PHYSICAL REVIEW B **72**, 134302 (2005)

Vibrational chirp in the dynamic Stokes-shift process due to ultrafast geometrical relaxation in a polydiacetylene

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(Received 2 October 2004; revised manuscript received 8 July 2005; published 10 October 2005)

Relaxation kinetics of photoexcitation in a blue-phase polydiacetylene has been investigated by difference absorption spectroscopy with extremely high time- and energy-resolution using broadband sub-5-fs optical pulses. One-fs-step tracking of an induced emission peak has enabled us to separate the vibrational dynamics during geometrical relaxation and internal conversion into modulations of transition-peak energy and transition probability. The peak energy shows redshift of about 60 meV and the instantaneous frequency of the "C≡C" stretching mode is positively "chirped" starting from $1600\pm100\ \mathrm{cm}^{-1}$ (21 ± 2 fs) and ending in $2100\pm100\ \mathrm{cm}^{-1}$ (16 ± 1 fs). This positive chirp indicates a huge dynamic structural change from $(\text{—C}R\text{=}C\text{=}C\text{=C}R'\text{—})_n$–like to $(\text{=C}R\text{—C}\equiv\text{C—C}R'\text{=})_n$–like structured bonds in the polymer backbone during the internal conversion process within 100 fs. This corresponds to the reduction of the bond length from 1.32 ± 0.04 Å to 1.19 ± 0.04 Å by about 0.13 Å, which was estimated from the bond lengths in literatures determined by the x-ray analysis for several polydiacetylenes.

DOI: 10.1103/PhysRevB.72.134302 PACS number(s): 78.66.Qn, 78.47.+p, 82.35.Ej

I. INTRODUCTION

Various optical spectroscopic properties of conjugated polymers have been studied extensively because of their unique properties as a model compound system of one-dimensionality. However, the primary photophysical phenomena in the relaxation kinetics of π-conjugated polymers have not yet been fully understood in spite of their growing technological impact and important optoelectronic applications such as electroluminescence devices.[1] Elucidating the early electron-lattice dynamics in the vibrational nonequilibrium after photoexcitation in these systems encourages engineering appropriate materials for the applications,[2] which require the reduction of the nonradiative rate to enhance the luminescence efficiency.

Among many conjugated polymers, polydiacetylenes (PDAs) have especially attracted much attention of many scientists,[3] because they have many interesting features from various viewpoints. They have several phases named according to their colors, i.e., blue, yellow, and red phases. They can also have various morphologies, i.e., single crystals, cast and spin coated films, Langmuir films, and solutions.[4–8] The ultrafast optical responses in PDAs have been intensively investigated using femtosecond absorption and fluorescence spectroscopies, and time-resolved Raman spectroscopy.[9–20] They exhibit characteristic features due to their low dimensionality. It includes ultrafast relaxation resulting in the ultrafast large optical nonlinearity assisted by the excitonic nature.[9–11,13,16–29] They exhibit several nonlinear optical effects such as phonon-mediated optical Stark effect,[26] phonon-mediated hole burning,[27] inverse Raman scattering,[9] optical Stark effect,[30–32] and Raman gain processes.[11,16] These features are deeply related to the formation of localized nonlinear excitations such as polarons and a self-trapped exciton (STE) formed via a strong coupling between electronic excitations and lattice vibrations.[10,11,33–35] This STE is sometimes called an exciton polaron or a neutral bipolaron.[10]

Electronic states in PDAs are well characterized theoretically by the Pariser-Parr-Pople-Peierls model,[36] which includes both the electron correlation (Pariser-Parr-Pople) and the electron-lattice (Peierls) coupling. One important consequence of the electronic correlation is the reversal of the energy-level positions of the photoexcited $1\,^1B_u$ and the $2\,^1A_g$ states.[37] Recent experimental and theoretical studies have revealed that the lowest excited singlet state in a blue-phase PDA to be an optically forbidden $2\,^1A_g$ state lying about 0.1 eV below a $1\,^1B_u$-free-exciton (FE) state.[17,38] It is because the blue-phase PDAs have long enough conjugation lengths for the $2\,^1A_g$ state to be substantially stabilized. The $2\,^1A_g$ state possesses a two-triplet character that induces large repulsive interaction between the two triplet "components" due to the Pauli exclusion principle. The repulsive interaction relaxes in a long chain and as in ordinary organic molecules, "two-triplet state" ($2\,^1A_g$) is more stabilized than a corresponding singlet state ($1\,^1B_u$-FE) in such a long chain systems. Blue-phase PDAs (Refs. 10 and 28) have a smaller fluorescence yield than 10^{-5} due to their efficient internal conversion (IC) ($1\,^1B_u \rightarrow 2\,^1A_g$) faster than 170 fs along with fast geometrical relaxation (GR).[16–18] The GR has been explained in terms of STE.[39] However, since the fluorescence from the strongly allowed $1\,^1B_u$-STE state has not been observed in isolated blue-phase chains,[40] it is, if present, considered to experience very fast relaxation to the nonfluorescent $2\,^1A_g$ state.[18]

Recent progress in femtosecond pulsed lasers has enabled us to study molecular dynamics on a 10-fs timescale.[12,13,17,20,41–45] In previous works by Bigot and others, a wave packet motion of C=C stretching mode with a period of 23 fs was found in the photon-echo and transient bleaching signals from PDA-pDCH (poly[1,6-di(*N*-carbazolyl)-2,4 hexadiyne]) films by using 9–10 fs pulses.[12,13]

During the initial GR in the blue-phase PDAs, the polymer chains are expected to undertake a configuration change by decreasing contribution of butatriene-like configuration $(-\mathrm{C}R{=}\mathrm{C}{=}\mathrm{C}{=}\mathrm{C}R'-)_n$[13,16] to an acetylenelike structure $(=\mathrm{C}R-\mathrm{C}\equiv\mathrm{C}-\mathrm{C}R'=)_n$, the latter being a more stable conformation.[46] Here, R and R' represent substituted side groups attached to the main chain. However, it had been difficult to observe modulated spectra by molecular vibrations during the initial relaxation ($1\,{}^1B_u \rightarrow 2\,{}^1A_g$). In this paper, we, for the first time, could real-time observe the primary dynamics associated with frequency-varying molecular vibrations from the optically allowed $1\,{}^1B_u$-FE state to the forbidden geometrically relaxed $2\,{}^1A_g$ state by a peak-tracking method. Thus, the primary dynamics provides the first real-time clarification of the Stokes shift due to the geometrical configuration change associated with chirped molecular vibration.

II. EXPERIMENT

Sub-5-fs pump-probe spectroscopy was applied to a cast film of blue-phase PDA-3BCMU (poly[4,6-decadiyn-1,10-diol (*N*-butoxycarbonylmethylurethane)]) on a glass substrate. PDA-3BCMU has side groups of

$$R = R' = -(\mathrm{CH_2})_3\mathrm{OCONHCH_2COO}(\mathrm{CH_2})_3\mathrm{CH_3},$$

attached to the backbone chain of

$$(=R\mathrm{C}-\mathrm{C}\equiv\mathrm{C}-\mathrm{C}R'=)_n.$$

PDA-3BCMU is one of the well-known soluble PDAs. The samples were prepared by the following way. Oxidative coupling of 4-pentyn-1-ol (Tokyo Kasei) by a Hay's method[47] was used to obtain 4,6-decadiyn-1, 10-diol with the yield of 79%. The diol compound reacted with butyl isocyanatoacetate at 296 K using triethylamine in tetrahydrofuran (THF) solution resulting in the production of 3BCMU (monomers) with the yield better than 98%. The purity of the obtained monomers after the refinement in the synthesis process was evaluated to be better than 99% from the data of nuclear magnetic resonance (NMR) and liquid chromatography. The monomer film of 3BCMU was irradiated by solid-state polymerization of an appropriate dose of ^{60}Co γ-ray irradiation. The total dose was ca. 150 kGy. The crystal of 3BCMU after the ^{60}Co γ-ray irradiation process was washed sufficiently with methanol to remove the unreacted monomers and oligomers that dissolve in the methanol. The obtained polymer (PDA-3BCMU) was dried under vacuum.

A sample PDA-3BCMU film (thickness of about 0.6 μm) was prepared by a doctor-blade method from chloroform solution of about 0.1 wt. %. By the doctor-blade method, the solution of polymer was dropped onto a washed glass plate, stretched by a glass rod, and then dried at room temperature.

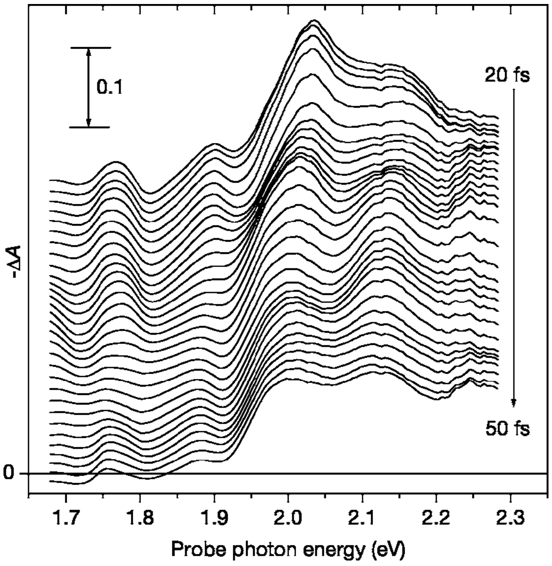

FIG. 1. Difference absorption spectra of blue-phase PDA-3BCMU at a delay time of 20–50 fs with a 1-fs step probed at 1.68–2.28 eV. Each curve is shifted up by $\Delta A = 0.0125$ from the next later delay step by 1 fs. The mark 0 on the ordinate corresponds to null ΔA for the bottom curve.

Both the pump and probe pulses were derived from a noncollinear optical parametric amplifier (NOPA) seeded by a white-light continuum.[48–50] The duration of the NOPA output pulses was reduced with a 5-fs pulse compressor system[48–50] composed of a pair of prisms and chirp mirrors. The source of this system was a commercially supplied regenerative amplifier (Spectra-Physics, Spitfire), of which pulse duration, central wavelength, repetition rate, and average output power are 50 fs, 790 nm, 5 kHz, and 800 mW, respectively. The visible pulse was shorter than 5 fs in duration and covered the spectral range of 520–750 nm, within which it carried a nearly constant spectral phase, indicating that the pulses are close to the Fourier-transform limited condition. The pulse energies of the pump and probe were about 35 and 5 nJ, respectively. Since the spot size of the laser beams on the sample was about 100 μm, the density of excitation was estimated to be $\sim 10^{14}$ photons/cm^2. Here, we have taken into account the transmitted and reflected intensities of the pump. This corresponds to a volume density of excitation of $\sim 10^{18}$ excitons/cm^3, considering the thickness of about 1 μm of the sample. All the measurements were performed at room temperature (295 ± 1 K).

Difference optical density $[\Delta A(\omega,t)]$ (Fig. 1) was calculated by Eq. (1) from the normalized difference transmission spectra $[\Delta T(\omega,t)/T(\omega,t)]$ at pump-probe delay time from −50 to 1949 fs with every 1-fs step.

$$\Delta A(\omega,t) = -\log_{10}\left(1 + \frac{\Delta T(\omega,t)}{T(\omega,t)}\right), \tag{1}$$

where ω and t are the optical frequency and the probe delay with respect to the pump, respectively. The difference transmittance probed in the wavelength range from 541 to 740 nm (corresponding to the photon energy of 1.68–2.28 eV) was detected simultaneously using a multichannel lock-in amplifier with a 300 grooves/mm grating

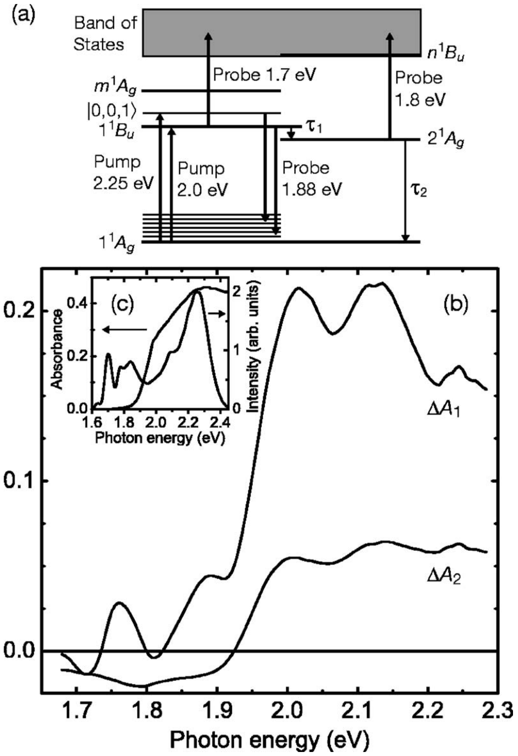

FIG. 2. (a) The essential states to the nonlinearity and the excited-state transitions (Refs. 51 and 52) relevant to this pump-probe experiment. (b) Decomposed difference absorption spectra: ΔA_1 due to the population distribution $P_1(t)$ in 1 ^1B_u state and ΔA_2 due to the population distribution $P_2(t)$ in 2 ^1A_g state. (c) Laser spectrum of the sub-5-fs pump and absorption spectrum of the blue-phase PDA-3BCMU sample.

monochromator for polychromatic purpose. The spectral resolution was about 2.6 nm (7.8 meV) limited by the monochromator.

III. RESULTS AND DISCUSSION

Essential states to the imaginary part of the third-order nonlinear susceptibility, $\mathrm{Im}[\chi^{(3)}(-\omega_{\mathrm{pr}};\omega_{\mathrm{pu}},-\omega_{\mathrm{pu}},\omega_{\mathrm{pr}})]$, in the pump (pu)-probe (pr) absorption spectroscopy[51,52] are schematically shown in Fig. 2(a). The time constants of the processes 1 $^1B_u \rightarrow 2\ ^1A_g$ and 2 $^1A_g \rightarrow 1\ ^1A_g$ are denoted as τ_1 and τ_2, respectively, in Fig. 2(a). As shown in Fig. 1, $\Delta A(\omega,t)$ shows complex behavior including long-term spectral shifts and oscillations with frequencies of molecular vibrations, which are superimposed on the slowly varying signal. However, it is still worth elucidating the relaxation kinetics of photoexcited 1 ^1B_u excitons taken place in 2 ps by a conventional model that the photoexcited 1 ^1B_u state undertakes sequential one-way decay to 2 ^1A_g state followed by the quantum tunneling to the ground state, which was inquired in previous extensive studies.[17,18] In order to investigate the nonoscillating decay of population induced in the excited states by the sub-5-fs pump, we have smoothed out the oscillating signal due to molecular vibrations by convoluting $\Delta A(t)$ with a rectangular time window of 30 fs in width. A decomposed formula for the smoothed $\Delta A(\omega,t)$ is obtained as shown in Eq. (2). Here, we have performed the singular-value decomposition of the smoothed two-dimensional data in the probed range: 1.68–2.28 eV and 20–1948 fs. We successively carried out a global fitting for the decomposed traces in the temporal and the spectral domains by using functions of time, $P_1(t)$ and $P_2(t)$, which are presented in Eqs. (3) and (4). The time range shorter than 20 fs, where the pump and probe pulses are not well separated, was excluded in the analysis to eliminate coherent artifacts and other nonlinear effects such as optical Stark and inverse Raman effects, which may exist.

$$\Delta A(\omega,t) = \Delta A_1(\omega)P_1(t) + \Delta A_2(\omega)P_2(t), \qquad (2)$$

where $\Delta A_1(\omega)$ and $\Delta A_2(\omega)$ represent the difference optical densities attributed to the population distribution: $P_1(t)$ and $P_2(t)$ in 1 ^1B_u and 2 ^1A_g excited states, respectively. The $P_1(t)$ and $P_2(t)$ are given by solving the rate equations of 1 ^1B_u and 2 ^1A_g states as follows:

$$P_1(t) = \exp(-t/\tau_1), \qquad (3)$$

$$P_2(t) = \frac{1}{1-\tau_1/\tau_2}[\exp(-t/\tau_2) - \exp(-t/\tau_1)], \qquad (4)$$

and the origins of $\Delta A_1(\omega)$ and $\Delta A_2(\omega)$ are described, respectively, as follows:

$$\Delta A_1(\omega) = [A_{\mathrm{BL}_1} + A_{\mathrm{PIE}}]\ (1\ ^1A_g \leftrightarrow 1\ ^1B_u) + A_{\mathrm{PIA}_1}(1\ ^1B_u \rightarrow m^1A_g), \qquad (5)$$

$$\Delta A_2(\omega) = A_{\mathrm{BL}_2}(1\ ^1A_g \rightarrow 1\ ^1B_u) + A_{\mathrm{PIA}_2}(2\ ^1A_g \rightarrow 1\ ^1B_u), \qquad (6)$$

where A_{BL}, A_{PIE}, and A_{PIA} denote the difference optical densities ascribed, respectively, to the bleaching (BL) (1 $^1A_g \rightarrow 1\ ^1B_u$) due to the ground-state depletion, the photoinduced emission (PIE) (1 $^1B_u \rightarrow 1\ ^1A_g$), and the photoinduced absorption (PIA). The subindex of $\Delta A(\omega)$ is also attached for A_{BL} and A_{PIA} for distinction. The initial population distribution $P_1(0)$ in 1 ^1B_u state, generated impulsively by the 5-fs pump, was normalized to unity. As a result, the lifetime of 1 ^1B_u and 2 ^1A_g states were determined to be $\tau_1 = 60 \pm 3$ fs and $\tau_2 = 890 \pm 40$ fs, respectively. The time constants are consistent with the values reported previously for a blue-phase PDA with different substituent groups.[17]

The decomposed spectra; $\Delta A_1(\omega)$ and $\Delta A_2(\omega)$ are shown in Fig. 2(b). ΔA_1 reveals the transient absorption spectrum due to the 1 ^1B_u state with a short lifetime of about 60 fs. Negative optical density in ΔA_1 is ascribed to both the PIE (A_{PIE}) (1 $^1B_u \rightarrow 1\ ^1A_g$) and the bleaching ($A_{\mathrm{BL}_1}$) (1 $^1A_g \rightarrow 1\ ^1B_u$). Conversely, the PIA ($A_{\mathrm{PIA}_1}$) (1 $^1B_u \rightarrow m\ ^1A_g$) positively contribute to ΔA_1. Positive and negative contributions to ΔA_2 are attributed to the PIA (A_{PIA_2}) (2 $^1A_g \rightarrow n\ ^1B_u$) and the bleaching ($A_{\mathrm{BL}_2}$) (1 $^1A_g \rightarrow 1\ ^1B_u$), respectively.

However, higher-order nonlinear effects of the pump can also contribute to the observed difference optical density in the first 100 fs, if the pump intensity is not sufficiently weak. We thus reduced the photon density of excitation using an aperture to decrease the beam diameter before focusing to 0.7 mm as well as the pulse energy of the incident pump to 35 nJ. The sample was located at 120 mm away from the surface of a off-axis parabolic mirror with a reflected focal length of 102 mm. As a result, the spot size of the pump beam was about 0.1 mm as mentioned before and the volume density of excitation was evaluated to be $\sim 10^{18}$ excitons/cm^3. Previously, the saturation density of excitons was estimated to be 2.0×10^{20} excitons/cm^3 and an exciton length of 33 Å was deduced in PDA-TS (polydiacetylene-toluene sulfonate) from femtosecond time-resolved transient reflectivity measurements.[53] Since the sample used in this study was prepared by doctor-blade methods, polymer chains should contain certain amount of disorder compared to PDA-TS that is a single crystal of PDA. This results in the delocalized length of an exciton shorter than that in PDA-TS and the estimate of ~30 Å is consistent with effective conjugation lengths evaluated in other conjugated polymers.[54,55] Therefore, we can safely assume the excited-exciton density in the present experiment to be smaller than the saturation density of exciton.

The transient spectrum at 20 fs in Fig. 1 has a negative peak of $\Delta A(\omega)$ at about 2.03 eV, which is higher than the energy of the zero-phonon transition from the ground state. The latter corresponds to the shoulder of the absorption spectrum at 2.0 eV in Fig. 2(c). This shift is also observed as the difference between the photon energies of the corresponding peaks of $\Delta A_1(\omega)$ and $\Delta A_2(\omega)$ in Fig. 2(b). $\Delta A_1(\omega)$ has a negative peak at 2.01 eV, which is slightly higher than the photon energy of the corresponding peak of $\Delta A_2(\omega)$ at 2.00 eV. Two possible reasons can be suggested to explain the observed difference between the peak energies. One is the difference in the sources of the two spectra. As shown in Eqs. (5) and (6), the spectral shape of $\Delta A_1(\omega)$ is determined not only by the bleaching ($1\,{}^1A_g \to 1\,{}^1B_u$) but also by the PIE ($1\,{}^1B_u \to 1\,{}^1A_g$) and the PIA ($1\,{}^1B_u \to m\,{}^1A_g$), whereas the PIA ($2\,{}^1A_g \to n\,{}^1B_u$) partly affects the photon-energy dependence of the $\Delta A_2(\omega)$. The other is the blueshift of the spectrum due to exciton-exciton repulsive interaction known as phase-space filling effect that is observed at high photoexcitation levels in semiconducting quantum wires.[56] However, in this study, the density of excitation was well below the exciton-saturation level. Therefore, the latter effect would bring about only a minor change in the ΔA spectrum.

In the blue-phase PDA films, the triplet state with a long lifetime of $\sim 18\ \mu$s is excited through the Auger recombination process between the two lowest $1\,{}^1B_u$ singlet excitons leading to the ionization of one exciton of the two.[57] However, in this study, excitation photon density was decreased to $\sim 10^{14}$ photons/cm^2, which provides negligibly small amount of the triplet state.

Both the differential optical densities, $\Delta A_1(\omega)$ and $\Delta A_2(\omega)$ have vibrational progressions as shown in Fig. 2(b). The stationary absorption spectrum of the same sample is also shown in Fig. 2(c). The absorption spectrum has a shoulder due to $1\,{}^1B_u$ exciton at 2.0 eV.[10,18] as well as a broad and intense phonon side band that indicates the existence of electron-lattice coupling in the polymer chains. Lécuiller *et al.* reported Stokes-shift free fluorescence spectrum peaked at 2.28 eV with a longer lifetime than 10 ps in isolated red-phase chains of PDA-3BCMU.[40] However, the concentration of the red-phase chain is reported to be about a thousand times smaller than that of the blue chain in the monomer matrix of PDA-3BCMU,[40] and the phonon sideband in the fluorescence spectrum of isolated red-phase chains is much weaker than that of the usual red-phase PDAs.[18] Therefore, the PIE from the red-phase chains cannot be responsible for the short-lived PIE with a lifetime of 60 fs observed at 1.9 eV in this work.

The spectrum of the pump pulses have a relatively narrow feature around 2.25 eV with a full width of about 0.21 eV at half maximum as shown in Fig. 2(c). The width is comparable to the phonon energies of single-, double-, and triple-bond CC stretching modes in the polymer backbone, which lie in the range 0.15–0.26 eV. The absorption spectrum also has a broad feature peaked around 2.3 eV. Therefore, partially selective excitation of the allowed $|1\,{}^1A_g\rangle|0,0,0\rangle \to |1\,{}^1B_u\rangle|0,0,1\rangle$ (C≡C) transition takes place at 2.25 eV, where $|1\,{}^1A_g\rangle$ and $|1\,{}^1B_u\rangle$ denote the electronic states, and integers l, m, and n in $|l,m,n\rangle$ represent, respectively, the vibrational quantum numbers of CC stretching modes of single, double, and triple bonds [Fig. 2(a)] within the framework of adiabatic approximation. The spectral feature of the pump pulse induces partial "femtosecond hole burning,"[58] which reduces the inhomogeneity in ΔA and enables the detection of the vibrational structure buried in the inhomogeneity.

The coherent molecular vibrations continue on a few ps time scale in the $2\,{}^1A_g$ excited state after the IC ($1\,{}^1B_u \to 2\,{}^1A_g$) process is completed.[20] Therefore, the vibrational thermalization is not completed in the first 100 fs. The PIE from the nonthermalized $1\,{}^1B_u$-exciton state is then expected in the photon-energy region above the energy of zero-phonon transition ($|1\,{}^1B_u\rangle|0,0,0\rangle \to |1\,{}^1A_g\rangle|0,0,0\rangle$) as well as below the absorption edge. Since the bleaching spectrum has a vibrational progression, the spectrum of PIE ($1\,{}^1B_u \to 1\,{}^1A_g$) is also expected to have a corresponding vibrational progression. In fact, the PIE spectrum similar to the mirror image of the bleaching spectrum is observed below absorption edge only in $\Delta A_1(\omega)$ in Fig. 2(b), although the spectral shape is distorted by the PIA ($1\,{}^1B_u \to m\,{}^1A_g$). We note again that the $\Delta A_1(\omega)$ is the difference optical density due to $1\,{}^1B_u$ exciton with a decay constant of 60 fs, which was derived from $\Delta A(\omega,t)$ after subtracting the oscillating components due to molecular vibrations. The results indicate that the negative-peak structure of ΔA below absorption edge is attributed to the PIE from the $1\,{}^1B_u$ state, not the saturated absorption from the ground state nor the PIA from the $2\,{}^1A_g$ state.

To characterize the dynamics of $\Delta A(\omega,t)$, we have introduced a "peak-tracking" method. In general, wave-packet motion driven by the pump pulse modulates both the time-dependent photon-energy, $\omega_0(t)$, of a peak of ΔA in its dependence on the probed photon energy and the difference optical density at $\omega_0(t)[\Delta A(\omega_0(t))]$.[59,60] $\omega_0(t)$ and $\Delta A(\omega_0(t))$ correspond to the peak values of the energies and the prob-

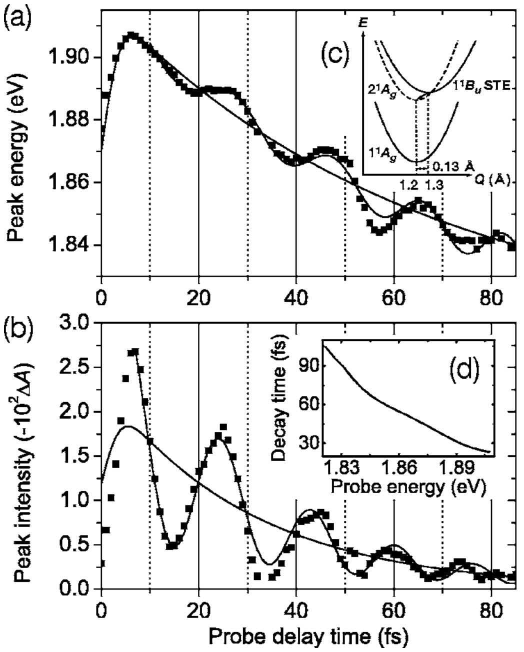

FIG. 3. Time traces of (a) the energy and (b) the intensity of an induced emission peak near 1.89 eV. Smooth monotonically decaying curves are single-exponential fits convoluted with the pulse duration. Oscillating curves represent the best fits to Eq. (7). (c) A schematic cross-section diagram of the potential hypersurfaces of $1\,^1A_g$, $1\,^1B_u$-STE, and $2\,^1A_g$ states along the C≡C stretching coordinate in configuration space. (d) Short-decay time determined by the biexponential decay fitting for the time trace of ΔA at each probe energy.

abilities, respectively, of transitions from the electron-phonon states composing the wave packet. Decomposed signals provide the correct time evolution of the transition energy and the transition probability unaffected by the crosstalk between the two. Even the vibrational-phase information can also be obtained from the signals. In our previous paper,[59,60] we separated the contribution by utilizing the simulation of vibrational amplitude spectrum in terms of the zeroth and first derivatives of absorbance change with respect to the probed photon energy. However, the present method can directly separate the contribution without any ambiguity induced in the previous fitting.

Figures 3(a) and 3(b) show the time traces of the energy and the intensity, respectively, of a negative peak of ΔA observed at 1.88 eV in Fig. 2(b). The peak energy of 1.88 eV is close to the photon energy of the fluorescence peak from the $1\,^1B_u$ state.[18] We thus assigned the peak, which was observed below the absorption edge and appeared only in the spectrum of $\Delta A_1(\omega)$, to the PIE from the $1\,^1B_u$ state to the ground state. The peak intensity was extracted by subtracting the smooth background signal from the observed absorbance change in the photon-energy range within ±0.08 eV around the peak.

The peak energy in Fig. 3(a) shows redshift from 1.90 to 1.84 eV during the first 80 fs with an oscillating signal superimposed. There are two possible interpretations. One is the usual dynamic Stokes shift due to the vibrational energy redistribution to a bath of dark modes with lower frequencies. The other is the electronic-energy change that results from the GR in the carbon backbones and the IC to the $2\,^1A_g$ state. The latter interpretation is believed to be more appropriate because of the following three reasons: (i) the oscillating signal in Fig. 3(a) does not show critical damping during the redshift of the peak; (ii) in the present experiment, the pump pulse excites the ground level and the first-excited vibrational level of the C≡C stretching mode in the $1\,^1B_u$ excited state, which are less subject to dissipative channels of the vibrational energy, compared to the higher vibrational levels; (iii) the efficient IC ($1\,^1B_u \rightarrow 2\,^1A_g$) and the GR accompanied with large structure change between acetylene and butatriene types have been observed in previous experiments[13,16] and inquired by theoretical calculations.[61–63] Previously, a vibrational mode coupling between C═C and C—C stretching modes via a torsion mode with a 145-fs oscillation period is observed in the geometrically-relaxed $2\,^1A_g$ state.[17] Vibrational phases of the CC stretching modes also suggests the coherent nuclear motions in the relaxed $2\,^1A_g$ state.[20] These results indicate that the peak shift is attributed to the potential-energy change in the transient "$1\,^1B_u^{(*)}$" state. Here, the symbol (*) denotes that the $1\,^1B_u^{(*)}$ is not the "pristine" $1\,^1B_u$ state but the electronic state that is nonadiabatically coupled with the $2\,^1A_g$ state. The effects of the diabatic coupling between the $1\,^1B_u$ and the $2\,^1A_g$ states on the vibrational coherence are discussed theoretically by Turki *et al.*[61] The coupling reduces both the oscillator strength of the $1\,^1B_u^{(*)} \rightarrow 1\,^1A_g$ transition and the photon energy of the PIE peak.

The PIE peak intensity decreases rapidly in the consequence of the IC from the $1\,^1B_u$ state to the geometrically relaxed $2\,^1A_g$ state. The modulation periods of the transition-peak energy and the intensity are both about 20 fs (Fig. 3), which is shorter and longer than the oscillation periods of the C═C (22.8 fs) and C≡C (16.0 fs) stretching modes, respectively.[20] Since the geometrically relaxed $2\,^1A_g$ state have the "acetylenelike" structure with well-defined C═C and C≡C bonds,[20] the transition state during the GR is expected to have a configuration with time-varying contributions of the two resonant "acetylenelike" $(\text{═C}R\text{—C≡C—C}R'\text{═})_n$, and "butatrienelike" $(\text{—C}R\text{═C═C═C}R'\text{—})_n$, configurations.[13,16] The C≡C-bond length and the corresponding vibrational frequency of the C≡C stretching is, therefore, presumed to vary reflecting the change in the electronic structure during the GR. In order to describe the population and coherence decays in Fig. 3, we have used the following phenomenological function $M(t)$,[64] assuming that the instantaneous vibrational frequency, $\Omega(t)$, is characterized by a linear positive chirp: $\Omega(t)=\Omega+\Delta\Omega\cdot t$.[65]

$$M(t) = A\exp(-t/\tau_v)\cos((\Omega+\Delta\Omega t/2)t+\theta) + B\exp(-t/\tau) + C, \tag{7}$$

where τ_v and τ are the time constants of the oscillating and nonoscillating signals, respectively, and A, B, and C are constants. Ω is the initial frequency and $\Delta\Omega$ gives frequency change with time. The time-dependent frequency $\Omega(t)$ means that the mode is not a normal mode and is coherently coupled with other modes, which include torsion modes of the chain. The deformation of the carbon backbone activated by the torsion modes breaks the C_2 symmetry of the polymer chains and induces the electronic coupling between the $1\,^1B_u$ and $2\,^1A_g$ states, which results in the electronic-structure change of the backbone. It is to be noted that not only "dynamic mode coupling" observed in our previous papers[17,43,44] but also "transient mode coupling" is taking place. It means that the mechanism of the coupling due to another mode (there may be even more than one) is not stable. The coupling disappears after some short time.

As a result, the time constants τ of dynamic Stokes shift (redshift of the stimulated-emission peak energy) and the decay in the peak intensity were determined to be 70 ± 10 fs and 30 ± 5 fs, respectively. The relaxation time τ_1 in Eq. (2) is the average of the "apparent" decay constant in Fig. 3(d), the range of which is induced by the redshift. The oscillation amplitude of the peak intensity shows damping with the time constant $\tau_v=30\pm5$ fs same as τ of the peak-intensity decay due to IC. In contrast, the energy oscillation suffers no decay ($\tau_v \gg 80$ fs) in Fig. 3(a), revealing that the vibrational coherence is maintained during GR and IC even though they are chirped. An analogy in optics to this time-dependent instantaneous frequency appears in a chirped "coherent" pulse. The $C\equiv C$-bond length changes continuously during the processes in the analogy of adiabatic change of the string length of a pendulum in a kinematic model. This kind of coherent vibrational frequency chirp was also observed in stilbene[65] and stilbene derivatives[66] during the isomerization process. The fitting curves in Figs. 3(a) and 3(b) indicate the instantaneous period varies from 21 ± 2 to 16 ± 1 fs during the relaxation. The variation of the oscillating period from 23 fs in the initial $1\,^1B_u$ state to 17 fs in the geometrically-relaxed $2\,^1A_g$ state is also reported in a theoretical simulation performed by Turki *et al.*[61] The corresponding frequency change from 1600 ± 100 cm^{-1} to 2100 ± 100 cm^{-1} suggests that the large structure change takes place for about 80 fs after photoexcitation as was proposed in Ref. 13. The reduction of carbon-carbon bond length during the relaxation is estimated to be 0.13 ± 0.04 Å. The bond-length reduction was deduced from the x-ray diffraction data in the ground state of PDA-TS in Ref. 67. We took a linear interpolation of the bond lengths, determined by x-ray diffraction,[67] as a function of the corresponding stretching frequencies; 1220 cm^{-1} for $C-C$ (1.428 Å),[20] 1480 cm^{-1} for $C=C$ (1.356 Å),[26] and 2080 cm^{-1} for $C\equiv C$ (1.191 Å).[26] As a result, we derived the bond lengths; 1.32 ± 0.04 Å from 1600 ± 100 cm^{-1} and 1.19 ± 0.04 Å from 2100 ± 100 cm^{-1}.

The electronic structure in the nonequilibrium excited state is characterized by the butatriene type rather than the acetylene type.[13] The efficient IC to the $2\,^1A_g$ state involves the recovery of the acetylenelike electronic configuration. This large structural change is consistent with the theoretical predictions.[61–63] The $1\,^1B_u$-FE is expected to convert rapidly (<20 fs) to the transient state with butatrienelike conformation, but it cannot be observed in this study because of the limited time resolution. We summarized the structural change in a simplified schematic potential curves in Fig. 3(c).

The intensity decay in Fig. 3(b) reflects the time dependence of the ensemble-averaged population probability of the $1\,^1B_u$ state.[61,68] About 80 fs after the 5-fs pulse excitation, the peak intensity of the IE ($1\,^1B_u \rightarrow 1\,^1A_g$) is diminished because of the even symmetry of the relaxed electronic structure in $2\,^1A_g$ state. The peak energy provides the instantaneous transition-peak energy ($1\,^1B_u \rightarrow 1\,^1A_g$) and shows a redshift of about 60 meV with a 70-fs decay constant associated with the relaxation from the $1\,^1B_u$ state to the geometrically-relaxed $2\,^1A_g$ state. The oscillation of the peak energy is due to the vibrational modulation of the shift energy during the dynamic Stokes-shift process.[69] The lifetime of the $1\,^1B_u$ state is estimated to be <40 fs from the low quantum yield of fluorescence ($<10^{-5}$) in PDA-3BCMU (Refs. 10 and 28) and the oscillator strength (~1.5) of $1\,^1B_u$ exciton.[70] The decay time of the IE intensity of 30 fs obtained in this study is consistent with the estimate. The energy shift (60 meV) is also consistent with the reported Stokes shift in the stationary spectra.[7,18,28]

IV. CONCLUSION

In conclusion, we have performed the peak-tracking analysis for an induced emission peak observed in the difference absorption spectra. Decomposed time traces of the peak energy and the probability of transitions have revealed the relaxation dynamics during GR and IC in blue-phase PDA. We thus observed for the first time coherent vibration during the dynamic Stokes-shift process prior to the energy redistribution among various modes in the polymer chains. The frequency change during the process provides the evidence of the transient structural change in the carbon backbone during the initial relaxation with the change of carbon-carbon bond length by about 0.13 Å. These results offer valuable information about the extremely fast IC and GR, and may stimulate the theoretical investigations of the electron-phonon and electron-electron interactions in nondegenerate conjugated polymers. More generally, the present method will provide invaluable information about the structures of excitons and excited-state molecules and activate the investigations of the "real-time" structural dynamics in the excited state and in the process of photochemical reactions.

ACKNOWLEDGMENTS

The authors would like to thank T. Saito, S. Adachi, K. Nishimura, T. Taneichi, and N. Ishii for enlightening discussions. This research was supported partly by the Grant-in-Aid for Specially Promoted Research (Grants No. 14002003) and partly by the program for the "Promotion of Leading Researches" in Special Coordination Funds for Promoting Science and Technology from the Ministry of Education, Science and Culture.

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