PHYSICAL REVIEW B **70**, 214301 (2004)

Phase analysis of vibrational wave packets in the ground and excited states in polydiacetylene

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(Received 11 May 2004; published 2 December 2004)

Molecular vibration of several modes in blue-phase polydiacetylene-3-butoxycarbonylmethylurethane (PDA-3BCMU) was real-time observed by 5-fs pump-probe measurement. The contribution of the vibrational wave packets in the ground state and in the excited state in the signal were separated by multichannel measurement. The C=C stretching mode in the ground state starts to oscillate π-out-of-phase with the C≡C stretching mode. The structure of PDA-3BCMU in the geometrically relaxed state is not pure butatriene type but more like acetylene type. The frequencies of C=C and C≡C stretching modes there were determined by singular value decomposition method to be $1472\pm6\ \mathrm{cm}^{-1}$ and $2092\pm6\ \mathrm{cm}^{-1}$, respectively. The double and triple bond stretching frequencies in the ground state are $1463\pm6\ \mathrm{cm}^{-1}$ and $2083\pm6\ \mathrm{cm}^{-1}$, respectively.

DOI: 10.1103/PhysRevB.70.214301 PACS number(s): 78.47.+p, 78.66.Qn, 82.35.Ej

I. INTRODUCTION

Optical and electrical properties of conjugated polymers have been attracting many scientists because of their potential applications to electronics, optoelectronics, and photonics.[1,2] The examples are flexible conductors, light-emitting diodes, and all-optical switches. The polymers are of interest not only because of the above technological applications but also due to fundamental physics, since they have large optical nonlinearities and are model materials of one-dimensional system with outstanding characteristic features including excitonic spectrum and ultrafast relaxation studied by spectroscopy. These features are deeply related to the formation of localized nonlinear excitations such as solitons, polarons, and a self-trapped exciton (STE) formed via a strong coupling between electronic excitations and lattice vibrations. STE is sometimes called exciton polaron or neutral bipolaron.[3–16]

Among conjugated polymers polydiacetylenes (PDAs) hold special interest, because PDAs have several phases named according to their colors and also can have various morphologies, i.e., single crystals, cast films, Langmuir films, and solutions.[17–20] The ultrafast optical responses in PDAs have been intensively investigated using femtosecond spectroscopy and time-resolved Raman spectroscopy.[2,6,10,11,21–30]

From previous extensive studies,[2,6,10,11,21–30] the initial changes in electronic absorption spectra and their ultrafast dynamics in a femtosecond region after photoexcitation of polydiacetylene (PDA) are explained in terms of the geometrical relaxation (GR) of a free exciton (FE) to a STE within 100 fs.[2] The STE is well established to be a geometrically relaxed state with admixture of butatrien-type configuration $(\text{—C}R\text{=C=C=C}R'\text{—})_n$ from an acetylene-type chain $(\text{=C}R\text{—C≡C—C}R'\text{=})_n$.[21,22] Here, R and R' represent substituted side groups attached to the main chain. All of the stretching vibrations of carbon atoms are considered to be coupled to the photogenerated FE and induce various nonlinear optical processes different from those in most inorganic semiconductors.[10–13,28,31] Recent experimental and theoretical studies have revealed the lowest excited singlet state in a blue-phase PDA to be an optically forbidden $2\ {}^1A_g$ state lying ~0.1 eV below an allowed $1\ {}^1B_u$-FE state, which provides characteristic intense blue color.[3,32–36] The internal conversion (IC) is then expected along with self-trapping,[12,13] but the dynamical processes of IC and GR have not yet been fully characterized.[12,13] Recent progress in femtosecond pulsed lasers has enabled study of molecular dynamics on a 10-fs time scale.[23,24] In the previous works, 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 of PDA-DCAD [poly(1,6-di(*n*-carbazolyl)-2,4 hexadiyne)] films by using 9–10 fs pulses.[21,22]

The real-time observation of the geometrical relaxation in PDA has been enabled by the recent development of sub-5-fs visible pulse generation based on noncollinear optical parametric amplification (NOPA) system, which satisfies all of the pulse-front matching, phase matching, and group-velocity matching conditions.[37–39] Utilizing compressors such as prism pair, grating pair, chirped mirror, and deformable mirror, the shortest visible—near-infrared pulse was obtained.[37,39] The trace of the delay-time dependence of the normalized difference transmittance $\Delta T(t)/T$ induced by an ultrashort pump pulse is called "real-time spectrum," which means a spectrum in a time domain. By time-resolved analysis of the Fourier transform of the real-time spectrum, the dynamic features of self-trapping, IC, and coupling between stretching and bending modes in the relaxed state in a PDA have been elucidated using sub-5 fs pulses.[30]

However, these experiments have a remaining problem of ambiguity in the assignment of the origins of the pump-probe signal traces to either the ground state or the excited states, because the ultrashort laser pulse with wide enough spectrum can drive the coherent vibrations in both ground and excited states. This prevents us from the well-defined discussion of the dynamics of the wave packet after being photogenerated.

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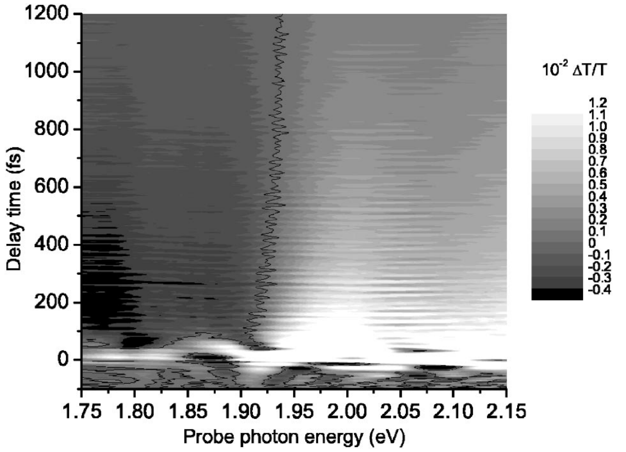

FIG. 1. Time dependence of the normalized difference transmittance $[\Delta T(t)/T]$ displayed two dimensionally (probe-photon energy versus probe delay time).

In this study, we could attribute the origins of the oscillation signals in pump-probe traces either to the ground or the excited state by utilizing precise multichannel detection method.

II. EXPERIMENT

The sample used in the present study is a cast film of blue-phase PDA-3BCMU (poly [4,6-docadiyn-1, 10-diolbis (n-butoxycarbonylmethylurethane)]) on a glass substrate. PDA-3BCMU has side groups of

$$R = R' = -(\mathrm{CH}_2)_3\mathrm{OCONHCH}_2\mathrm{COO}(\mathrm{CH}_2)_3\mathrm{CH}_3,$$

in the backbone chain structure of $(=R\mathrm{C}-\mathrm{C}\equiv\mathrm{C}-\mathrm{C}R'=)_n$. PDA-3BCMU is one of the well-known soluble PDAs. The laser pulses for both pump and probe are produced by NOPA seeded by a white-light continuum with a 5-fs pulse compressor system.[29,39–41] The source of this system is a commercially supplied regenerative amplifier (Spectra-Physics, model Spitfire), of which pulse duration, central wavelength, repetition rate, and average output power are 100 fs, 790 nm, 5 kHz, and 800 mW, respectively. The spectrum of the pump and probe pulses covers a spectral range from 520 to 730 nm with a nearly constant phase, providing a Fourier transformed temporal shape. Laser pulse energies of the pump and probe pulses are about 35 and 5 nJ, respectively. Time trace of normalized difference transmittance $[\Delta T(t)/T]$ was obtained as a function of pump-probe delay-time (t) from -100 to 1200 fs with every 1-fs step. Simultaneous measurement was performed by a multichannel lock-in amplifier designed by EG&G over the spectral range extending from 540 to 740 nm using a 300 grooves/mm grating monochromator with spectral resolution of about 3.6 nm. All the measurements were performed at room temperature $(295 \pm 1\ \mathrm{K})$.

III. RESULTS AND DISCUSSION

Figure 1 shows the observed the normalized difference transmittance $\Delta T(t)/T$ of the blue-phase PDA-3BCMU sample displayed two dimensionally (probe-photon energy versus probe delay time). Figure 2 exhibits several examples of $\Delta T(t)/T$ traces at several energies of probe photon. All of the traces have signals of finite size at negative delay times, and sharp and intense peaks around zero probe-delay time. The former is due to the perturbed free-induction decay process associated with the third-order nonlinearity of the sequential interaction of probe-pump-pump fields modified with molecular vibrations. The latter signals are due to pump-probe coupling induced by the nonlinear process of the pump-probe-pump time ordering. There is another contribution from the interference between the scattered pulses and the probe pulses, durations of which are elongated in the polychromator. The details of the vibrational modulation observed at delay times longer than 100 fs are free from the distortions due to the above two mechanism. Figure 3 shows the measured normalized difference transmittance spectra at a few probe-delay times. In the probe-photon energy region above 1.95 eV the normalized difference transmittance is

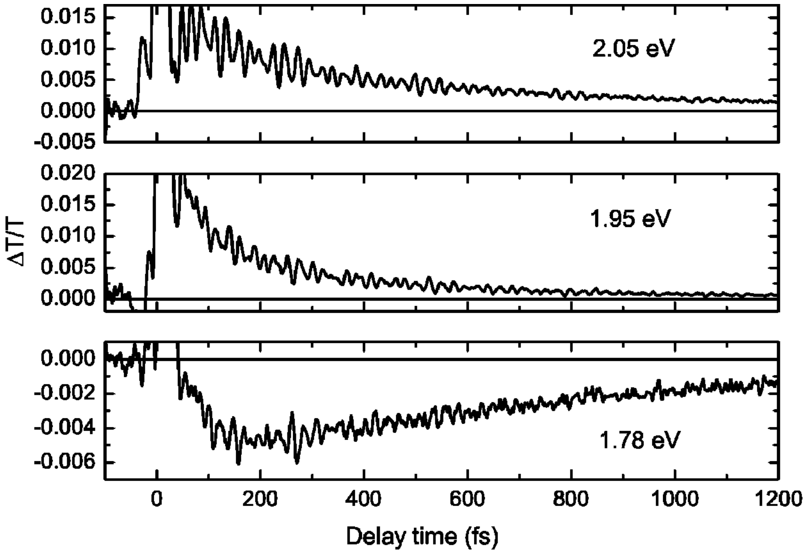

FIG. 2. Pump-probe delay time dependence of the normalized difference transmittance $[\Delta T(t)/T]$ on the probe delay time at three probe photon energies.

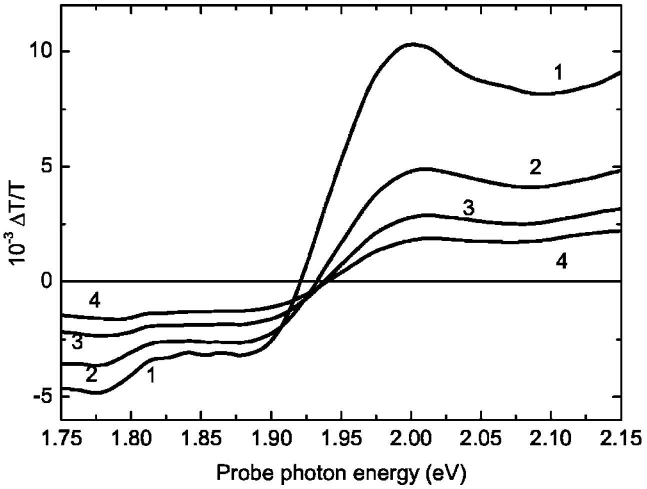

FIG. 3. Normalized difference transmittance spectra ($\Delta T/T$); (1) delay at 200 fs; (2) 500 fs; (3) 800 fs; (4) 1100 fs.

positive because of photobleaching of the 1 ^1B_u-FE absorption peaked around 2.0 eV. In the probe-photon energy region below 1.90 eV the normalized difference transmittance signals are negative due to the photoinduced transition from the geometrically relaxed 2 ^1A_g state to the higher excited nB_u state, which is one of the four essential states.[30,42] The 1 ^1B_u-FE state decays within 100 fs into the geometrically relaxed 2 ^1A_g state.[2,31,43]

The power spectrum of Fourier transform of $\Delta T(t)/T$ at 128 probe-photon energies probed by using the multichannel lock-in amplifier is shown in Fig. 4. For the calculation the signal data in the probe delay time ranging from 400 to 900 fs were used after high-pass step-function filtering with a cutoff frequency of 1000 cm^{-1}. In the wide range of probe-photon energy, three peaks were observed at 1220, 1460, and 2080 cm^{-1}, corresponding to the C—C, C═C, and C≡C stretching modes, respectively.[44–46] All three modes have peaks around 1.78, 1.95, and 2.05 eV in common.

In order to investigate the vibrational mode more deeply, we analyzed the pump-probe signal by a linear prediction singular value decomposition (LP-SVD) method. By LP-SVD, single or multiple mode(s) of damped oscillation were extracted from the data such as $y(t)=A\exp(-t/\tau)\cos(\Omega t+\theta)$, where A is an initial amplitude of the signal modulation of $\Delta T(t)/T$ due to molecular vibration, τ is the decay time, Ω is the mode frequency, and θ is the initial phase. The value of each vibrational mode of C—C, C═C, and C≡C was extracted by the LP-SVD method from the 200–900-fs data after rectangular frequency filtering of the Fourier power spectrum (1150–1290, 1395–1535, and 2010–2150 cm^{-1}) at each probe-photon energy independently. The amplitude at 300 fs of each mode is shown in Fig. 5. The spectrum of amplitude of C—C stretching mode in Fig. 5(a) does not resemble the FFT power spectrum of C—C mode in Fig. 4. The signal of vibration of C—C stretching mode was not strong enough for the mode signal to be extracted out from the real-time data to analyze the decay time and initial phase precisely. From here on we concentrate on the pump-probe signal of only C═C and C≡C stretching modes extracted by LP-SVD.

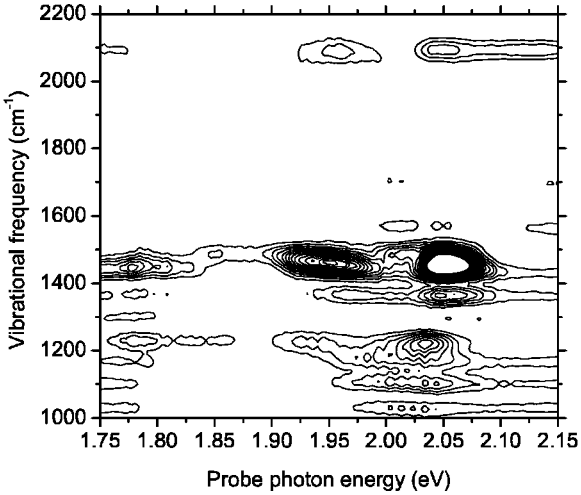

FIG. 4. Two-dimensional Fourier power spectra of the $\Delta T/T$ traces.

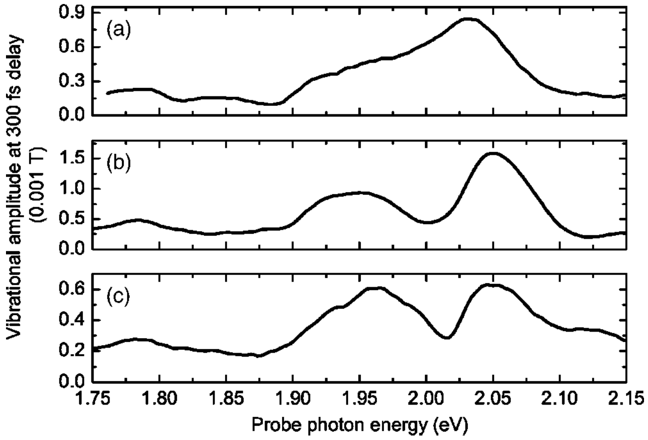

FIG. 5. Fourier amplitude at the probe delay of 300 fs extracted from the normalized difference transmittance by the method of LP-SVD for the modes of (a) C—C; (b) C═C; and (c) C≡C stretching.

The absolute initial phase of the C═C and C≡C modes is shown in Fig. 6. In order to explain the features of the phase spectra in Fig. 6, we propose a simple model as follows. In Figs. 7(a) and 7(c), transition from the ground state to 1 ^1B_u-FE state and that from the geometrically relaxed 2 ^1A_g state to nB_u state, respectively, are represented on the potential curves of PDA. The FWHM of pulse of the NOPA output used as a pump is shorter than the oscillation periods of C═C 23 fs and C≡C vibrations 16 fs. Therefore, it can generate vibrational wave packets impulsively in the ground state and 1 ^1B_u-FE state. The wave packet in the ground state is made at point B in Fig. 7(a), which is located at the bottom of potential curve surface of the ground state, and begins to oscillate on the potential curve as $B\rightarrow A\rightarrow B\rightarrow C\rightarrow B\ldots$ (or $B\rightarrow C\rightarrow B\rightarrow A\rightarrow B\ldots$). After the wave packet is generated, absorption intensity increases when the wave packet is located at the probe-photon frequency corresponding to the vertical transition energy at the position of the wave packet. Therefore, the oscillation of wave packet results in the

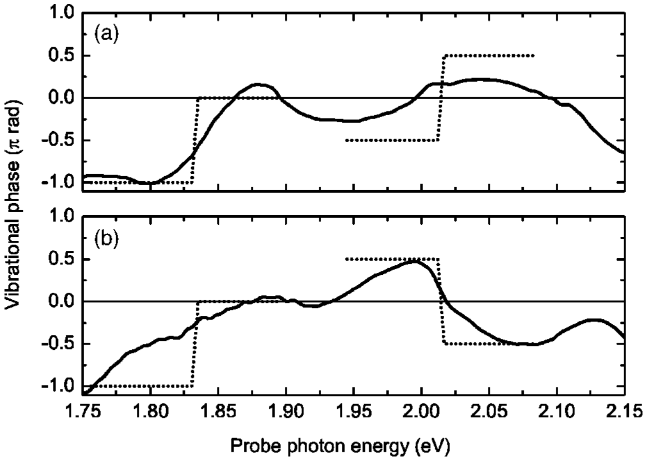

FIG. 6. Initial phase (solid curve) of each vibrational mode of normalized difference transmittance by the method of LP-SVD for the modes of (a) C=C; and (b) C≡C stretching. The expected phase (dotted line) of vibration from the model of the wave packet motion in the ground state (1.95–2.07 eV) and in the excited state (1.76–1.88 eV).

modulation of normalized difference transmittance with the vibrational frequency.

If the wave packet photoproduced at B starts to oscillate as described by $B \rightarrow A \rightarrow B \rightarrow \ldots$, the transmittance at probe photon energy E_A starts to decrease initially, and at the same time the transmittance at E_C starts to increase. Here, E_X is the transition energy from position $X(=A,B,C,D,E,$ or $F)$ on the lower state to the upper state. In this case the phase of the vibration of $\Delta T(t)/T$ is $\pi/2$ at probe photon energy higher than E_B, and $-\pi/2$ at that lower than E_B as shown in Fig. 7(b). If the wave packet starts to move in the reverse direction $(B \rightarrow C \rightarrow B \rightarrow \ldots)$, the phase is $-\pi/2$ for the probe-photon energy higher than E_B, and $\pi/2$ at the lower than E_B.

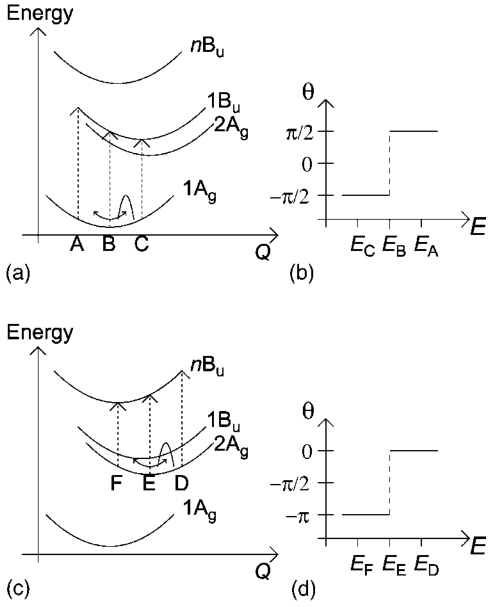

FIG. 7. (a) Transition from the ground states on potential energy curves of PDA. Point B is located at the bottom of the curve of the ground states. (b) The model phase of vibration by the motion of the wave packet in the ground state. E_X is the energy of transition from position X. (c) Transition from the excited states on potential energy diagram of PDA. Point E is located at the bottom of the curve of the ground states. (d) The model phase of vibration by the motion of the wave packet in the excited state.

Figure 6(a) shows that the phases determined for the C=C stretching mode from about 1.9 to 2.0 eV are negative, while those between about 2.0 and 2.1 eV are positive. These features can be explained using Figs. 7(a) and 7(b), where E_B is 2.0 eV, which corresponds to the 1 ^1B_u-FE absorption peak. The phase of the C=C stretching mode at 2.02 eV is positive, while that of the C≡C stretching mode at 2.02 eV in Fig. 6(b) is close to zero. This energy (2.02 eV) corresponds to the photon energy shifted by the C=C stretching energy (0.18 eV) from 2.2 eV of the peak of the probe, which is expected to give a $\pi/2$ phase. Therefore, it can be concluded that the phases around 2.02 eV in C=C are shifted to positive due to the contribution of the Raman gain signal. The phases of C≡C stretching are positive from about 1.93 to 2.02 eV and are negative between about 2.02 and 2.15 eV. It is concluded that the wave packet of C≡C mode generated on the ground-state potential curve starts to move in the reverse direction to that of the C=C mode.

The phases of C=C mode around 1.95 and 2.05 eV are neither $\pi/2$ nor $-\pi/2$. It can be explained in the following way. Intense signal of photoinduced absorption modulated by the wave packet of C=C mode in the excited state is expected also to be generated relatively strongly in the photon energy region. Then, the phases of C=C mode are considered to be zero as expected for a wave packet in the excited state. Because of the overlap of the vibrational signals due to the ground state and to the excited state, the observed values of the phases are expected to correspond to the weighted averages of the two contributions.

From the fact that the phases at 1.95 and 2.05 eV have opposite sign to each other, it can be concluded that the vibrational-amplitude peaks at 1.95 and 2.05 eV are due to the modulation of the intensity of 1 ^1B_u-FE absorption (resonant at 2.00 eV) by the motion of the vibrational wave packet induced by the stimulated Raman scattering (SRS) process in the ground state.

Figure 7(c) represents the diagram of photoinduced absorption from the geometrically relaxed 2 ^1A_g state. The pump pulse makes wave packets not only in the ground state but also in the 1 ^1B_u-FE state. The wave packet photoexcited in the 1 ^1B_u-FE state soon (<100 fs) after generation relaxes into the geometrically relaxed 2 ^1A_g state. In our group we found that this relaxation time was determined to be 60±20 fs.[47] The oscillation of the wave packet on the geometrically relaxed 2 ^1A_g state potential curve modulates the probe signal. A wave packet is produced at point F in Fig. 7(c) at the beginning, and then starts to move as $F \rightarrow E \rightarrow D \rightarrow E \rightarrow F \ldots$, where point E is located at the bottom of the geometrically relaxed 2 ^1A_g state potential curve along the corresponding stretching-mode coordinate.

The expected phases of the oscillation of the photoinduced-absorption signal in the case of $E_D > E_F$ are shown in Fig. 7(d), i.e., they are zero, $-\pi/2$, and $-\pi$ at E_D, E_E, and E_F, respectively, in the analogy of the ground state.

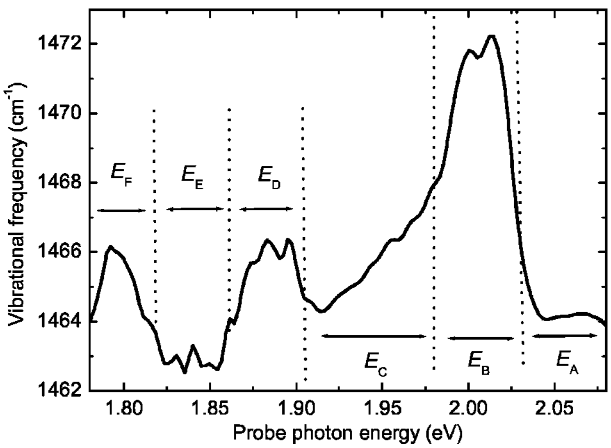

FIG. 8. The probe photon energy dependence of vibrational frequency of C=C stretching mode. E_A and E_C are energy regions in which the pump-probe signal is modulated by the motion of the wave packet in the ground state strongly rather than the excited state. E_D and E_F are energy regions in which the pump-probe signal is modulated by the motion of the wave packet in the ground state strongly rather than the excited state. In E_B and E_E, the signal is modulated by the motion of the wave packet only in the excited/ground state, respectively.

The spectrum of absorption from the geometrically relaxed $2\,^1A_g$ state to nB_u states has a peak around 1.8 eV.[28] If E_E is 1.83 eV, the phases of the C=C mode in Fig. 6(a) correspond to the model phase in Fig. 7(d). The phases of C≡C mode at 1.77 and 1.87 eV are $-\pi$ and zero, respectively, in the same way as the phases of C=C mode. Therefore, it is concluded that not only the vibrational wave packet of C=C mode but also that of C≡C mode is generated in the geometrically relaxed $2\,^1A_g$ state. This clearly demonstrates that the full geometrically relaxed butatriene-type structure is not formed, but it can still be described in the form of acetylene-type structure, as discussed previously by one of the present authors.[30]

Figure 8 shows that the frequencies of C=C mode at 128 probe-photon energies extracted by LP-SVD from the real-time traces. From the previous discussion, the signal due to the wave packet motion in the ground state appears strongly at the probe-photon energies of 2.04–2.07 and 1.92–1.95 eV, which correspond to E_A and E_C, respectively, in Fig. 7. The oscillatory motion of the wave packet in the geometrically relaxed $2\,^1A_g$ state appears strongly at the probe-photon energies of 1.87–1.90 and 1.79–1.81 eV, indicated by E_D and E_F regions in the figure. At the probe-photon energies of 2.00 and 1.84 eV, which are marked with E_B and E_E, respectively, the vibration of wave packet in the geometrically relaxed $2\,^1A_g$ state and that of the ground state, respectively, appear nearly exclusively. Figure 8 shows that the vibrational frequencies determined for the probe-photon energies of E_B, E_D, and E_F are higher than those of E_A, E_C, and E_E. Hence, it can be concluded that the frequency of C=C stretching in the geometrically relaxed $2\,^1A_g$ state is close to that determined for E_B probe photon energy. Therefore, the frequency of the C=C stretching in the excited state is concluded to be 1472 ± 6 cm^{-1} and that in the ground state which is 1463 ± 6 cm^{-1} concluded for E_E probe photon energy. The error was estimated from the value that induces shifting of the vibrational phase by $\pm\pi/4$ after the experimental time span of 700 fs, and can easily be detected in the present method. The frequency of C≡C stretching mode in the geometrically relaxed $2\,^1A_g$ state is determined to be 2092 ± 6 cm^{-1}, while that in the ground state is 2083 ± 6 cm^{-1}. It can be concluded that each of the frequencies of the C=C and C≡C stretching in the excited state is higher by about 10 cm^{-1} than each of those in the ground state.

IV. CONCLUSION

In conclusion, we separated the ground-state and the excited-state contributions in the real-time vibrational signals due to the wave packet motions from the different transmittance spectra obtained by multiwavelength sub-5 fs spectroscopy. The wave packet of C=C stretching mode in the ground state was found at first to oscillate to the *opposite* direction to that of C≡C stretching mode. Also, the vibration of C≡C stretching mode in the geometrically relaxed $2\,^1A_g$ state was observed as well as C=C mode even after the FE is converted to the geometrically relaxed state within 100 fs. This clearly demonstrates that the full geometrically relaxed butatriene-type structure is not formed; instead, it can still be described by the acetylene-type structure with small admixture of butatriene-type configuration. The frequencies of C=C and C≡C stretching modes in the geometrically relaxed $2\,^1A_g$ state were determined to be 1472 ± 6 and 2092 ± 6 cm^{-1}, respectively. The corresponding frequencies in the ground state were calculated as 1463 ± 6 and 2083 ± 6 cm^{-1}. Each of the former is higher by about 10 cm^{-1} than each of the latter.

ACKNOWLEDGMENTS

This research was supported partly by the Grant-in-Aid for Specially Promoted Research (No. 14002003) and also 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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