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Takayoshi Kobayashi, Haibo Wang, Zhuan Wang, and Tetsuo Otsubo

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Confined breather-type excitation in a quinoidal thiophene after sub-5 fs pulse excitation

Takayoshi Kobayashi^{a)}

Department of Physics, University of Tokyo, Hongo 7-3-1, Bunkyo, Tokyo, 113-0033, Japan;
Institute of Laser Engineering, Osaka University, Ibaraki 567-0047, Japan; and Department
of Electrophysics, National Chiao Tung University, Hsinchu 300, Taiwan

Haibo Wang and Zhuan Wang

Department of Physics, University of Tokyo, Hongo 7-3-1, Bunkyo, Tokyo, 113-0033, Japan

Tetsuo Otsubo

Department of Applied Chemistry, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

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A quinoidal thiophene molecule which is a prototype of the repeated unit of *s-trans-cis*-polyacetylene was studied by sub-5 fs spectroscopy. A breatherlike mode modulation of both the amplitude and frequency of the C=C stretching was observed for the first time. It generates two sidebands of 2238 and 700 cm⁻¹ with a separation of 769 cm⁻¹ corresponding to the modulation frequency. The latter mode is very close to the C-S-C ring deformation, which indicate that this mode mediates coupling between the breather mode and the C_β-C_β stretching mode. It was also found that the breather-type excitation has a longer lifetime (2–3 ps) than in all-*trans*-polyacetylene (50 fs) due to its confinement. © 2006 American Institute of Physics. [DOI: 10.1063/1.2213977]

I. INTRODUCTION

Polyacetylene (PA) is the simplest π -conjugated polymer that consists of a CH chain and is regarded as a prototype of quasi-one-dimensional electronic system. All-*trans*-polyacetylene (*t*-PA) has especially attracted a lot of interest because of nonlinear excitation such as soliton formation, which originates from its twofold degeneracy of the ground states.¹ The soliton formation is related to anomalous (10¹³-fold) increase in conductivity by chemical doping.² According to the simulation performed using the Su-Schrieffer-Heeger (SSH) Hamiltonian,³ a photogenerated electron-hole (*e-h*) pair evolves into a soliton-antisoliton ($S\bar{S}$) pair within 100 fs following photoexcitation because of the barrier-free relaxation in the one-dimensional system. It was resolved to be as short as about 60 fs in our previous paper.⁴ It has also been theoretically predicted^{5–11} that within this initial time the soliton pair is spatially localized to form a dynamic bound state which is 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.

The breather mode excitations 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.¹² However, no direct evidence was presented in the paper either due to the limited time resolution. In our previous paper,⁴ 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 this letter, we could, for the first time, observe a breatherlike excitation in a quinoidal-type thiophene derivative which is a good model for studying nonlinear excitation in an *s-trans-cis*-polyacetylene. The breather was found to be formed more stable than in all *trans*-polyacetylene because of the confinement in a short polyene structure of the quinoid-type thiophene molecule.

II. EXPERIMENT

A sample used in the present study is quinoidal thiophene with push-pull charge-transfer groups. The molecular structure is shown in the inset of Fig. 1. Hereafter the molecule is abbreviated as QT1. The molecule QT1 was dissolved in tetrahydrofuran (THF) solution. The thiophene substitute with an electron-donative 1,3-dithiol-2-ylidene unit and an electron-withdrawing dicyanomethylene unit at the two ends of the molecule.¹³ Because of the quinoidal structure the molecule has a *s-trans-cis*-configuration, and hence it is considered to be a good prototype of a repeat unit in polyacetylene. This is quite different from that of the thiophene oligomer with an aromatic structure containing both *s-trans* and *s-cis* configurations with equal amount.

Both the pump and probe pulses were from a nonlinear optical parametric amplifier (NOPA) seeded by a white-light continuum.^{14–16} The pulse duration of the NOPA output was compressed with a system^{14–16} composed of a pair of prisms and chirp mirrors. The pump source of this NOPA system is a commercially supplied regenerative amplifier (Spectra Physics, Spitfire), whose central wavelength, pulse duration, repetition rate, and average output power

^{a)}Electronic mail: kobayashi@ils.uec.ac.jp

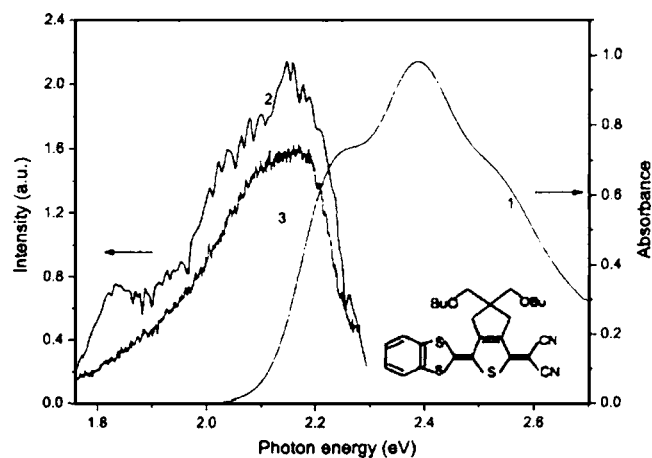


FIG. 1. The absorption, fluorescence spectra of the thiophenes and sub-5 fs laser spectra. Curve 1: absorption spectra of the thiophene; curve 2: sub-5 fs NOPA output spectrum; and curve 3: fluorescence spectrum of the thiophenes excited at 470 nm. Real-time vibrational.

were 790 nm, 50 fs, 5 kHz, and 800 mW, respectively. A typical visible near infrared pulse was slightly 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 were nearly Fourier-transform limited. The pulse energies of the pump and probe were about 35 and 5 nJ, respectively. All the measurements were performed at room temperature (295 ± 1 K).

III. RESULTS AND DISCUSSION

The absorption and fluorescence spectra are shown in Fig. 1 together with the sub-5 fs NOPA output spectrum. The molecule QT1 is considered to be a good model compound of short polyene with one dimensionality such as polyacetylene and polythiophene. Especially the quinoidal structure of the molecule QT1 can be regarded as a short model of an *s-trans-cis*-polyacetylene oligomer only with three C=C double bonds organized in a *cis* configuration. The molecule is stable and more suited to be studied by femtosecond spectroscopy than short polyene such as hexatriene or retinal, the stability of QT1 is the result of the ring structure which is absent in the polyene oligomers as in the case of hexatriene. All short polyenes are very unstable and easily degraded both by ultraviolet radiation and by thermal process. It is also extremely difficult to isolate isomers from the mixtures chemical synthetically prepared or extracted from natural materials.

Figure 2 depicts the eight traces in the range of probe photon wavelength (energy) from 623 nm (1.988 eV) to 634 nm (1.954 eV) of the sub-5 fs pump-probe induced absorbance changes for QT1 in THF solution. The Fourier spectra of traces are shown on the right side of the figure. They show several characteristic features. The most intense peak is located at 1469 cm^{-1} and there are three mode relatively high intensity peaks at 1607, 1379, and

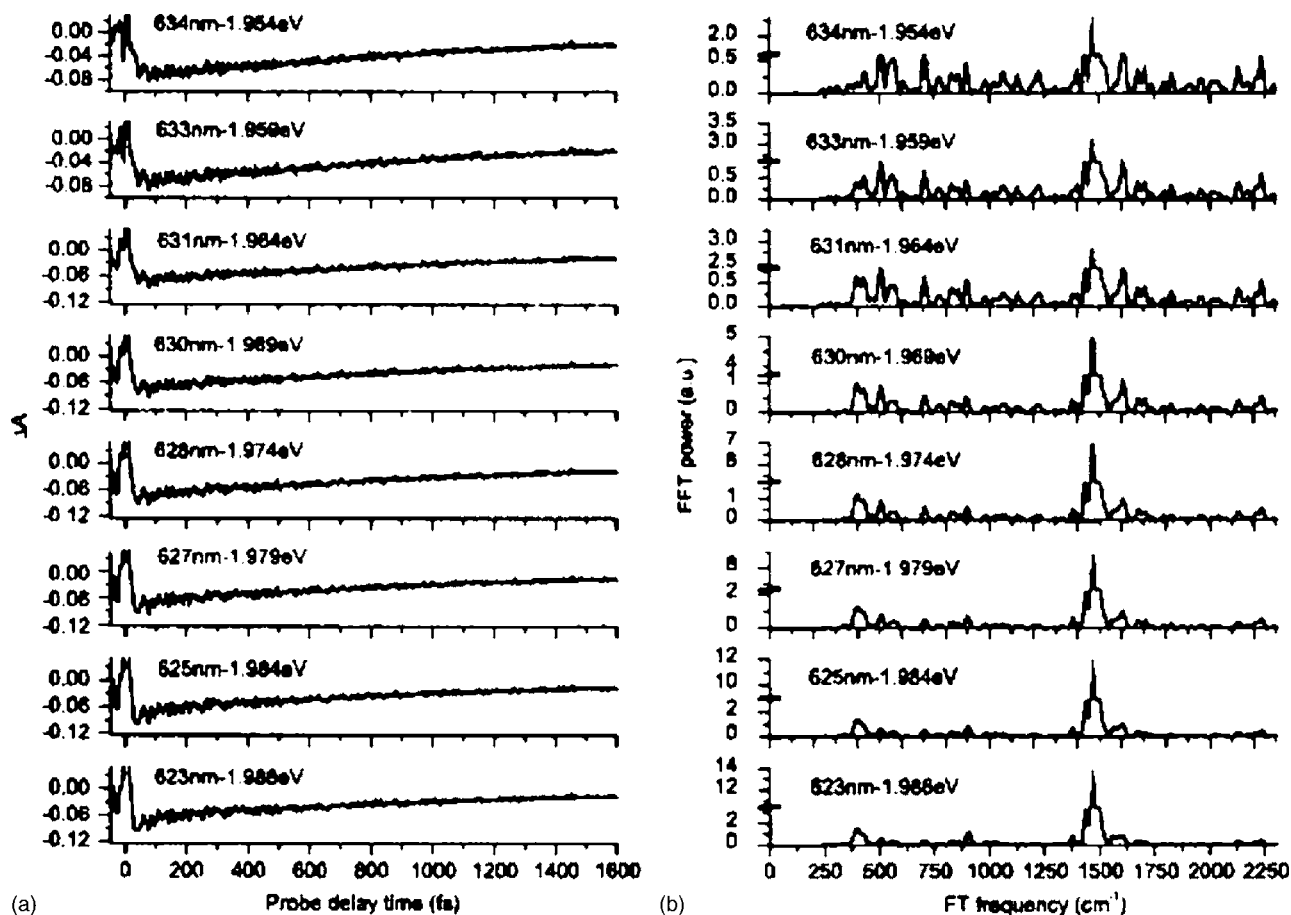


FIG. 2. Real-time vibrational spectra and FT power spectra of molecular vibration at eight different probe wavelengths. (a) The change in the absorbance as a function of pump-probe delay time at various probe photon energies and (b) the (FFT) power spectra of real-time vibrational spectra at the corresponding probe energies.

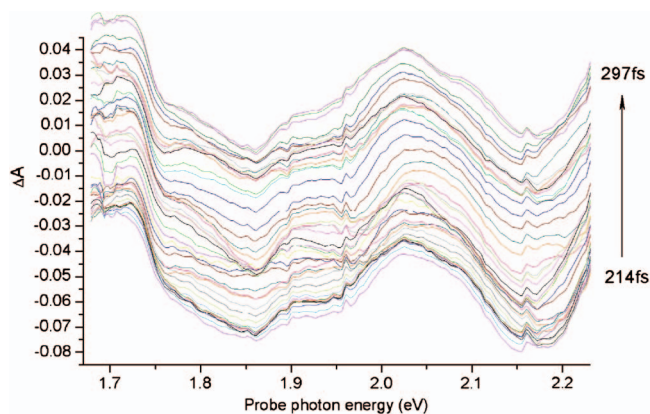


FIG. 3. (Color) The time-resolved pump-probe spectra probed at 48 delay-time points between 214 and 297 fs with a time step of 1 fs from 214 to 224 fs and a 2 fs step from 225 to 297 fs.

700 cm^{-1} . From the Raman spectrum measured for the thiophene, some of them could be assigned as described later.

Figure 3 shows the time-resolved pump-probe spectra probed at 48 delay-time points between 214 and 297 fs with a time step of 1 fs from 214 to 224 fs and a 2 fs step from 225 to 297 fs. The scale on the left axis is for 214 fs and for each time step the absorbance is upshifted by 0.0017.

Figure 4 shows the two-dimensional power distribution of the molecular vibration coupled to the electronic transitions. There are several intense peaks whose frequencies appear in the spectral range between 2.05 and 1.90 eV as shown in the figure. Among these modes 911 cm^{-1} was attributed to the totally symmetric ring breathing mode in the solvent THF molecule. There is a very high frequency mode at 2238 cm^{-1} , which could be assigned to the carbon-nitrogen triple bond stretching according to the molecular structure in the present study. The other frequency components were attributed in our previous paper using assignment in the literature,^{17,18} antisymmetric $C_{\beta}-C_{\beta}$ stretching (1667 or 1603 cm^{-1}), $C_{\beta}-C_{\beta}$ symmetric stretching (1469 cm^{-1}), $C_{\alpha}-C_{\beta}$ stretching (1379 cm^{-1}), and C-S-C ring deformation (700–704 cm^{-1}) modes. There are several other modes at

1590, 1558, 565, 505, 430, and 394 cm^{-1} . The first two modes are two modes of C-C stretching. It is very difficult to assign the other mode. Among them 1590, 565, and 394 appear also at 1600, 560, 406 cm^{-1} , respectively in Raman spectrum excited at 488 nm.

There are two modes of interest in Fig. 4 even though they are relatively weak at 2238 and 700 cm^{-1} . The frequency difference between the former 2238 cm^{-1} and the C=C ($C_{\beta}-C_{\beta}$) stretching mode at 1469 cm^{-1} is 769 cm^{-1} . The difference between the stretching mode frequency of 1469 and 700 cm^{-1} is again 769 cm^{-1} in a good agreement with the above difference frequency between the former and the high frequency mode at 2238 cm^{-1} . The value is very close to the modulation frequency of C-C single and C=C double bonds appearing as sidebands or the stretching modes due to the breather modes. The widths of these modes at 2238 and 700 cm^{-1} are about 13 and 11 cm^{-1} , respectively. This means that the duration times of 2238 and 700 cm^{-1} are 2.5 and 3 ps, respectively, assuming the decay being exponential.

Figure 5 shows dependence of FT powers of the modes of 2238 and 700 cm^{-1} on the probe photon energy. Both of them are peaked around 1.96 eV and similar full width of half maximum of about 80 meV. In the figure the difference spectra between the difference absorption spectrum at 214 and at 297 fs was also shown. The time between them is 83 fs and it corresponds to the odd integer (11) multiple of the half period (7.45 fs) of the mode with frequency of 2238 cm^{-1} . This pair of difference absorption spectra was selected to extract the maximum spectral change taking place in this molecular vibration. The three spectra are quite similar among themselves and it shows that the two modes are strongly correlated in the probe wavelength dependence indicating that the two modes are working together to change the electronic spectra. These two are the sidebands generated by the modulation of 1469 cm^{-1} C=C stretching mode and modify together the spectrum in the range between 1.90 and 2.02 eV. This modulation can be due either to amplitude modulation and/or frequency modulation of the 1469 cm^{-1} mode. In the case of amplitude modulation, upper and lower

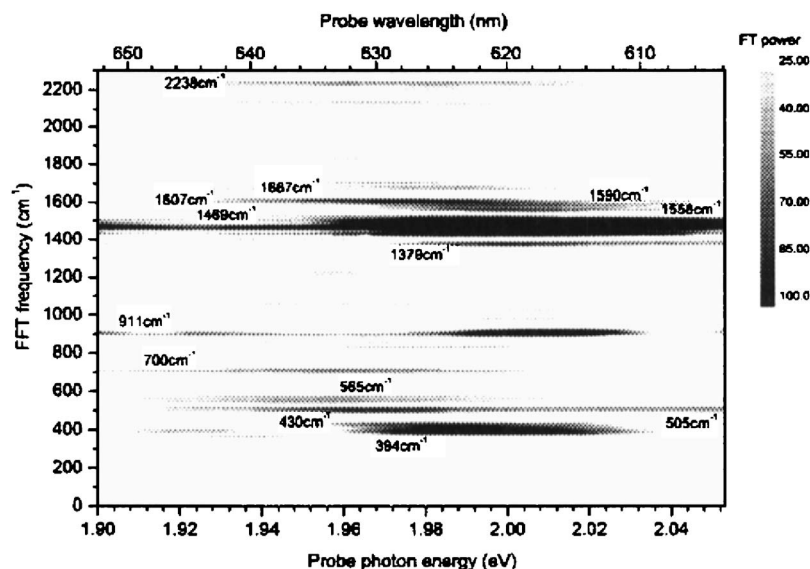


FIG. 4. The two-dimensional power of the molecular vibration coupled to the electronic transitions.

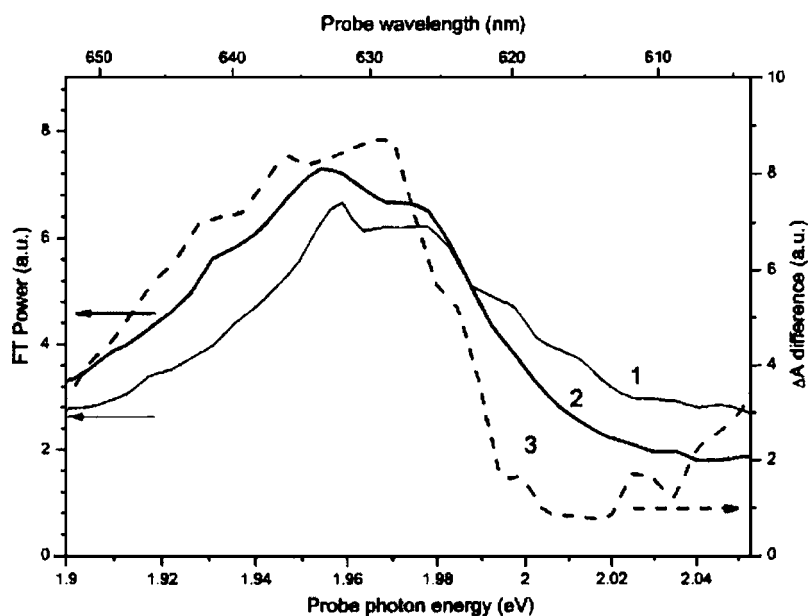


FIG. 5. The probe photon energy dependence of FT powers at 2238 and 700 cm^{-1} . Curve 1: 700 cm^{-1} mode; curve 2: 2238 cm^{-1} mode; and curve 3: the difference between the absorption spectrum at 214 fs and that at 297 fs.

sidebands separated from main band (1469 cm^{-1}) by 769 cm^{-1} are theoretically expected to have the same sign with the same amplitude. While in the case of frequency modulation, they are calculated to have opposite signs with the same size associated with higher order overtones with alternative signs. Therefore if both of the amplitude and phase modulations take place in the C=C stretching mode at 1469 cm^{-1} , the intensities of the higher frequency (2238 cm^{-1}) and the lower frequency (700 cm^{-1}) are imbalanced, depending on the amount of the two contributions. From the intensity ratio of the higher and lower bands after correction of the detection band width due to limited time resolution, the contribution of the amplitude modulation and the phase modulation was calculated to be 3:1.

The frequency of lower sideband is 700 cm^{-1} and it is very close to the C-S-C ring deformation mentioned earlier with frequency of $700\text{--}704 \text{ cm}^{-1}$. It is highly probable that this mode is in the resonance with the breather mode and mediate coupling between the breather and the $C_{\beta}\text{--}C_{\beta}$ stretching mode.

The lifetimes of the two sidebands are similar as mentioned before. The upper band has a lifetime of about 2.5 ps and the lower one has a duration time of about 3.0 ps. The small difference between the lifetime may be due to the difference in the duration of frequency and amplitude modulation. The lifetimes are relatively long while in the case of all *trans*-polyacetylene the lifetime was determined to be as short as $50 \pm 10 \text{ fs}$.⁴ This lifetime is due to the rapid formation of soliton-antisoliton pair in all *trans*-polyacetylene. In the present system the long life time is due to the incapability of a pair of solitonlike excitations to be dissociated due to the very limited length of short polyene (triene).

THF is a solvent with high polarity so it may affect the nonlinear excitation of the breather mode, soliton, and/or bipolaron generation. The interaction between the polar solvent and the solute molecule after excitation is expected to be highly relevant to the formation process. Such experiment is being planned to be performed in near future.

In conclusion we found for the first time a breatherlike

excitation in a quinoidal short polyene (triene). The breatherlike excitation modulates both amplitude and frequency of C=C stretching mode as in all *trans*-polyacetylene. It generates upper and lower frequency sidebands with the separation of 769 cm^{-1} corresponding to the modulation frequency. This frequency is very close to that (760 cm^{-1}) found in all *trans*-polyacetylene. The breatherlike excitation has much longer lifetime (2–3 ps) than in all *trans*-polyacetylene (50 fs) due to its confinement.

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