

Sub-5-fs spectroscopy of a thiophene derivative with a quinoid structure

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Abstract

Sub-5-fs spectroscopy of a thiophene derivative with an electron donative and an acceptive moieties and quinoid structure provided the experimental evidence of dynamic mode coupling. It was shown that two out-of-plane bending modes mediate the dynamic mode coupling between 1469 and 1379 cm^{-1} and between 1603 and 1469 cm^{-1} . These couplings are considered to be associated with geometrical relaxation relevant to the neutral bipolaron formation in all-*s-trans* polyacetylene.

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1. Introduction

Thiophene-based oligomers have been extensively studied theoretically and experimentally for a better understanding of physical properties of polythiophene, which has been one of most popular conjugated polymers since 1990's [1–11]. They are also promising materials for various devices [7,12–15], such as light-emitting diodes [16–18].

Vibrational spectroscopy has shown [8] that polythiophenes contain all-*s-trans* sequences of thiophene rings linked at α - and α' -positions with a distribution of sequential lengths, so-called the conjugation length. The distribution of conjugation lengths has been ascribed to the existence of disordered structures in the polymer chain. Since polythiophene has a nondegenerate ground state, the optical properties of doped polythiophene have been discussed in terms of polarons and bipolarons [10,11], which are self-localized excitation in conjugated polymers. A positive polaron (a radical cation in chemical terminology) is created when an electron is removed

from a polymer chain by acceptor doping. The charge $+e$ and spin $1/2$ are localized over several thiophene rings with geometrical changes. If another electron is removed from the chain, a positive bipolaron corresponding to a dication, $+2e$, but without spin is formed. The electronic state of polarons and bipolarons have been discussed mainly in the framework of theories incorporating electron-lattice interaction [10,11]. It is of interest to study the processes following the creation of electron and hole by photoexcitation. It may generate a bound pair of the opposite charge forming exciton and relax to a self-trapped exciton or the pair may be separated into oppositely charged geometrically relaxed localized excitation, namely two oppositely charged polarons. Experimental studies have been made on the vibronic coupling in thiophene oligomers with electron-donating and accepting groups attached to the oligomer to explore the effect of charge on the branching ratio of neutral bipolaron (which is equivalent to self-trapped exciton) and two charged polarons with opposite charges separated from each other [1,11,12].

In the present study, we have performed sub-5-fs spectroscopy of a derivative of quinoidal thiophene (Fig. 1) and found that this molecule is a good model as a repeat unit of polythiophene with all-*s-trans* conformation.

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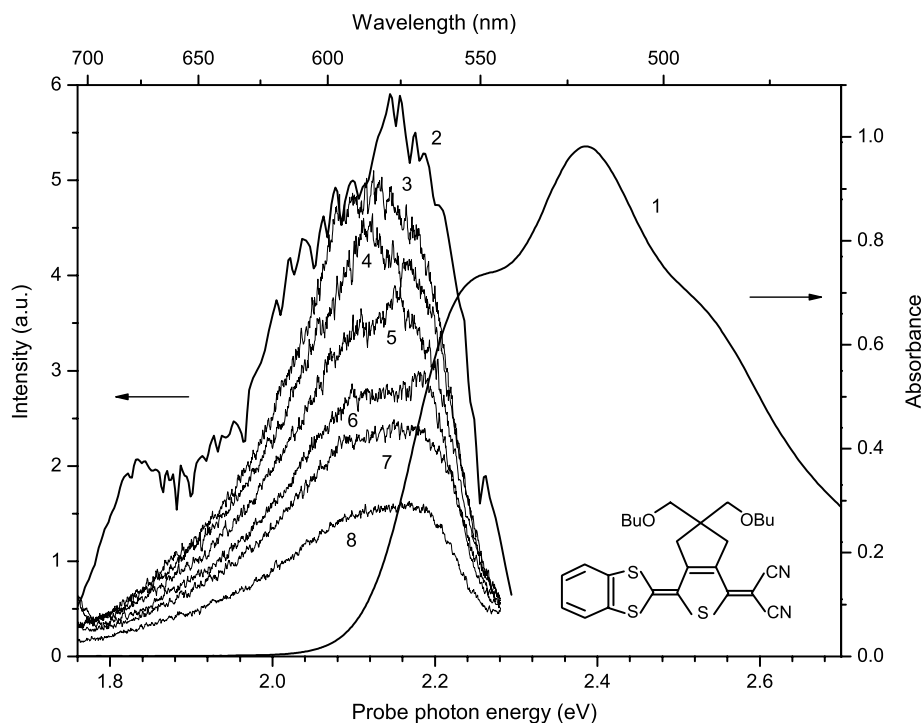


Fig. 1. Electronic spectra of QT1: (1) absorption spectrum, (2) output spectrum sub-5 fs NOPA laser, and fluorescence spectra excited at (3) 530, (4) 520, (5) 510, (6) 500, (7) 480, and (8) 470 nm.

2. Experimental

The sample used in the present study is a novel synthesized quinoidal thiophene with push-pull charge-transfer groups [19,20], abbreviated as QT1, dissolved in tetrahydrofuran (THF) solution. This thiophene substitute has an electron-donating 1,3-dithiol-2-ylidene unit and an electron-withdrawing dicyanomethylene unit at the terminals. Because of the quinoidal structure, this molecule has an all-*s-trans cis* polyacetylene configuration, and hence it is a good prototype of a repeat-unit in polyacetylene. This is quite different from that of thiophene oligomer with an aromatic structure containing *s-trans* and *s-cis* configurations.

The pump and probe pulses were both produced from a noncollinear optical parametric amplifier (NOPA) seeded by a white-light continuum [21–23]. The pulse of the NOPA output was compressed with a system composed of a pair of prisms and chirp mirrors [21–23]. The pump source of this NOPA system was a regenerative amplifier (Spectra Physics, Spitfire) with central wavelength: 790 nm, pulse duration: 50 fs, repetition rate: 5 kHz, and average output power: 800 mW. 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).

3. Results and discussion

3.1. Fourier analysis of vibrational signals

Fig. 1 shows the absorption and fluorescence spectra, and the output spectrum of the sub-5 fs NOPA laser. The fluorescence spectra, 3–8, change with the excitation wavelength. This is ascribable to reabsorption, which reduces the fluorescence intensity in the shorter wavelength range when excited at a longer wavelength. The fluorescence peak shifts from 500 to 580 nm when the excitation wavelength is moved from 470 to 530 nm. This is because the absorption depth for a longer wavelength excitation is deeper so that the effect of reabsorption is more serious.

Fig. 2a shows the change in the absorbance as a function of the pump–probe delay time at various probe photon energies. The signals are composed of slow dynamics and highly oscillating signals. The former and the latter are mainly assignable to the electronic and vibrational dynamics. However, the slow dynamics have a little complicated feature, namely, they seem to be composed of very slow oscillation with an oscillation half period as long as 1 ps. It is hard to determine the vibrational decay time, because the low vibrational mode corresponds to ≈ 16 cm^{-1} . Highly oscillatory signals exist up to 600 fs after excitation. The results of our Fourier transform (FT) analysis of these oscillatory signals are shown in Fig. 2b. This FT analysis was performed after averaging over 100 fs to remove the slow decay dynamics due to those in the relevant electronic states. There are two distinct components at 1469 and

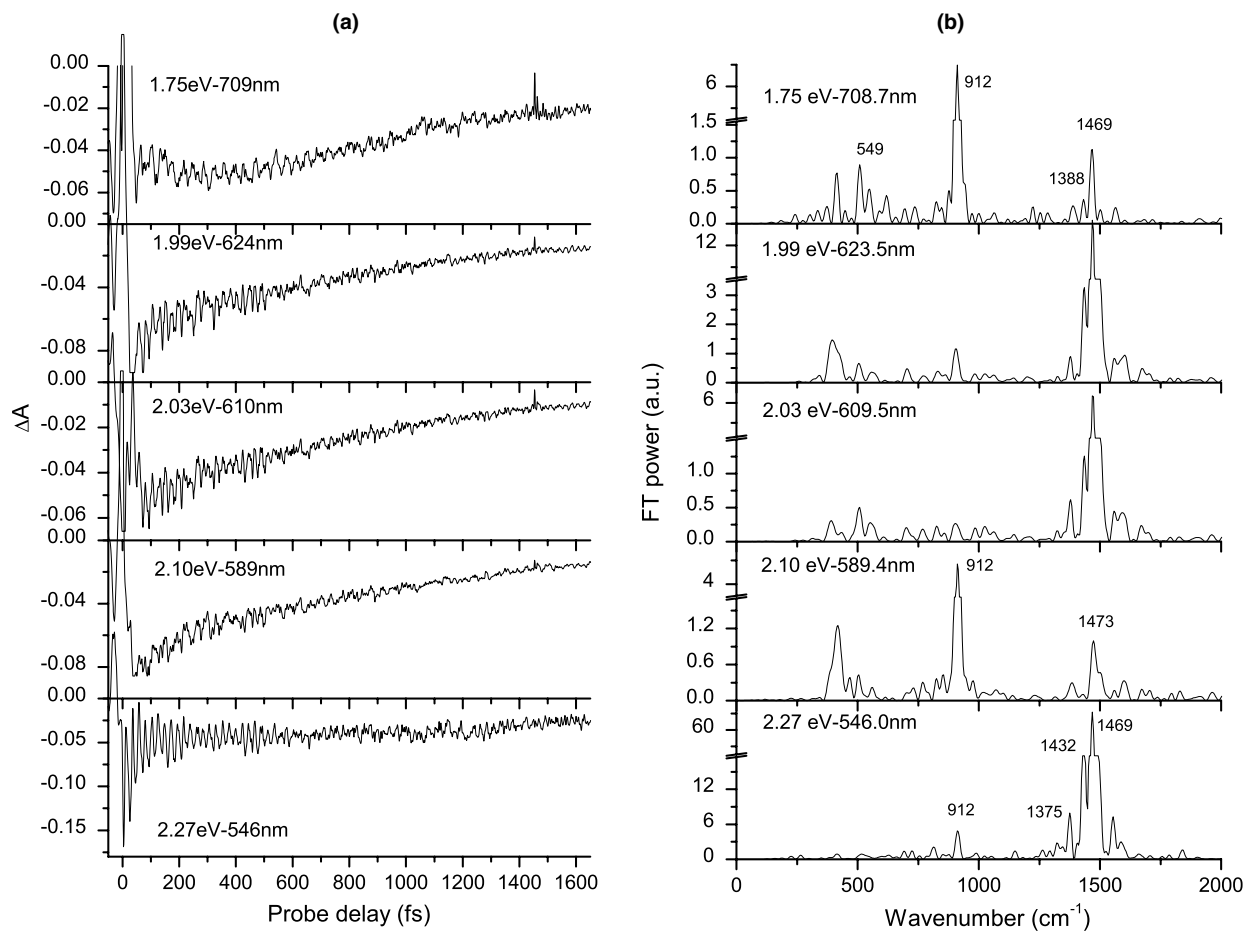


Fig. 2. Real-time vibration spectra and FT power spectra of the vibrations of QT1 at five different probe wavelengths: (a) changes in the absorbance vs. the pump-probe delay time and (b) Fast FT (FFT) power spectra of real-time vibration spectra.

911 cm^{-1} . Since the latter one also appears for the sample without the solute molecule, it can be attributed to the solvent molecule of THF [24]. The former one, assigned to the C–C stretching mode, is also found in the Raman spectra excited with 488 nm , near-resonant to the electronic transition of $S_1 \leftarrow S_0$.

At probe wavelengths (photon energies) of 709 nm (1.75 eV) and 589 nm (2.10 eV), a very intense peak appears at 911 cm^{-1} . This peak also appears in the Raman spectrum at the same wavenumber, as shown in Fig. 3. This corresponds to the totally symmetric breathing mode in the solvent molecule. This mode is the most intense signal in some spectral range, and there are several other modes at 1450 , 1225 , 618 , and 590 cm^{-1} . The FT power spectra provide many modes to be assigned to the QT1 solute instead of the THF solvent molecule. Since the overlap of the laser spectrum and absorption spectrum of QT1 is smaller than 1000 cm^{-1} , the vibrational modes with wavenumbers higher than this are excited only in the ground electronic state. This can also be concluded from the phase of the vibration. The vibrational modes were first assigned using Ref. [25], as summarized below.

The Raman spectrum of regioregular poly(3-decylthiophene) excited at 514.5 nm was studied. The band at

1518 cm^{-1} was assigned to the $C_\alpha\text{--}C_\beta$ antisymmetric mode in the aromatic thiophene ring [26,27]. The band near $1445\text{--}1455\text{ cm}^{-1}$ is due to symmetric $C_\alpha\text{--}C_\beta$ stretching deformations. The band at 1378 cm^{-1} is due to $C_\beta\text{--}C_\beta$ stretching deformations in the aromatic thiophene ring, and the peak at 726 cm^{-1} is due to C–S–C ring deformations.

From the assignment of the vibration modes observed in the Raman spectra, the peaks at $1469\text{--}1473\text{ cm}^{-1}$, $1379\text{--}1375\text{ cm}^{-1}$, and $700\text{--}704\text{ cm}^{-1}$ in the power spectra (shown in Fig. 3a–c) of the real-time data can be attributed to the $C_\beta\text{--}C_\beta$ and $C_\alpha\text{--}C_\beta$ stretching modes and C–S–C ring deformation mode, respectively. The change of the assignment between $C_\alpha\text{--}C_\beta$ and $C_\beta\text{--}C_\beta$ originates from the difference in the π -electron distributions in the aromatic and quinoidal thiophene rings.

3.2. Spectrogram analysis of time dependent vibrations

In order to discuss the dynamics of the interaction among the modes, the spectrograms for the real-time data were calculated with a Blackman window function with a 150 fs window width. The instantaneous wavenumbers and intensities of the peaks are plotted in Fig. 4a, b against the delay time of peak of the Blackman window.

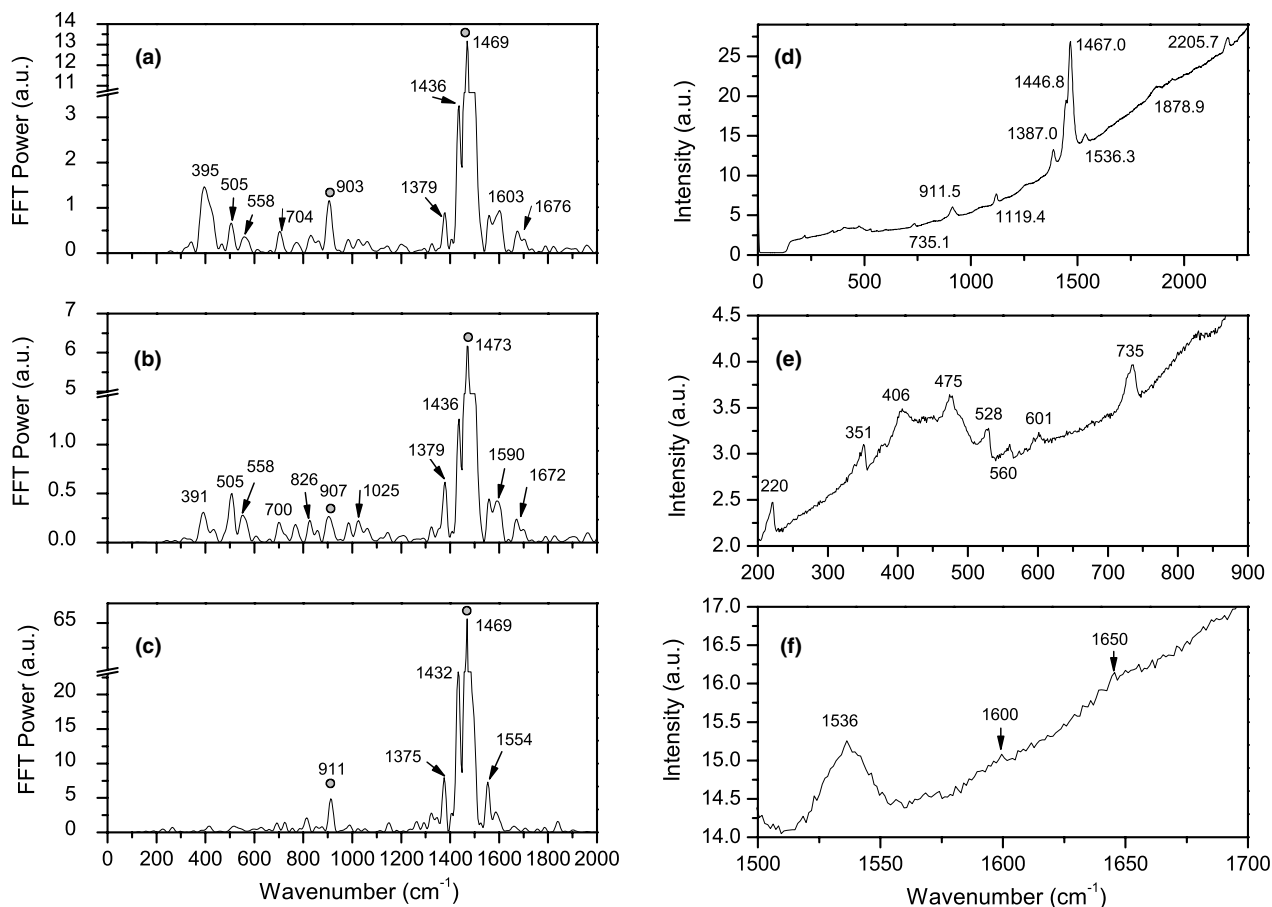


Fig. 3. FFT power spectra and Raman spectra of QT1. FFT spectra probed at (a) 1.99, (b) 2.03, and (c) 2.2 eV; in arbitrary units but mutually comparable, (d) Raman spectra excited at 488 nm, (e) and (f) expanded Raman spectra.

Fig. 5 shows the Fourier power spectra of the molecular vibration real-time signal together with those of wavenumber and intensity modulations of the 1469 cm^{-1} component in the spectrogram at 624 nm below 300 cm^{-1} . In the wavenumber and intensity modulation spectra probed at 624 nm, there are two peaks located at 90 and 182 cm^{-1} , and 130 and 260 cm^{-1} , respectively. The difference in the wavenumbers of 90 and 130 cm^{-1} is very close to that between the peaks at 1469 and 1379 cm^{-1} , and 1603 and 1469 cm^{-1} , respectively. One could argue that the two spectral components within the FT of this window can couple with each other through an artificial interference. Therefore, the observed modulation with frequencies of 90 and 130 cm^{-1} would in principle be ascribed to this artifact.

However, this possibility can be ruled out for the following two reasons:

In the first place, the second harmonic of the modulation wavenumbers at 182 cm^{-1} ($\approx 90\text{ cm}^{-1} \times 2$) and 260 cm^{-1} ($= 130\text{ cm}^{-1} \times 2$) are observed with high intensities. Their ratios, $[I(182)/I(90) = 0.28$ and $I(260)/I(130) = 0.50]$, cannot be expected for ordinary overtones.

The second reason is that the peaks at 90 and 182 cm^{-1} appear only in the intensity modulation whereas those at

130 and 260 cm^{-1} only in the frequency modulation. If they were artificial interferences, these modulations should have appeared simultaneously.

The artifact being ruled out, this behavior can be explained in terms of dynamic mode coupling [28,29]. Experimentally, the two sets of components, (1469 and 1379 cm^{-1}) and (1603 and 1469 cm^{-1}), appear alternatively in the frequency or intensity modulation, as reported above.

It is difficult to assign the modes of the 90 and 130 cm^{-1} vibrations. The presence of the strong overtone indicates that they are out-of-plane bending modes, because the mirror symmetry of the π -electron distribution with respect to the molecular plane and deformation in the out-of-plane mode has a planar configuration in one oscillation period. The two modes of 90 and 130 cm^{-1} can be accounted for in the following way from the above observation. The former mode is probably such that modifies the intensity of 1469 cm^{-1} (the symmetric $C_{\beta}-C_{\beta}$ stretching mode), while the latter modifies the bond order of the $C_{\beta}-C_{\beta}$ bond. The former mode corresponds to the processes in which the symmetric $C_{\beta}-C_{\beta}$ stretching mode couples with the $C_{\alpha}-C_{\beta}$ stretching deformation through the out-of-plane bending mode of 90 cm^{-1} . The latter effect may be

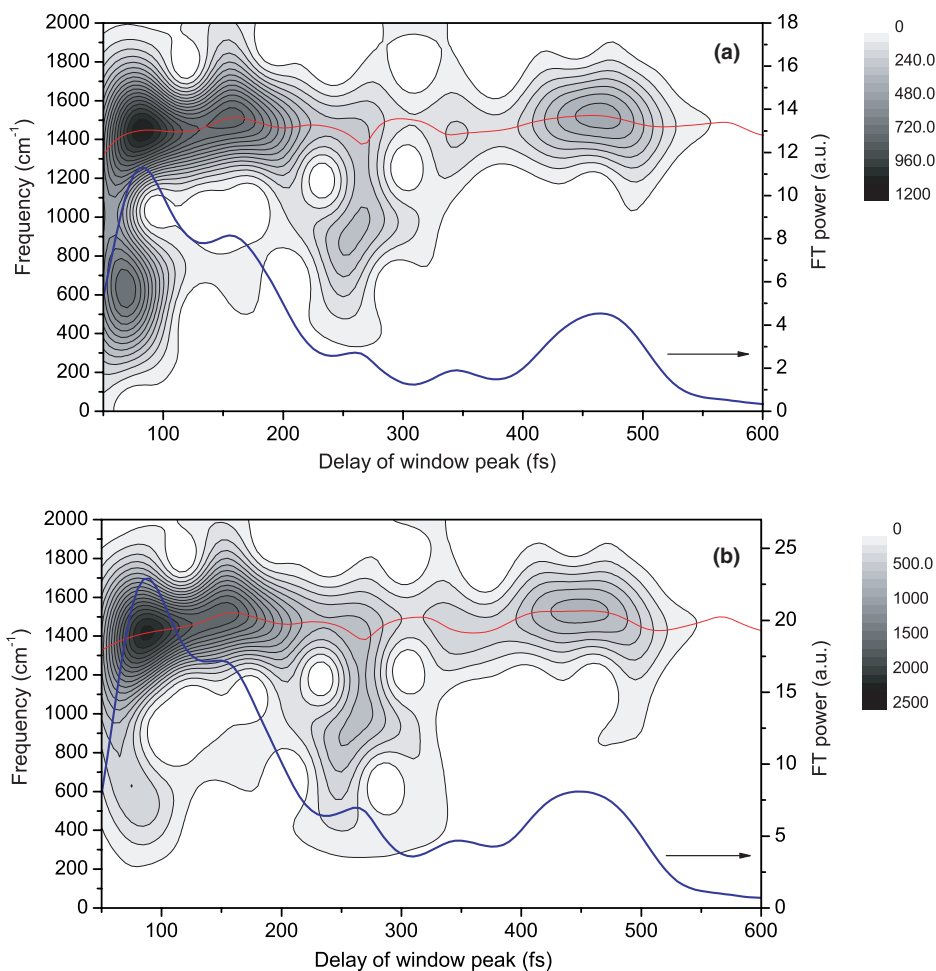


Fig. 4. Contour maps of the spectrograms for the real-time data calculated at 610 nm (a) and 624 nm (b). Thick and thin lines denote intensity and frequency modulations, respectively.

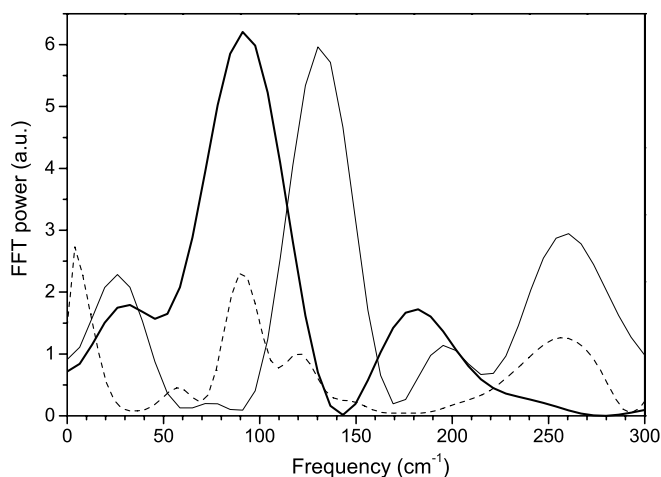


Fig. 5. Fourier power spectra. Thick and thin solid lines denote FT spectra of intensity and frequency modulations, respectively, and dashed line the real-time spectra. All lines were analyzed at the probe wavelength of 624 nm.

rephrased as that the vibration energy is transformed between the symmetric $C_{\beta}-C_{\beta}$ stretching mode of 1469 cm^{-1} and the other mode of 1603 cm^{-1} , which is

probably the antisymmetric $C_{\beta}-C_{\beta}$ stretching mode, through the 130 cm^{-1} out-of-plane bending mode. In both cases, the three modes, ω_1 , ω_2 , and ω_3 , involved in the couplings satisfy the Fermi resonance condition, $\omega_1 + \omega_2 = \omega_3$. A similar effect has been reported for polydiacetylene [1].

In summary, we conclude that the two out-of-plane bending modes mediate the dynamic mode coupling between 1469 and 1379 cm^{-1} and that between 1603 and 1469 cm^{-1} . These couplings are considered to be a model associated with the geometrical relaxation relevant to the formation of nonlinear excitations such as neutral bipolaron (self-trapped exciton, exciton bipolaron) and charged bipolarons in all-*s-trans* polyacetylene.

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