

# Real-time vibrational mode-coupling observed using a few-cycle pulse laser

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We observe the instantaneous frequency and amplitude modulations of the C–C stretching mode with a central frequency of  $1343\text{ cm}^{-1}$  in a poly (substituted thiophene) using 6.3 fs laser pulses by the method of real-time vibrational spectroscopy. Spectrogram analysis shows that both amplitude and instantaneous frequency of the mode with a central frequency of about  $1343\text{ cm}^{-1}$  are modulated. Both modulation frequencies are found to be  $120\text{--}130\text{ cm}^{-1}$ , which provides evidence of dynamical coupling between a stretching mode and another stretching mode mediated by a low-frequency bending mode.

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Polythiophenes have significant potentials in the development of electronic devices such as field-effect transistors, solar cells, batteries, and diodes<sup>[1,2]</sup>. Over the last three decades, continuous attention has been paid to polythiophene and its derivatives because of their significant potential applications<sup>[3–8]</sup>. Detailed understanding of the dynamics of their photoexcitations is highly desired for practical reasons. However, most of the morphology of conjugated polymer systems is amorphous except for a few polymers. Therefore, such amorphous polymers have highly inhomogeneous electronic states due to the distributed degrees of polymerization and conjugation lengths. Additionally, the relaxation dynamics of electronic states are very complicated due to the different dynamics in their inhomogeneous surroundings. They are also expected to be inhomogeneous in their vibrational properties. Therefore, the relaxation dynamics of electronic states coupled to vibrational levels are considered to be very complicated because of the various contributions of the inhomogeneous systems to the relaxation mechanisms depending on the properties of electronic states and vibrational levels.

To excite the molecular coherent vibration in the time domain, the basic requirement for the pump laser pulse is for the pulse duration of the optical pump pulse to be shorter than the vibration period. For example, a laser pulse with a 10-fs duration is capable of exciting the coherent vibration frequency smaller than  $3000\text{ cm}^{-1}$ . Therefore, the few-cycle laser pulse is highly desirable in the study of real-time vibration spectroscopy. In addition, to disentangle the complexity of decay dynamics in the inhomogeneous systems mentioned above, measuring the two dynamics at the same time using both same light source and detection system is more advantageous. Generally, however, the electronic relaxation dynamics is studied by conventional pump-probe experiments, degenerate four-wave mixing, and several other

methods such as pulsed light pump-photoacoustic probe. Vibrational relaxation has been mainly studied by time-resolved Raman scattering spectroscopy or time-resolved infrared absorption spectroscopy. In these experiments, most frequently, an ultraviolet or visible pump pulse generates excited states or starts a photochemical reaction, and a probe pulse detects the change in the Raman or Infrared (IR) spectrum and/or intensity<sup>[9–11]</sup>. In the present experiment, simultaneous measurement of electronic relaxation and vibrational dynamics in a broad spectral range were performed in a quinoid-benzenoid polythiophene by the femtosecond pump-probe real-time spectroscopy technique.

A noncollinear optical parametric amplifier (NOPA) seeded by a white-light continuum was used as a light source for both pump and probe pulses<sup>[12–14]</sup>. The pump source of this NOPA system was a commercially supplied regenerative amplifier (Spectra Physics, Spitfire), whose central wavelength, pulse duration, repetition rate, and average output power were 800 nm, 50 fs, 5 kHz, and 650 mW, respectively. Pulse duration of the NOPA output was compressed with a system composed of a pair of Brewster angle prisms that have an apex angle of  $68^\circ$  and chirp mirrors. A typical visible near IR pulse with a pulse duration of 6.3 fs covered the spectral range extending from 515 to 716 nm (Fig. 1), which indicates that the pulses were nearly Fourier-transform limited. Pulse energies of the pump and probe were typically about 50 and 6 nJ, respectively.

The pump-probe signal was detected by the combination of polychromator and multi-channel lock-in amplifier. The probe signal was measured at pump-probe delay times from  $-200$  to  $1800$  fs with a spectral resolution of 1.5 nm. In the present experiment, we used a high time resolution electronic stage to achieve the probe signal with a delay time step of 0.2 fs. The sample studied here is a poly [(3-hexylthiophene-2,5-diyl)-(p-

dimethylaminobenzylidenequinoidmethene)] (PHTDMA BQ), whose monomer is a derivative of a thiophene molecule. Stationary absorption and fluorescence spectra of PHTDMABQ were measured with an absorption spectrometer (Shimadzu, UV-3101PC), as shown in Fig. 1. PHTDMABQ was dissolved in methanol and cast on a quartz substrate for the measurement of stationary and time-resolved spectra.

Real-time absorbance change  $\Delta A(t, \omega)$  traces shown in Fig. 2 (a) were analyzed using global fitting as functions of probe delay time  $t$  and probe frequency  $\omega$  by

$$\Delta A(t, \omega) = a(\omega)e^{-t/\tau_1} + b(\omega)e^{-t/\tau_2} + c(\omega)e^{-t/\tau_3}. \quad (1)$$

Here,  $a(\omega)$ ,  $b(\omega)$ , and  $c(\omega)$  represent the signal amplitude parameters of each probe photon energy, and  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$  denote the time constants we are interested in. The values of these three time constants are obtained as  $\tau_1 = 62 \pm 2$  fs,  $\tau_2 = 750 \pm 20$  fs, and  $\tau_3 \gg 3$  ps. The relaxation dynamics can be interpreted in the following way, as shown in Fig. 2(c). Just after the excitation to the higher vibrational level of the lowest excited electronic state  $S_1$  corresponding to the Franck-Condon state ( $S_1^{\text{FC}}$ ), the first step is the relaxation to the geometrically relaxed state ( $S_1^{\text{GR}}$ )<sup>[15]</sup>, which is the exciton polaron or sometimes called self-trapped exciton (STE), in the relaxation time of  $\tau_1 = 62 \pm 2$  fs. The second relaxation step is the thermalization to a state named as  $S_1^{\text{Th}}$  with time constant of  $\tau_2 = 750$  fs. The third process follows decay into the distributed higher vibrational levels in the ground electronic state followed by decaying to  $S_0$  and/or in the lowest triplet state  $T_1$  state with a much longer time than 3 ps.

To discuss the vibrational dynamics during relaxation processes, we calculated the Fourier powers of molecular vibration modes coupled to the probed electronic transition as shown in Fig. 2(b). There are three prominent peaks at 1111, 1343, and 1465  $\text{cm}^{-1}$ . The highest, medium, and lowest frequencies are considered to correspond to modes with the largest contribution of C=C double bonds, medium contributions of both double and single bonds, and the largest contribution of C-C single bonds, respectively.

To utilize real-time trace in the vibrational dynamic study, we calculated the spectrograms. A 2D plot of the

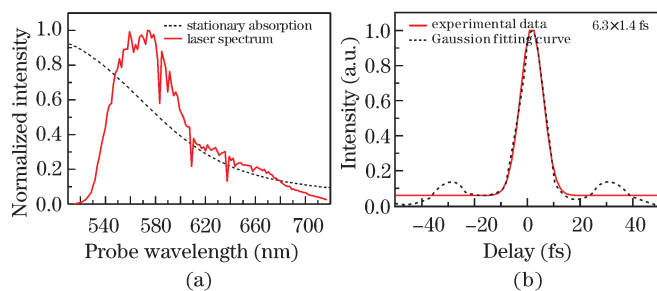


Fig. 1. (a) Stationary absorption spectrum of the PHTDMABQ and the NOPA laser spectrum; (b) Typical intensity autocorrelation of the laser pulse. The experimental data are shown by the solid curve, and the Gaussian fitting curve by the dotted line.

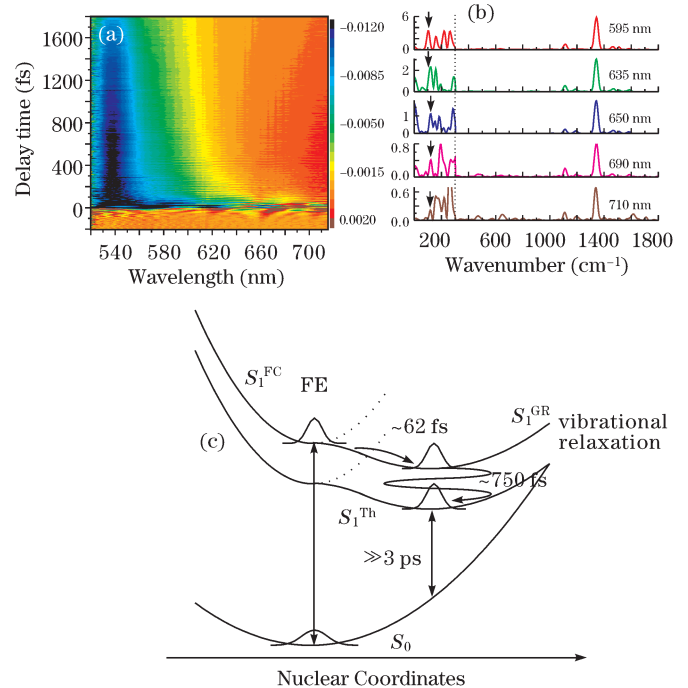


Fig. 2. (a) Two-dimensional (2D) real-time absorbance change; (b) Fourier power spectra at 5 random wavelengths; (c) Model of the relaxation dynamics.

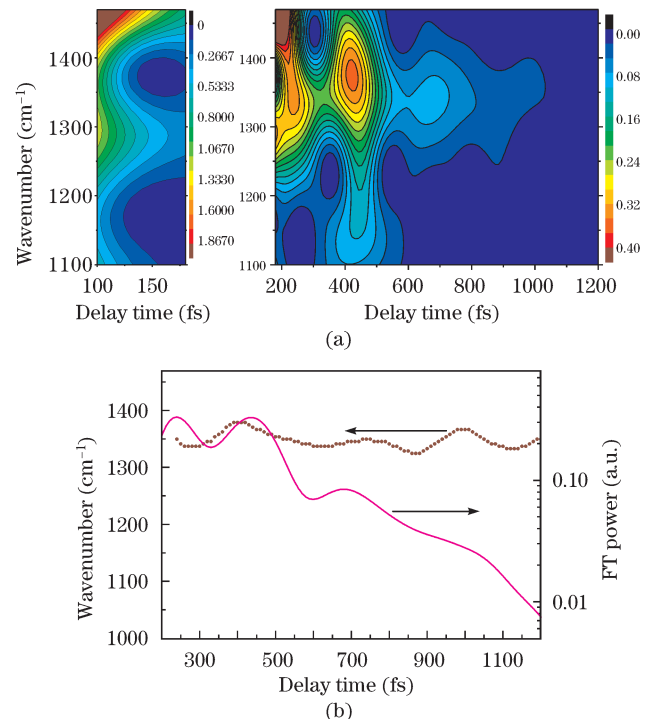


Fig. 3. (a) Contour plot of the 2D spectrogram calculation for real-time vibrational traces probed at 635 nm; (b) Peak track of the frequency modulation (dotted line) and that of the integrated intensity (solid line).

spectrogram is shown in Fig. 3(a). Both the instantaneous frequency and the amplitude are clearly modulated for the C-C stretching mode at 1343  $\text{cm}^{-1}$ . The modulation trace of frequency together with that of the integrated amplitude is depicted in Fig. 3(b). After taking

their fourier transform (FT), the modulation frequencies of  $122\pm 6$  and  $130\pm 10$   $\text{cm}^{-1}$  were obtained for frequency and amplitude modulation, respectively.

In our previous works, we have observed the similar phenomena of instantaneous frequency modulation for bacteriorhodopsin (bR<sub>568</sub>) and polydiacetylene (PDA)<sup>[16,17]</sup>. In the former work, the modulation frequency was calculated to be  $160$   $\text{cm}^{-1}$  from the FT calculation, which correspond to about 200-fs oscillation period. This can be attributed to the twist mode around the C=C bond. As for PDA, the frequencies of C=C and C-C stretching modes are modulated at the vibrational period of the C=C-C out-of-plane bending mode (145 fs) for  $\sim 2$  ps. Therefore, in the present letter, the bending is a candidate of the observed low-frequency mode in our quinoid-benzenoid polythiophene. This bending mode could be attributed to the C-C=C out-of-plane bending or chain-deformation mode<sup>[18,19]</sup>. The latter chain-deformation mode is considered to involve the out-of-phase translation of adjacent thiophene monomer units. In Ref. [18], the frequency of the deformation mode observed in tetrathiophene was reported to be  $160$   $\text{cm}^{-1}$ . However, the decreasing frequency of this mode was expected when the number of thiophene rings increased. Therefore, the deformation mode with the lower frequency of either  $122$  or  $130$   $\text{cm}^{-1}$  than  $160$   $\text{cm}^{-1}$  in the polymer with many more thiophene rings and longer conjugation lengths is another possible candidate of the modulation mode with  $120$ – $130$   $\text{cm}^{-1}$ .

If the observed modulation is due to the bending mode, it is expected to appear in real-time traces. As we expanded the FT power below  $300$   $\text{cm}^{-1}$  in Fig. 2(b), a low frequency located at  $114$ – $122$   $\text{cm}^{-1}$  could be observed at all the probe wavelengths, which is considered to correspond to  $122$  or  $130$   $\text{cm}^{-1}$ . The difference between the values is caused by possible errors due to a too small cycle number in real-time traces in order to obtain its precise frequency. The existence of this low frequency mode provides evidence that the modulation is caused not by the artificial interference during spectrogram calculation but by mode coupling with bending modes. The mode coupling between the C-C stretching mode and the bending mode is maintained until the vibrational dephasing destroys the coherence of relevant modes.

Modulations of both instantaneous vibrational frequency and amplitude were observed for the C-C stretching mode with the central frequency of  $1343$   $\text{cm}^{-1}$  in a polythiophene thin film. Spectrogram analysis shows that both amplitude and instantaneous frequency of the mode are modulated. Both the modulation frequencies were found to be  $120$ – $130$   $\text{cm}^{-1}$ , which provides evidence of the dynamical coupling between a stretching mode and another stretching mode mediated by a low-

frequency bending mode.

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