± 3 fs from the frequency separation between the main mode and the satellite bands, which on the average is 760 cm^{-1}. This estimate agrees with the theoretical prediction of 33–50 fs [3–6]. Moreover, this simulation readily explains the growth of the amplitude of the main modes t_1 and t_2 (Fig. 2) during the initial time following the photoexcitation. Finite rise time of photoinduced absorption signals shown in Fig. 1(a) can also be explained by the duration time of breather mode. After photoexcitation to the conduction band (CB), gap states from the bottom of the CB and the top of the valence band are split off. It takes finite time for the elevation of the hole gap state and the lowering of the electron gap state. The induced absorption signals reflect a broad transition from the midgap soliton breather state to the conduction band state. The rise-time constant of the induced absorption signal is estimated to be 41 ± 2 fs after the removal of the exponentially decaying component. This result is consistent with the modulation lifetime of 50 ± 10 fs. Therefore it could be confirmed the formation of the breather by the agreement of the rise time of the corresponding absorption and the decay time of the frequency modulation due to the breather mode.

In conclusion, this work demonstrates the first experimental evidence of the formation and the decay of a dynamical bound state formed by a soliton pair, also known as the breather state, which is created in t-PA after photoexcitation. Thus, the real-time dynamics of this state is for the first time clarified with a sub-5 fs pulse laser developed in our group. It is well known that the oscillation period depends on the relative importance of the underlying electron-phonon coupling on the one side and electron-electron correlation on the other. The competing views, on which of the two coupling mechanisms is dominant, is a long-standing issue dating back to the argument of Peierls vs Hubbard models [23,24]. The obtained parameters of the oscillation period and damping rate of the breather are expected to encourage theorists to

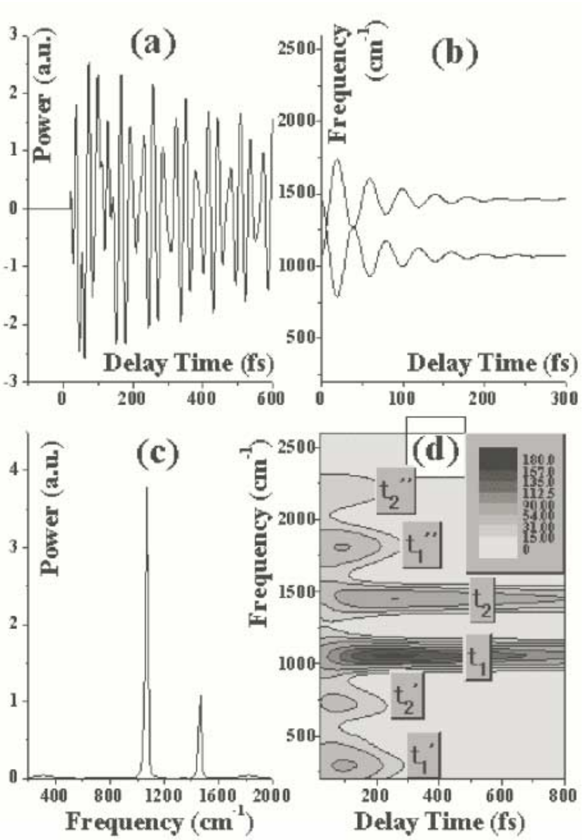

FIG. 3. Simulation based on the theoretical predictions [3–6]. (a) Time trace. (b) Frequency distribution. Instantaneous frequencies corresponding to the vibrational modes t_1 and t_2 are modulated with the modulation period of 44 fs and the modulation duration time of 50 fs. (c) Fourier power spectrum and (d) Spectrogram are calculated using the simulation signal. Short-lifetime modes (t_1', t_1'', t_2', and t_2'') are the result of modulation of the instantaneous frequencies. These figures reproduce typical features of the spectrogram in Figs. 1(c) and 2(a) which are obtained from the experimental result.

determine the relative contribution of the electron correlation and electron-phonon coupling.

The authors would like to thank Mr. T. Saito for his help in experiments and Dr. A. Baltuska, Dr. T. Fuji, and Dr. E. Tokunaga for careful reading. The work is partially supported by Research for the Future Program run by the Japan Society for Promotion of Science.

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