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## The relation between the symmetry of vibrational modes and the potential curve displacement associated with electronic transition studied by using real-time vibrational spectroscopy

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**Abstract.** The relation between the vibronic coupling strength of the vibronic state combined with the optical transitions with short pulses and the symmetry of the coupled vibrational modes was studied by using multi-wavelength vibrational real-time spectroscopy. A pump–probe experiment of thiophene oligomers using 6.7 fs pulsed laser as an ultrashort pulse light source and a multi-channel lock-in amplifier as a broadband detector was performed to obtain simultaneously the real-time traces at 128 wavelengths. At all wavelengths, the absorbance changes were plotted against pump–probe delay time, which was between –200 and 2000 fs. The vibronic coupling in both the ground and excited states was classified into two types: the displaced (D) type with displaced potential surfaces

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and the non-displaced (ND) type with non-displaced potential surfaces between the two electronic studies. The D and ND types were found to be related to inversion anti-symmetric and symmetric molecular vibrations, respectively, with respect to the center of the pseudo-inversion symmetry of the molecule. The symmetry center is located at the middle point of the C=C bond connecting the two quinoid-type thiophene rings. It was shown that multi-wavelength measurement of the vibrational real-time spectroscopy provides information on the mechanism of vibronic coupling in the process of transition from the ground state to the excited state and that between the two excited states.

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## 1. Introduction

For the study of real-time vibrational spectroscopy, an ultrashort few-cycle pulse laser source has been available in the UV, visible and near infrared ranges by using non-collinear phase-matched optical parametric amplification [1]–[9]. Non-collinear optical parametric amplifiers (NOPAs) based on this scheme have been used to generate sub-5 fs pulses [5, 6] and even 4 fs pulses in the visible spectral range [7, 8]. Such ultrashort laser pulses can be applied to the study of vibrational dynamics utilizing the intensity modulation of electronic transition by a wave-packet motion associated with coherent molecular vibration through electron–vibration (vibronic) coupling in a molecule. The mechanism of vibronic coupling has been extensively studied theoretically [10]–[12].

Coherent molecular vibration is well formulated by a time-dependent nuclear wave-packet description. Using the wave-packet description, one may be able to set theoretical bases for models of chemical reaction pathways and geometrical changes associated with the electronic excitations from the experimental results and even predict novel phenomena. In particular, the wave-packet dynamics in the excited states of molecules is important for coherent control of molecular systems [13]–[19]. Under some conditions, vibrational coherence can be generated rather than destroyed during chemical reaction. Real-time spectroscopy can be used to study the mechanism of chemical reactions in such a case [20, 21].

Thiophene oligomers, one of which is studied in this paper, are attracting the attention of many scientists from both fundamental and application viewpoints. The thiophene chain is basically of importance because it is a model of a one-dimensional system with *cis-cisoid*-polyacetylene configuration and hence is also a model system of confined solitons [22]–[26]. It has possible applications in organic light emitting diodes (LED) and field-effect transistor technologies. For the LED application, it is of importance to clarify the mechanism of vibronic coupling, which can reduce the luminescence quantum yield through radiationless relaxation. The radiationless process is introduced by the vibronic coupling resulting in conversion from electronic energy to vibrational energy. There is another important relaxation channel that is widely observed in all organic molecules. It is the intersystem crossing (ISC), in which an excited singlet state relaxes to a triplet state. In some cases, phosphorescence from the triplet state can contribute to LED to overcome the spin multiplicity limit of 25% [27]. Therefore it is also important to investigate what is the key factor that determines the rate of ISC. ISC takes place via spin–orbit coupling between the excited singlet state and the triplet state and in some cases the vibronic coupling also contributes to the mixing of the lowest excited triplet state with the higher excited singlet state(s), from which efficient spin–orbit coupling can take place to the relevant triplet state(s). Therefore, it is highly desired to study the vibronic coupling mechanism, which controls wave-packet dynamics in molecular systems. Since the size of the transition probability change induced by the vibronic coupling is expected to be dependent on the symmetry relation between the two electronic states relevant to the transition and that of vibrational modes, it is of interest to study the vibronic coupling mechanism in terms of the symmetry of the vibration.

In this paper, we could classify the mechanism of dynamic mode coupling into two types from the spectral change during the molecular vibration: the displaced (D) and non-displaced (ND) types in terms of the relation between the two electronic states. The former and the latter types were found for the modes with anti-symmetric and symmetric molecular deformations, respectively, with respect to the center of the pseudo-inversion symmetry of the molecule.

## 2. Femtosecond vibrational spectroscopy

A schematic diagram of 6.7 fs spectroscopy is shown in figure 1. It is composed of NOPA used as the light source, a pump–probe setup and a data acquisition instrument as described below.

### 2.1. NOPA

The pump source of this NOPA system was a regenerative amplifier (Spectra Physics, model Spitfire) with the following operation parameters: central wavelength, 805 nm; pulse duration, 50 fs; repetition rate, 5 kHz; and average output power, 740 mW. A small fraction of the fundamental was focused on to a 1 mm thick sapphire glass to generate white light continuum through a stable single filament [28]–[30]. The second harmonic (SH) was generated in a 0.17 mm thick BBO (type I,  $\theta = 29.2^\circ$ ) with a 25  $\mu$ J pulse energy and then separated from the fundamental and utilized as a pump in the non-collinear optical parametric process.

The external non-collinear angle between the pump beam and seed is  $6.4^\circ$  at the BBO crystal corresponding to an internal angle of  $3.7^\circ$ , which gives the broadband phase matching.

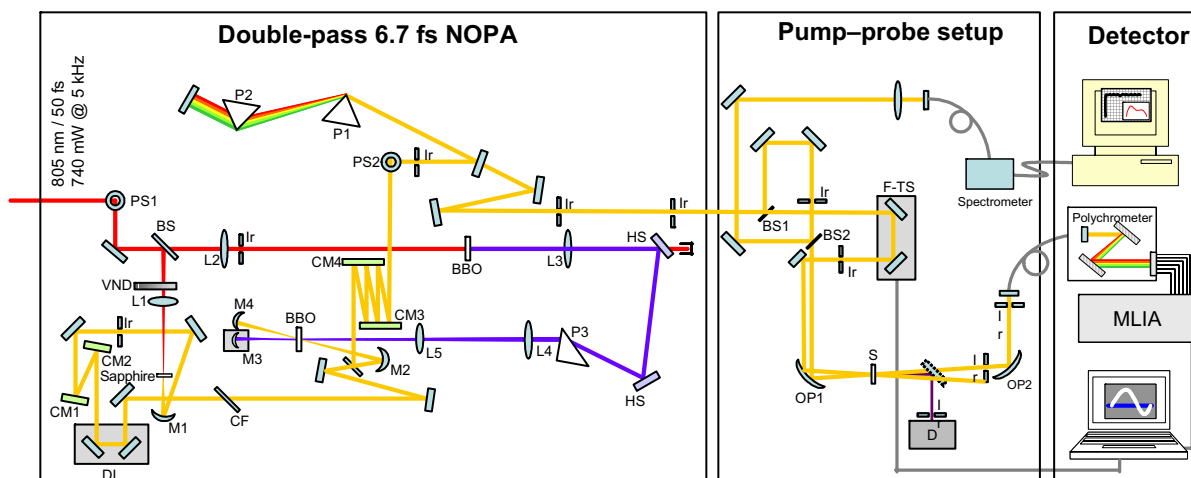


**Figure 1.** Schematic diagram of the 6.7 fs NOPA. BS, beam splitter; L1, L2, L3, L4, L5, lenses with the focal lengths of 100, 600, 250, 200 and 71 mm, respectively; CM1, CM2, CM3, CM4, chirp mirrors; M1, M2, M3, M4, concave mirrors with radii of curvature of 100, 250, 200 and 100 mm, respectively; CF, cut-off filter; P1, P2, Brewster angle prisms; P3, 45° prism; HS, harmonic separator; PS, periscope; Ir, iris; DL, delay line; VND, variable neutral-density filter; BS1, BS2, Cr-coated beam splitters; F-TS, feedback translation stage; OP, off-axis parabolic mirror; PMT, D, photomultiplier and spectrometer in the case of autocorrelation and second-harmonic generation frequency-resolved optical gating (SHG-FORG) measurements, respectively; MLIA, multi-channel lock-in amplifier.

The amplified signal pulse after the double-pass NOPA with a spectrum extending from 535 to 725 nm was compressed with a pair of chirp mirrors and then with a prism pair, resulting in a pulse duration of 6.7 fs, which is nearly Fourier transform (FT) limited. The pulse from the NOPA was split into two: the pump and probe pulses with energies of about 45 and 5 nJ, respectively.

## 2.2. Detection system for the pump-probe experiment

In the present study, pump-probe spectroscopy was employed with a combination of a polychromator and a multi-channel lock-in amplifier. The polychromator (300 grooves  $\text{mm}^{-1}$ , 500 nm blazed) was utilized to disperse the probe pulse and guide it to avalanche photodetectors (APDs) by a 128-channel fiber bundle. The multi-channel lock-in amplifier was designed for the purpose of detecting the signals simultaneously over the whole spectrum with a reference signal from a chopper. In the present experiment, the modulation frequency was set at 2.5 kHz. The spectral resolution of the total system was about 1.5 nm. The transmitted probe spectrum from the sample without the injection of the pump was recorded by averaging 50 000 laser shots. The transmission difference of the probe was accumulated every 3000 laser shots under the excitation conditions by the pump pulse. The pump-probe experiment was performed with a delay time step of 1 fs in the time range from  $-200$  to  $2000$  fs.

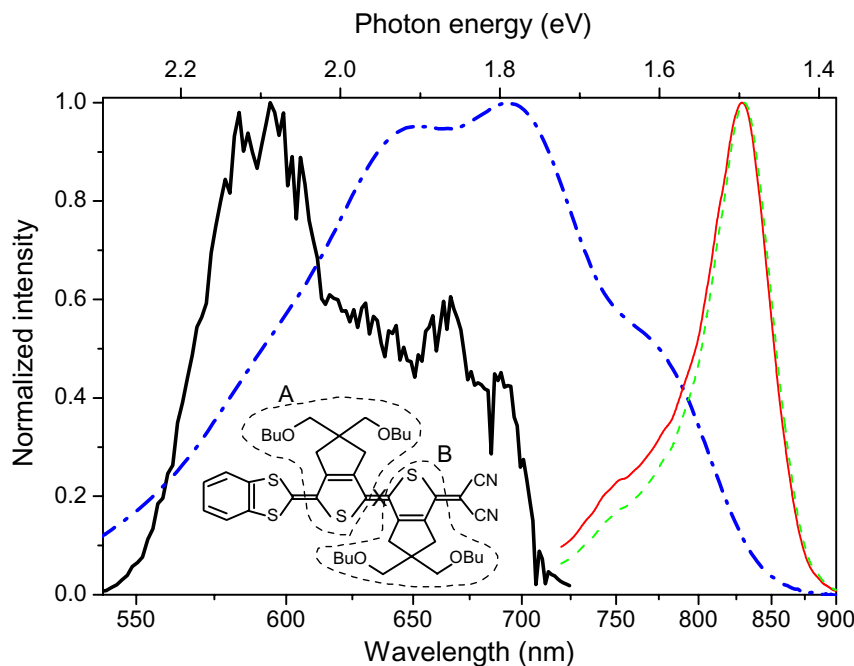


**Figure 2.** Laser spectrum (thick solid line), stationary absorption (thick dash-dotted line), fluorescence spectrum (thin solid line) and stimulated emission spectrum (dashed line). The inset shows the molecular structure used in the present study. A and B are the moieties containing the counterparts of the quasi-inversion symmetry of the molecules. The cross at the center of the C=C bond between two thiophene rings indicates the center of the inversion (quasi-) symmetry.

A small intensity fraction of the laser source was guided to a spectrometer (Ocean Opt. Inc., USB2000) to monitor the intensity fluctuation of the laser source with home-made LabView software.

### 2.3. Sample

The sample studied is a quinothal thiophene derivative (QT2, the structure is shown in the inset of figure 2) [31, 32], which has a quasi-inversion symmetry with respect to the center of the bond connecting the two thiophene rings as marked in the figure and it is suited to study the relation between the vibrational mode symmetry and the vibronic coupling mechanism. The optical density of QT2 ( $1.5 \times 10^{-4} \text{ mol dm}^{-3}$ ) solution in tetrahydrofuran was 1.6 at the absorption peak of 690 nm in a 1 mm thick quartz cell. The stationary absorption and the fluorescence spectra of QT2 shown in figure 2 were recorded with an absorption spectrometer (Shimadzu, model UV-3101PC) and a fluorophotometer (Hitachi, model F-4500), respectively. All experiments were performed at room temperature ( $293 \pm 1 \text{ K}$ ).

Dispersion due to the front plate of the quartz cell was pre-compensated. The effect of the dispersion caused by the sample liquid was also considered. The pump-probe delay time-dependent signal of the femtosecond spectroscopy was utilized to check the zero delay between the pump and probe pulses. In fact, there is no clear hint of the shift of the zero delay in the spectral range of the laser.

### 3. Quantum chemical calculation

The unrestricted Becke three-parameter hybrid exchange functional combined with the Lee–Yang–Parr correlation functional (B3LYP) [33, 34] was utilized with the 6-31+G\* basis sets for geometry optimizations and vibrational analyses [35]. As for the d orbital, 5d functions were used. And the calculation was performed without assuming symmetry. It was confirmed that all the frequencies are real. The quantum chemical calculations were performed using the Gaussian 03 program package. Instead of the butyl (Bu) group in QT2, a molecule with a substitute methyl (Me) group was selected as the model in the vibrational analysis. This is because if the butyl group is included, more than 81 conformers must be calculated and the computation time becomes extraordinarily long. This model compound is considered to have equal electronic states around the  $\pi$ -conjugated main chain as in the case of molecule QT2. Therefore the calculated results of molecular vibration modes expected for the  $\pi$ -conjugated main chain discussed in this paper should be nearly the same as molecule QT2.

Even though the absolute value of the frequencies determined may not be very precise, the order of the mode frequencies is not expected to be changed.

### 4. Results and discussion

#### 4.1. Experimental results

The stationary absorption and fluorescence spectra and the stimulated emission spectrum calculated from the latter spectrum of the QT2 sample, as well as the laser spectrum, are shown in figure 2. The stationary absorption spectrum has two peaks at about 650 and 690 nm and a shoulder around 760 nm. Figure 3(a) shows several examples of the pump–probe delay time dependence of the difference absorbance probed in the spectral range between 535 and 720 nm. The curves are called real-time traces hereafter. The real-time traces have information on both electronic relaxation and vibrational dynamics. The former is usually slower than the latter and shows more or less monotonic dependence on the probe delay time, whereas the latter is, in general, faster and periodically oscillating with frequency corresponding to the vibrational frequency.

From  $-200$  to  $2000$  fs, the Fourier cosine transform to the real-time traces was performed in the following three steps. Firstly, the slow electronic relaxation was obtained after removing the vibrational dynamics together with the experimental noise. This process was realized through smoothing the real-time trace by adjacent averaging. Secondly, by subtracting the slow electronic relaxation from the real-time traces, the vibrational dynamics together with the noise was obtained. Thirdly, fast Fourier cosine transform of the real-time traces in the time range from  $0$  to  $2000$  fs was performed, the results being shown in figure 3(b). They show more than 20 vibrational modes appearing as a modulation of the transition possibility probed at the corresponding wavelength. Among them, the eight most intense vibrational modes with frequencies of  $301$ ,  $785$ ,  $1172$ ,  $1343$ ,  $1376$ ,  $1420$ ,  $1453$  and  $1539$   $\text{cm}^{-1}$  were studied in terms of vibronic coupling. These modes from FT analysis are listed in table 1 together with the results of quantum chemical calculations. In the following, the value mentioned for the vibration mode will be from the FT analysis without any special indication.

Figure 4 shows the plots of the time-resolved difference absorption spectra from 535 to 720 nm in the probe delay time ranging from 100 to 200 fs, and from 400 to 500 fs with a

**Table 1.** Classification of the modes in terms of vibronic coupling mechanisms.

| Frequency (cm <sup>-1</sup> ) |        | VC <sup>b</sup> | PS <sup>c</sup> | Sym <sup>d</sup> | Modes <sup>e</sup>                                 |
|-------------------------------|--------|-----------------|-----------------|------------------|----------------------------------------------------|
| FT (CAL) <sup>a</sup>         | FT-CAL |                 |                 |                  |                                                    |
| 301 (303)                     | − 2    | C-1             | D               | u                | $\alpha$                                           |
| 785 (773)                     | 11     | NC-0            | ND              | g                | $\alpha$                                           |
| 1172 (1161)                   | 11     | C-2             | ND              | N                | $\beta$ (benzene)                                  |
| 1343 (1343)                   | 0      | C-1             | D               | u                | $\delta$ (CH <sub>2</sub> ); $\gamma$ (benzene CH) |
| 1376 (1407)                   | 31     | NC-0,1          | D               | g                | $\epsilon$ (CH <sub>2</sub> ); $\rho_s$ C=C        |
| 1420 (1425)                   | − 5    | C-1,2           | D + ND          | u                | $\epsilon$ (CH <sub>2</sub> ); $\rho_{as}$ C=C     |
| 1453 (1475)                   | − 22   | C-1w,2          | ND              | N                | $\gamma$ (benzene CH); $\nu$ C=C                   |
| 1539 (1549)                   | − 0    | NC-0,2w         | ND              | g                | $\nu$ C=C                                          |

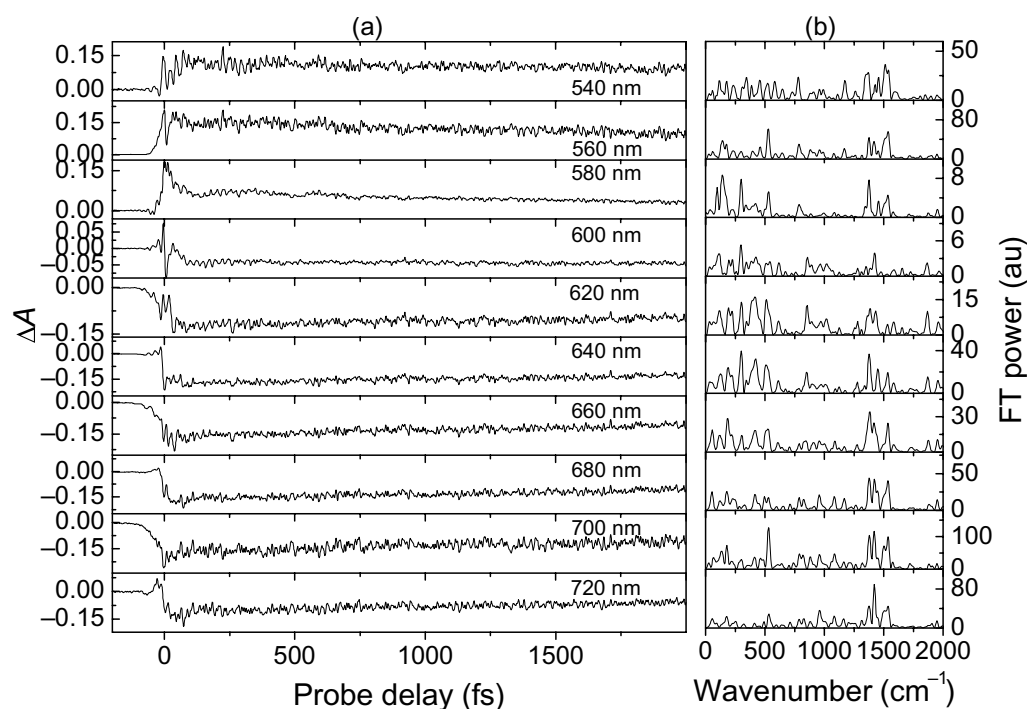
<sup>a</sup>FT: the frequencies obtained by the FT of the real-time trace; CAL: the frequencies obtained by the quantum chemical calculation.

<sup>b</sup>VC: vibronic coupling; C: the Condon mechanism; NC: the non-Condon mechanism; 0, 1, 2: derivative order; w: relatively weak contribution.

<sup>c</sup>PS: potential surface; D: displaced type; ND: non-displaced type.

<sup>d</sup>Sym: symmetry (g, gerade (symmetric); u, ungerade (anti-symmetric); N, no well-defined symmetry with the center of inversion), rather the mixed situation of g and u.

<sup>e</sup> $\alpha$  = in-plane skeletal;  $\beta$  = skeletal;  $\delta$  = twisting;  $\gamma$  = bending;  $\epsilon$  = wagging;  $\rho$  = degenerate bending;  $\nu$  = stretching.

**Figure 3.** (a) Real-time absorbance change at several probe wavelengths; (b) FT power spectra of the traces in (a).

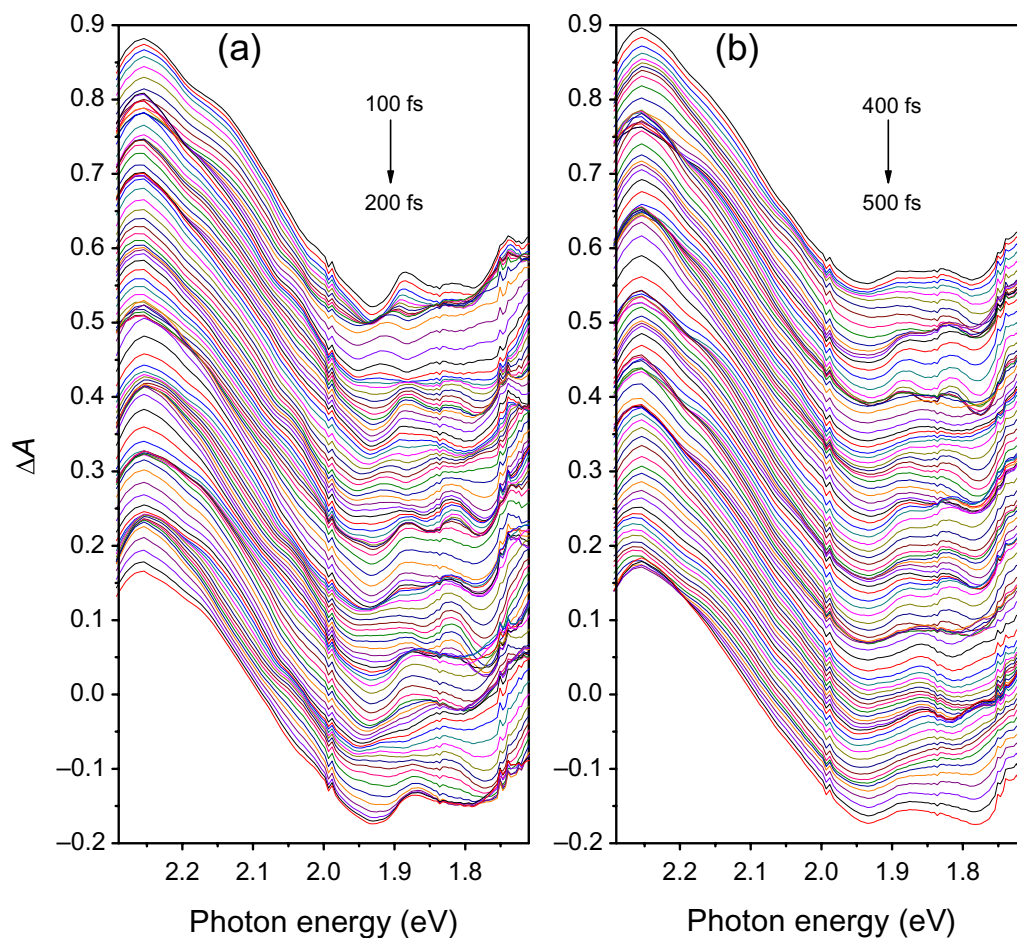


**Figure 4.** The time-resolved difference absorption spectra probed at delay time points (a) 100–200 fs and (b) 400–500 fs, with a 1 fs step. Each curve was down-shifted by 0.008 with an increasing delay time step of 1 fs. The values of  $\Delta A$  along the ordinate are for the bottom curves at 200 and 500 fs in the left and right columns, respectively.

1 fs step. They give a clear oscillation of spectral position and intensity modulation due to the coherent molecular vibration. Changes in spectral shape and intensity of the transient absorption difference were studied by tracking the characteristic spectral features including the frequency and intensity of the peak, spectral bandwidth and band-integrated intensity [36, 37]. They were used for the classification of the mechanisms of vibronic coupling.

#### 4.2. Modulation of electronic transition probability by a wave-packet motion

The real-time traces represent the intensity modulation due to the motion of a wave packet generated by the intense pump pulse. The origins of the intensity modulation are discussed below, which can be classified into two cases, namely the case when the Condon approximation is satisfied and the case when it is not satisfied. The former is due to the time-dependent Franck–Condon (FC) overlap due to the formation of a wave packet, which is the linear contribution of vibrational levels. The latter is the case when the electronic wavefunction is

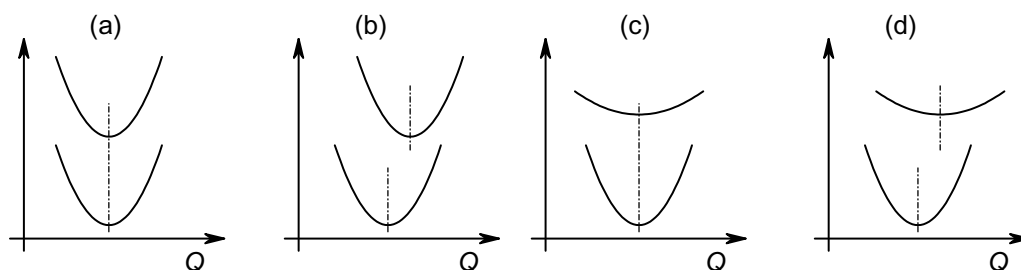


**Figure 5.** Four typical cases of the minima and curvatures of the potential curves: (a) neither minimum displacement nor a curvature change upon photoexcitation; (b) potential minimum displacement without a curvature change; (c) a curvature change without potential minimum displacement; and (d) with both potential minimum displacement and a curvature change. The dash-dotted lines indicate the minimum of the potential surfaces.

mixed with a third electronic state to introduce the borrowing of the electronic transition dipole. Following the wave-packet motion, the molecular structure is deformed and the corresponding electronic energies of these states are modified, and then the absorption intensity is modulated.

**4.2.1. Condon approximation satisfied case.** In this subsection, electronic transition with satisfied Condon approximation is discussed with a two-level system (2LS). In this case, the integrated intensity of the absorbance change covering the relevant electronic state does not change during the wave-packet motion. The 2LS has two harmonic potential curves belonging to the ground state and the lowest excited state. In the present case, the sets of potential curves of two electronic states for the mechanisms are shown in figure 5.

Here, we are discussing the wave packet generated only in the ground state. A similar discussion can also be made in the case of the wave packet generated in the excited state. There are four typical cases of the minima and curvatures of the potential curves: (a) neither displacement of the minimum nor change in the curvature upon photoexcitation; (b) potential minimum displacement but without a curvature change; (c) a curvature change but without a displacement of the potential minimum; and (d) both potential minimum displacement and a curvature change.

There are four different cases relevant to the above features of potential curves. They are: (a') generation of a vibrational eigenstate without any wave-packet motion because of the selection rule for the allowed transition; (b') generation of a wave packet in the ground state, which starts to displace along the potential curve; (c') generation of a wave packet in the ground state, whose size starts to breathe after photoexcitation; (d') generation of a wave packet in the ground state, which starts to displace along the potential curve and breathe at the same time.

Intensity modulation can be introduced by the time-dependent overlap of the molecular wavefunctions between the initial and the final electronic states associated with the transition. In such a case, the mechanism of the modulation of transition probability is the time-dependent FC overlap factor.

In the case when the molecular vibration is Fourier-analyzed to separate many modes into many normal modes, it can be described in terms of a one-dimensional harmonic potential curve. Then the FC factor is associated with the motion of a wave packet moving between two

equal-energy points of the potential curve along one of the normal coordinates on which the wave packet is located [38]. The time-dependent FC factor,  $F(t)$ , related to the two electronic states of initial and final states ( $i$  and  $f$ , respectively) coupled with the transition, is given in the following equation:

$$F(t) = \sum_l \sum_m c_l^* c_m \langle \tilde{\chi}_l^i(\hat{Q}) | \tilde{\chi}_m^f(\hat{Q}) \rangle = \sum_l \sum_m c_l^* c_m \langle \chi_l^i(\hat{Q}) | \chi_m^f(\hat{Q}) \rangle e^{i(l-m)\omega_v t}. \quad (1)$$

Here,  $|\tilde{\chi}_a(\hat{Q})\rangle = |\chi_a(\hat{Q})\rangle e^{ia\omega_v t}$  is the nuclear wavefunction with the vibrational quantum number of  $a = (l, m)$ , and  $\omega_v$  is the frequency of molecular vibration relevant to the vibronic coupling. The linear combination of the time-dependent (oscillating) terms with the sets of quantum numbers ( $l, m$ ) having weight factors related to the FC factor gives the wave-packet motion. The equation describing the spectral change due to the motion of a wave packet induced by the impulsive excitation is dependent on the FC factor, which is the prefactor of the sinusoidal function in equation (1). The coefficients  $c_l^* c_m$  are determined by the pump laser spectrum and the cross section of the ground (G) state absorption. If  $i$  and  $f$  are the G state and the excited (E) state, respectively, there are two possibilities for the wave packet to be generated by the pump: either in the  $i$  state by coherent vibronic excitation or in the  $f$  state by the stimulated Raman process. Then wave-packet motion takes place along the potential curve of the corresponding state.

Let us discuss the case that the potential minima is displaced along the potential surface of the  $i$  state with respect to that of the  $f$  state (figure 5(b)). This displaced-potential surface case will be called D type hereafter in the discussion about the mechanism of transition probability modulation. If the amount of shift due to the wave-packet motion is small, then the spectral change is small and can be given by the first derivative of the absorption spectrum. Then  $\pi$ -phase jump can be found at the peak of the absorption spectrum in the vibrational amplitude as a function of probe wavelength [39, 40].

In the case of no displacement between the ground state and the excited state (figure 5(c)), will be referred to as ND type hereafter), the wave-packet motion is not the oscillation between the two turning points of equal energy of the potential curve of either the excited state or the ground state. The main motion of the wave packet in such a case is due to the second-order difference between the initial state and the final state. Then the second-order difference is given by the breathing of the wave packet, in which the width of the wave packet oscillates with time with vibrational frequency. It means that the vibronic coupling due to this mechanism is of higher order than that of the FC type with respect to the spectral change due to the wave-packet motion from the FC point upon photoexcitation. The potential curves of the initial state and the final state are expected to be more or less similar to each other except in the case of dramatic geometrical relaxation after excitation. Then the difference between the potential energies can be Taylor expanded into the power series of the normal coordinate ( $Q$ ), the term of which is proportional to the  $n$ th derivative ( $\frac{\partial^n A(\omega)}{\partial \omega^n}$ ) of the absorption spectrum ( $A(\omega)$ ) [38]. The components of the power series are classified in terms of the strength of vibronic coupling. The coupling strength of the first-order term is the strongest in most cases.

As discussed above, the spectral change is determined approximately by the second derivative of the relevant transition spectrum in the case of breathing. When the wave-packet motion is in the ground state, the corresponding spectrum is the ground-state absorption spectrum to the excited state. If the wave packet is moving in the excited state, then the probe wavelength dependence of the vibrational amplitude is the second derivative of the stimulated emission spectrum and/or the bleaching spectrum.

The above discussion can be well understood by the following equation, which shows the modulation of absorbance change ( $\Delta A(\omega)$ ) at probe frequency  $\omega$ .

$$\begin{aligned}\delta\Delta A(t; \Omega, \omega) &\cong \Delta A(t; \Omega, \omega) - \Delta A_0(\omega) \\ &= \left( \delta\omega \frac{d\Delta A_0(\omega)}{d\omega} + \delta\Delta\omega \frac{d^2\Delta A_0(\omega)}{d\omega^2} \right) \cos(\Omega t + \phi).\end{aligned}\quad (2)$$

Here,  $\Omega$  is the frequency of the relevant molecular vibration mode.  $\Delta A_0(\omega)$  is the difference absorption spectrum free of molecular vibration. This can be obtained by smoothing the real-time vibrational trace over several vibration periods at each probe wavelength. This may be a composite of the spectra due to the gain and bleaching due to ground-state depletion.  $\delta\Delta A(\Omega; \omega)$  is the amplitude of the FT of the absorbance change with molecular vibrational frequency  $\Omega$ .  $\delta\Delta\omega$  is the change in the bandwidth ( $\Delta\omega$ ) of the absorption, gain or bleaching spectrum.

Up to this point, we studied the case when the Condon approximation is satisfied. This is called the C mechanism, which can be sub-classified into D and ND types. In the case of D type, the probe frequency dependence of  $\delta\Delta A(\Omega; \omega)$  can be mainly given by the first derivative of  $\Delta A_0(\omega)$ . In the ND type case, the main contribution is given by the second derivative of  $\Delta A_0(\omega)$ . For the configuration shown in figure 5(d), it is a mixture of D and ND types, thus a mixed probe wavelength dependence of first and second derivatives is expected.

**4.2.2. Condon approximation unsatisfied case.** In this subsection, the deviation from the Condon approximation can be introduced by taking another electronic state (a third state), which is radiationally coupled to the two states between which transition intensity is being monitored. Here, we discuss a three-level system (3LS) including the third state. The 3LS is composed of three electronic states,  $S_0$ ,  $S_1$  and  $S_2$ , energies of which are in increasing order. It is assumed that the vibronic coupling occurs predominantly between  $S_1$  and  $S_2$  states and the following three wavefunctions are considered:

$$|S_0(\hat{q}, \hat{Q})\rangle = |\psi_0(\hat{q}, \hat{Q})\rangle |\chi_n^0(\hat{Q})\rangle, \quad (3)$$

$$|S_1(\hat{q}, \hat{Q})\rangle = \frac{1}{\sqrt{1 + (H_{\text{vib}}/\Delta E_{21})}} \left( |\psi_1(\hat{q}, \hat{Q})\rangle - \frac{H_{\text{vib}}}{\Delta E_{21}} \hat{Q} |\psi_2(\hat{q}, \hat{Q})\rangle \right) |\chi_m^1(\hat{Q})\rangle, \quad (4)$$

$$|S_2(\hat{q}, \hat{Q})\rangle = \frac{1}{\sqrt{1 + (H_{\text{vib}}/\Delta E_{21})}} \left( |\psi_2(\hat{q}, \hat{Q})\rangle + \frac{H_{\text{vib}}}{\Delta E_{21}} \hat{Q} |\psi_1(\hat{q}, \hat{Q})\rangle \right) |\chi_m^2(\hat{Q})\rangle. \quad (5)$$

In the above equations,  $|\psi_X(\hat{q}, \hat{Q})\rangle$  and  $|\chi_k^X(\hat{Q})\rangle$  represent wavefunctions of the electrons and nuclei, respectively, for state  $X$  ( $= 0, 1$  and  $2$  for  $S_0$ ,  $S_1$  and  $S_2$ , respectively) as a function of the electron and nuclear coordinates,  $\hat{q}$  and  $\hat{Q}$ , respectively. In the nuclear wavefunctions  $|\chi_k^X(\hat{Q})\rangle$ , the vibrational quantum number is given by the suffixes  $k = n$  and  $m$ .  $\Delta E_{21}$  is the energy difference between  $S_2$  and  $S_1$ .  $H_{\text{vib}}$  is the interaction Hamiltonian. The states  $S_1$  and  $S_2$  are not necessarily the pair of first and second E states but can be any pair of electronic E states in general, i.e. electronic state  $S_2$  can be a higher E state than the second E state. In this way, the spectral change integrated over the relevant spectral range is not conserved to have a constant oscillator strength, but it changes with the vibrational motion of the mode, whose interaction  $H_{\text{vib}}$  is contributing to the mixing of the two electronic states. The mixing is controlled by the symmetries of the mode and electronic states.

Using equations (3)–(5), the transition dipole model between  $|S_0(\hat{q}, \hat{Q})\rangle$  and  $|S_1(\hat{q}, \hat{Q})\rangle$  can be given by the following equation:

$$\begin{aligned}\langle S_0 | \mu | S_1 \rangle &= \langle \varphi_0 | \langle \chi | \mu (|\varphi_1\rangle - \beta Q |\varphi_2\rangle) | \chi_m^1 \rangle \\ &= \langle \varphi_0 | \mu | \varphi_1 \rangle \langle \chi_n^0 | \chi_m^1 \rangle - \beta \langle \varphi_0 | \mu | \varphi_2 \rangle \langle \chi_m^0 | Q | \chi_m^1 \rangle, \\ \beta &\equiv \frac{H_{\text{vib}}}{\Delta E_{21}}.\end{aligned}$$

The transition probability is given by the following equation:

$$\begin{aligned}|\langle S_0 | \mu | S_1 \rangle|^2 &= |\langle \varphi_0 | \mu | \varphi_1 \rangle|^2 |\langle \chi_m^0 | \chi_m^1 \rangle|^2 - \beta^* \langle \varphi_0 | \mu | \varphi_1 \rangle \langle \varphi_0 | \mu | \varphi_2 \rangle^* \langle \chi_m^0 | \chi_m^1 \rangle \langle \chi_m^0 | Q | \chi_m^1 \rangle^* \\ &\quad - \beta \langle \varphi_0 | \mu | \varphi_1 \rangle^* \langle \varphi_0 | \mu | \varphi_2 \rangle \langle \chi_m^0 | \chi_m^1 \rangle^* \langle \chi_m^0 | Q | \chi_m^1 \rangle + \text{h.o.}\end{aligned}\quad (6)$$

In the case that both  $S_0 \rightarrow S_1$  and  $S_1 \rightarrow S_2$  are allowed transitions, further discussion becomes complicated. Therefore, we utilize a modified phenomenological equation (2) as follows:

$$\delta A(t; \Omega, \omega) \cong \left( \frac{\delta(\mu^2)}{\mu^2} \Delta A_0(\omega) + \delta\omega \frac{d\Delta A_0(\omega)}{d\omega} + \delta\Delta\omega \frac{d^2 \Delta A_0(\omega)}{d\omega^2} \right) \cos(\Omega t + \phi). \quad (7)$$

The first term represents the phenomenological modulation of the transition dipole moment  $\mu$  of the relevant electronic transition.

The non-conserved oscillator strength will destroy the Condon approximation, which indicates that the integrated intensity over the electronic transition is not maintained during the vibrational period. It is called the non-Condon (NC) mechanism hereafter. This NC mechanism can also be sub-classified into D and ND types.

The probe photon frequency dependence of  $\delta\Delta A(\Omega; \omega)$  for the NC mechanism is given as follows. In the case of D type, the probe photon frequency dependence of  $\delta\Delta A(\Omega; \omega)$  is given by the zeroth and first derivatives of  $A_0(\omega)$ . In the case of ND type, it is given by the zeroth and second derivatives of  $A_0(\omega)$ . For both D and ND types in the NC mechanism, the zeroth-order dependence of probe wavelength was added to fulfill the non-conserved integrated transition probability under the NC mechanism. The zeroth-order derivative can also be understood as the time-dependent contributions from the third electronic states, oscillating periodically with the vibrational frequency. These phenomena may be rephrased as alternating intensity borrowing and returning [41, 42].

**4.2.3. Classification of the vibrational modes.** According to the discussion in the above subsections, the representative vibrational modes were classified. There are several modes to be classified into the C mechanism from the fact that the integrated intensities of these modes do not change during the molecular vibration. Their frequencies are 301, 1172, 1343, 1420 and 1453  $\text{cm}^{-1}$ . The other modes with frequencies of 785, 1376 and 1539  $\text{cm}^{-1}$  are classified into the NC mechanism because of the destruction of the Condon approximation found by the change of the transition probability integrated over the transition band. A detailed data analysis and a discussion about the classification can be found in [37]. The results are listed in table 1.

Table 1 also lists the wavelength dependence of the transient absorbance change for each vibration mode [37]. According to this wavelength-dependent property in the C and NC mechanisms as discussed in section 4.2, the experimentally observed vibration modes could be sub-classified into D and ND types, the results being listed in table 1. For mode 785  $\text{cm}^{-1}$ , its probe wavelength dependence of spectral shape change is the zeroth derivative of the absorbance change spectrum in the NC mechanism; therefore it is classified under the ND type.

This is because no clear first-order contribution could be considered to be contradictory to displaced potential surfaces. Therefore, non-displaced potential surfaces were expected for this mode.

#### 4.3. Vibrational symmetry

Figure 6 shows several examples of the structural change during the molecular vibration and their vibrational amplitudes obtained by the quantum chemical calculation described earlier. The vibration mode assignment is listed in table 1. In this table, the vibrational frequencies obtained from the FT of the real-time traces and calculation are also listed. They are in agreement with each other within  $12\text{ cm}^{-1}$  except for modes with frequencies of  $1376$  and  $1453\text{ cm}^{-1}$ . The other differences are partly due to the limited calculation precision and experimental error. They may also be due to the limited frequency resolution resulting in the mixing of the mode frequency in the G state and the E state, which may be slightly different from each other. The calculated frequencies correspond to the G state and the observed ones can correspond to the G and/or E state. The mode with  $1581\text{ cm}^{-1}$  shown in figure 5 could not be identified in the FT power spectrum probably because of relatively weak vibronic coupling. These results were utilized to classify the vibration modes by the configuration change to the molecular structure with respect to the moiety of the quinoid thiophene oligomer part.

From the molecular structure of QT2 shown in the inset of figure 2, it was found that it has an inversion (quasi-) symmetry with respect to the center of the  $\text{C}=\text{C}$  bond connecting two thiophene rings. The classification is shown in table 1; they are inversion symmetric (gerade) and anti-symmetric (ungerade) groups. Interestingly, the modes whose vibronic coupling mechanism was classified under (inversion) anti-symmetric were attributed to the D type except for the modes with the frequency of  $1420\text{ cm}^{-1}$ , whereas the vibronic coupling of the modes classified under the inversion symmetric one were assigned to ND type except for the modes with the frequency of  $1376\text{ cm}^{-1}$ . Symmetric  $1376\text{ cm}^{-1}$  and anti-symmetric  $1420\text{ cm}^{-1}$  are only classified into NC and C mechanisms without clear D or ND type identification. The reason for these exceptions and the not well-defined symmetry for modes of  $1172$  and  $1453\text{ cm}^{-1}$  will be explained later. The relation between the mechanism of vibronic coupling and the vibration symmetry can be explained in the following way.

We name the two moieties of the oligomer as moieties A and B. At first, the configuration change of the molecular structure is considered to be in one of the two moieties, moiety A. The energy required for this configuration change is supposed to be  $E_A$ . In the case of gerade vibration, the destabilization energy for the configuration change is the same because of the symmetry. Therefore, the energy minimum does not change and the potential curve becomes symmetric. This is true both in the G state and in the E state and hence there is no shift of the minimum of the potential curve in the transition process from the G state to the E state through photoexcitation. Therefore, it is expected that there is no contribution to the time-dependent FC overlap in this case and then the deformation of molecular structure during molecular vibration has nothing to do with the change in the relevant electronic transition probability. This means that the contribution of the vibronic coupling to the change in the transition intensity is ND type.

While in the case of ungerade mode, the destabilization energy of moiety B can be  $E_B$ , which is different from  $E_A$  because the deformation in this case is not equivalent. Therefore, the potential curve is anti-symmetric with the possibility of a change in potential minima

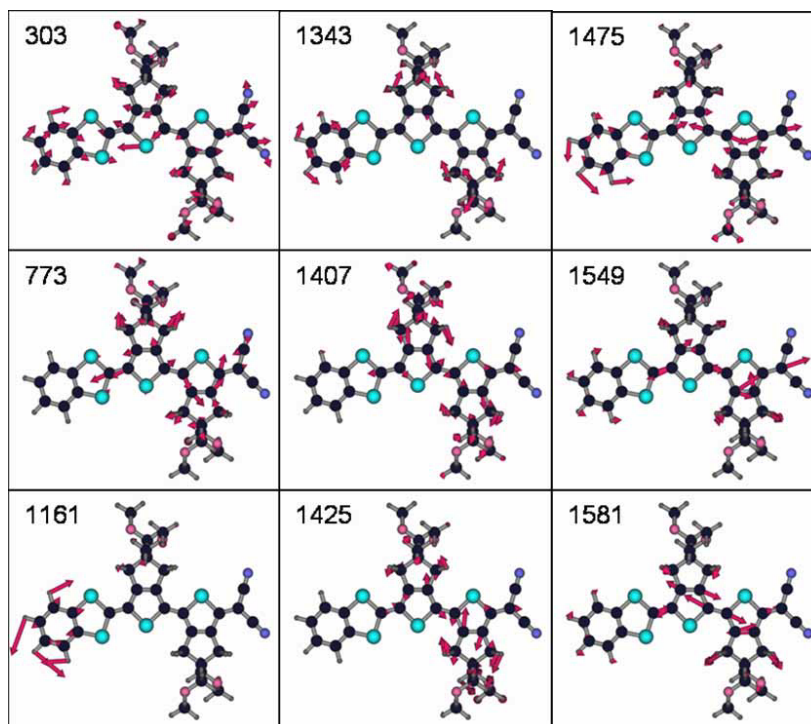


**Figure 6.** Examples of the structural change due to the vibration modes obtained by the quantum chemical calculation method of B3LYP [33, 34] with the 6-31+G\* basis sets for geometry optimization and vibrational analyses [35]. The numbers at the top left corners are the frequencies of the modes in wavenumbers.

between the G state and the E state induced by the asymmetry. Then the larger contribution to the vibronic coupling is that of the D type by time-dependent overlap of the FC factor due to the displacement of the potential minimum associated with photoexcitation.

The reason why the modes with frequencies of 1172 and 1453  $\text{cm}^{-1}$  do not follow the rule can be explained as follows. As can be seen in figure 6, the displacement amplitudes of atoms in the molecule are very large in the benzene ring but very small in the thiophene ring moieties. Therefore, these modes are not sensitive to the symmetry of the structural change in the thiophene ring moieties.

From the mode with a frequency of 1376  $\text{cm}^{-1}$ , the difference between the FT analysis and the quantum chemical calculation is 31  $\text{cm}^{-1}$ . This large difference might indicate that they are not the same mode, and hence the result of the vibronic coupling cannot be discussed in terms of the symmetry of the molecule obtained by the quantum chemical calculation.

For mode 1420  $\text{cm}^{-1}$ , the probe wavelength dependence of spectral shape change has nearly the same contribution from the first- and second-order derivative components, which indicates that the configuration of potential surfaces is given by the one shown in figure 5(d). It is a mixture of D and ND types, whereas the mode assignment from quantum chemical results shows that it is composed of a mixed contribution of the  $\text{CH}_2$  group wagging mode and the  $\text{C}=\text{C}$  stretching mode. Therefore, the mode does not follow the rule between the vibronic coupling mechanism and mode vibration symmetry.

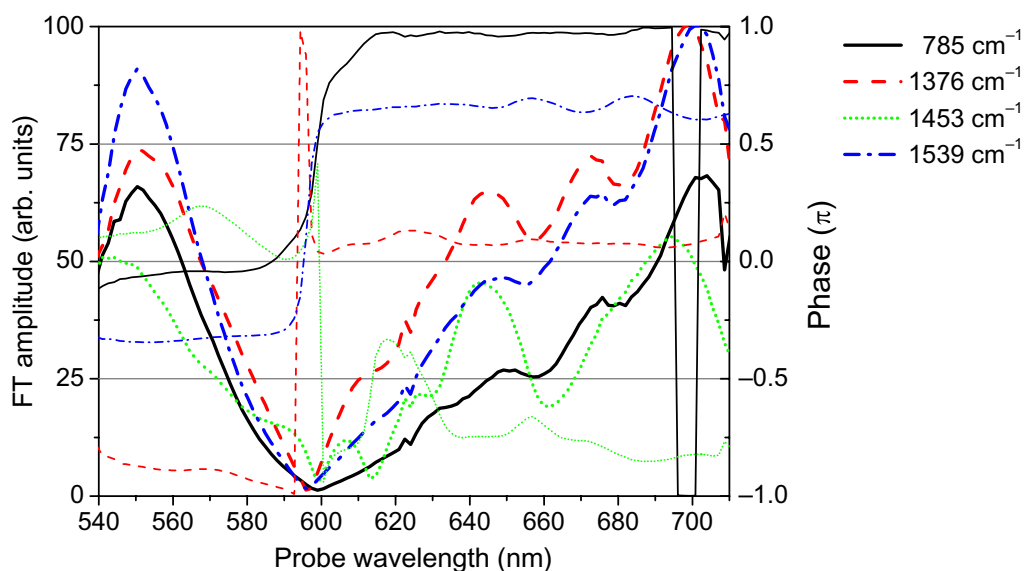


**Figure 7.** Probe wavelength dependence of FT amplitudes (thick line) and phases (thin line) of modes with frequencies of  $785\text{ cm}^{-1}$  (solid),  $1376\text{ cm}^{-1}$  (dashed),  $1453\text{ cm}^{-1}$  (dash-dotted) and  $1539\text{ cm}^{-1}$  (dot).

Figure 7 shows several examples of the probe wavelength dependences of vibrational amplitudes (vibrational amplitude spectrum) for modes with frequencies of 785, 1376, 1453 and  $1538\text{ cm}^{-1}$  in the wavelength range 540–600 nm. They show very complicated structures. In the following, the dependences will be discussed briefly. The modulation of transition probability inducing the real-time traces is due to the change in FC overlap and/or transition movement caused by molecular vibration.

After the generation of the wave packet either in the G state or in the E state, they introduce modulation of probabilities of electronic transitions from the G state to the relaxed E state, from the (relaxed) E state to the G state, and from the (relaxed) E state to the higher E state(s). Spectral features of these transitions make the probe frequency dependence of the vibrational amplitude complicated. The contributions of both G-state and E-state wave packets also make the vibrational phase as a function of probe frequency (vibrational phase spectrum) complicated. Full information on the probe frequency dependence may make it possible to separate various contributions of the G state and E state contributions and contributions due to transitions corresponding to breathing, stimulated emission and induced absorption.

The electronic difference spectrum is composed of bleaching, induced emission and induced absorption. They are expected to contribute to  $\delta\Delta A(\Omega, \omega)$  in a complex manner. In the present study, it is not possible to describe in full detail the probe photon frequency dependence of vibrational phase and amplitude shown in figure 7. Further study is in progress to resolve the problem. The dynamics of the vibrational-induced transition modulation can also provide information on the coupling among the photoexcited vibrational modes. By taking the amplitude of each mode separated by FT, the detailed dynamical process of internal vibrational relaxation (IVR) will be clarified.

## 5. Conclusion

In conclusion, we could classify the mechanism of dynamic mode coupling into two types from the spectral change during the molecular vibration: the D and ND types. In the former type, the spectral change is described by the first derivative (C mechanism) or the zeroth plus first derivatives (NC mechanism) of the spectra of ground-state absorption, induced emission and induced absorption. In the latter case, spectral change is given by the second derivative (C mechanism) or the zeroth plus second-order derivatives (NC mechanism) of the (combination of) relevant spectra. The former and the latter modes are found for the modes with symmetric (gerade) and anti-symmetric (ungerade) molecular deformations, respectively, with respect to the center of the inversion symmetry of the molecule. Therefore the detailed study of multi-wavelength measurement of vibrational real-time spectroscopy offers information on the mechanism of vibronic coupling in the process of transition from the G state to the E state and that between the two E states.

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