# Optical frequency- and vibrational time-resolved two-dimensional spectroscopy by real-time impulsive resonant coherent Raman scattering in polydiacetylene

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Real-time impulsive resonant Raman scattering induced by a 4-fs ultrashort laser pulse was spectrally resolved with a multichannel lock-in amplifier. An optical and vibrational two-dimensional spectrum was introduced to separate the effects of electronic and vibrational broadening in the power spectrum of the vibrations. Spectrally resolved real-time oscillations can identify the wave packet motion associated with the stretching vibrational mode of the carbon-carbon double and triple bonds of the polymer polydiacetylene. Calculated nonlinear polarizations which take into account the ground-state wave packets reproduced the observed dynamics fairly well. It is confirmed that the ground-state vibrations play a significant role in the dynamics of the wave packet even far below the absorption edge, as well as the excited-state vibrations.

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## I. INTRODUCTION

Recent advances in ultrashort lasers make it possible to observe real-time ultrafast dynamics in various materials on the femtosecond time scale, and many ultrafast processes in molecular systems in both excited and ground states have been revealed [1-3]. The dynamics in materials, in particular electronic excited-state dynamics, can be studied by transient nonlinear spectroscopy techniques such as transient absorption, transient grating, and stimulated Raman scattering. With these schemes, impulsive excitations of wave packets by ultrashort pulses can offer important information on vibronic coupling, conformational changes, and photochemical reactions [4–7]. In contrast to conventional stationary Raman scattering experiments, which are relevant to the groundstate vibrations, information about the excited-state vibrations can be obtained by real-time spectroscopy using ultrashort lasers. However, ultrafast spectroscopy has difficulty in separating the contributions of the excited-state vibrations from those of the ground-state vibrations, because an ultrashort laser pulse coherently induces both ground-state and excited-state vibrations with longer periods than the pulse duration. Only a limited number of experiments have overcome this difficulty so far, using chirped-pulse excitation [8,9] and detailed analysis of the delay-time dependence of pump-dump pulses in stimulated Raman scattering [10]. In fact, impulsive real-time nonresonant Raman scattering has been observed and applied to shortening the probe pulse durations [11,12]. This paper will demonstrate spectrally resolved real-time measurement of impulsive resonant Raman scattering, which allows us to study the ground-state vibrations exclusively. By using selective excitation, we limit the investigation of vibrational dynamics to two nonlinear processes. Figure 1 represents a schematic diagram of a relevant third-order nonlinear process in which ground-state vibrations are excited coherently without exciting coherent vibrations of an excited state. The laser spectrum is carefully adjusted to have appropriate overlap with the absorption of the sample [polydiacetylene-4-butoxy spectrum carbonylmethylurethane-(PDA-4BCMU)] to prevent coherent excitation of the vibrations of the excited state and to excite only the ground-state vibrations. After filtering out the high-energy components of the laser spectrum, it covers only the 0-0 transition and does not reach the 0-1 transition of the sample as shown in Fig. 1. (Here n-m indicates a transition between the *n*th vibrational level of the electronic ground state and the mth vibrational level of the electronic excited state.) To drive the 1-0 transition by the pump pulse and be able to detect the weak nonlinear polarization by a heterodyne scheme, the laser spectrum must cover the lowerenergy region  $E_e - E_v$ . The detailed analysis of the nonlinear processes will be discussed in the next section.



FIG. 1. Diagram of the relevant third-order nonlinear process, the energy levels, the arrangements of the laser spectrum covering energies from  $E_e$  to  $E_e - E_v$ , and absorption spectrum around  $E_e$  and  $E_e + E_v$  of a sample suitable for the excitation of ground-state vibrations.  $P^{(3)}$ , third-order nonlinear polarization;  $E_e$ , absorption energy of 0-0 transition;  $E_v$ , vibrational energy involved in the nonlinear process. Note: the transmittance change (dashed line in the right figure) occurs at  $E_e - E_v$  by this nonlinear polarization.

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FIG. 2. The three-level model and parameters.  $E_e$ , absorption energy of 0-0 transition;  $E_v$ , vibrational energy;  $T_2$ , electronic transverse dephasing time between the ground state and the excited state;  $T_4$ , vibrational transverse dephasing time between the vibrational states in the ground state; and  $\mu$ , transition dipole moment between the ground state and the excited state.

## **II. THEORY**

A three-level model is assumed and we analyze two thirdorder nonlinear processes contributing to the pump-probe signal by the theory of nonlinear ultrafast spectroscopy [13,14]. We consider two vibrational levels in the electronic ground state ( $|g\rangle$  and  $|g_v\rangle$ ) and one vibrational level in an electronic excited state ( $|e\rangle$ ) as described in Fig. 2. Figure 3 depicts the double-sided Feynman diagrams [14] for the two third-order nonlinear (NL) processes (*A* and *B*) representing vibrational excitations in the ground state.

Other nonlinear processes leading to the excitation of the ground-state vibrations are not detected in a (heterodyne) pump-probe experiment, because there is no spectral overlap between the probe pulse and the induced nonlinear polarizations. There are several other nonlinear processes which contribute to nonlinear pump-probe signals such as coherent anti-Stokes Raman scattering (CARS), coherent Raman scattering (CRS), induced photon emission, bleaching of the ground state, and induced absorption. However, in the following analysis of the vibrational dynamics, their contribution can be clearly separated, because their dynamics is de-



FIG. 3. Double-sided Feynman diagrams of the two nonlinear processes. In (a) (NL process A), the energy of the nonlinear polarization created by the final electronic coherence is lower than the absorption energy by the vibrational energy involved. In (b) (NL process B), the energy of the nonlinear polarization is the same as the absorption energy.

termined by the electronic longitudinal relaxation time [14–16], which is usually much longer than periods of typical molecular vibrations. Two important conclusions can be drawn from examining the diagrams in Fig. 3. First, the contributions of the NL processes A and B can be distinguished experimentally by frequency-resolving the pump-probe signal because of the energy difference  $E_v$  of the photons emitted by the nonlinear polarizations. Here we note that the frequency difference between the nonlinear polarizations induced by NL processes A and B corresponds to the energy gap between  $|g_{\nu}\rangle$  and  $|g\rangle$ . Second, generally the pump-probe signal at frequencies below the 0-0 transition can be influenced by both ground-state vibrations and excited-state vibrations. For frequencies above the 0-0 transition also, both ground-state and excited-state dynamics are generally present as a mixture of many nonlinear processes as in CARS, CRS, and so on. Therefore, in a conventional resonant pump-probe experiment, it is very difficult to find a certain spectral range within which the nonlinear signal will reflect excited-state dynamics exclusively. The polarizations of the NL processes A and B and the pump-probe signal were calculated with the help of the Feynman diagrams. The parameters described in Fig. 2 are defined as follows. The energy, the transition dipole moment, and the transverse dephasing time between  $|e\rangle$  and  $|g\rangle$  are  $E_e \equiv \hbar \omega_e$ ,  $\mu$ , and  $T_2$ , respectively, and those between  $|e\rangle$  and  $|g_v\rangle$  are  $E_e - E_v$  $\equiv \hbar(\omega_e - \omega_v), \mu$ , and  $T_2$ , respectively. The transverse dephasing time between  $|g\rangle$  and  $|g_v\rangle$  is  $T_4$ . The electrical fields of the pump and probe pulses are defined to have the same center frequency but different phases from each other. The phases of  $E_{pump}(t)$  and  $E_{probe}(t)$  are defined as  $\theta_{pump}$  and  $\theta_{probe}$ , respectively. The electrical field is then represented by

$$E(t) = E_{pump}(t)\exp(-i\omega_0 t - i\theta_{pump}) + E_{probe}(t)\exp(-i\omega_0 t - i\theta_{probe}) + \text{c.c.}$$
(1)

It is assumed that the pump and probe pulses interact with the sample twice and once, respectively. The pump pulse proceeds well ahead of the probe pulse in such a way that only the sequence pump-pump-probe of the interaction between pulses and the sample remains. The third-order non-linear polarizations of NL processes A and B are described using the rotating-wave approximation as

$$P_{A}^{(3)}(t,\tau) = \left(\frac{i}{\hbar}\right)^{3} \mu^{4} \int_{0}^{\infty} dt_{3} \int_{0}^{\infty} dt_{2} \int_{0}^{\infty} dt_{1}$$

$$\times E_{probe}(t-t_{3}) E_{pump}(t-t_{3}-t_{2}+\tau)$$

$$\times E_{pump}^{*}(t-t_{3}-t_{2}-t_{1}+\tau)$$

$$\times \exp[-i\{(\omega_{e}-\omega_{v}-\omega_{0})t_{3}-\omega_{v}t_{2}-(\omega_{e}-\omega_{0})t_{1}+\omega_{0}t+\theta_{probe}\}] \exp\left(-\frac{t_{1}}{T_{2}}-\frac{t_{2}}{T_{4}}-\frac{t_{3}}{T_{2}}\right)$$
(2)

and

$$P_{B}^{(3)}(t,\tau) = \left(\frac{i}{\hbar}\right)^{3} \mu^{4} \int_{0}^{\infty} dt_{3} \int_{0}^{\infty} dt_{2} \int_{0}^{\infty} dt_{1}$$

$$\times E_{probe}(t-t_{3}) E_{pump}^{*}(t-t_{3}-t_{2}+\tau)$$

$$\times E_{pump}(t-t_{3}-t_{2}-t_{1}+\tau)$$

$$\times \exp[-i\{(\omega_{e}-\omega_{0})t_{3}+\omega_{b}t_{2}+(\omega_{e}-\omega_{0})t_{1}+\omega_{0}t_{2}+\theta_{probe}\}] \exp\left(-\frac{t_{1}}{T_{2}}-\frac{t_{2}}{T_{4}}-\frac{t_{3}}{T_{2}}\right),$$
(3)

respectively. The ultrashort envelopes of the pump and the probe electrical fields are assumed to be  $\delta$  functions in order to Fourier transform Eqs. (2) and (3). The induced intensity change of the incident pulse is proportional to the imaginary part of the nonlinear polarization multiplied by the conjugate of the incident electric field. The pump-probe signals, expressed as the change of the optical transmission of the sample for the NL processes *A* and *B*, can be written as follows:

$$\frac{\Delta T_A(\omega,\tau)}{I(\omega)} \propto \frac{-(\omega_e - \omega_v) \text{Im}[\tilde{E}_{probe}^*(\omega)\tilde{P}^{(3)}(\omega)]}{|\tilde{E}_{probe}(\omega)|^2} \\ \propto (\omega_e - \omega_v) \exp\left(-\frac{\tau}{T_4}\right) \\ \times \frac{-\Omega \sin(\omega_v \tau) + \gamma_2 \cos(\omega_v \tau)}{\Omega^2 + \gamma_2^2}$$
(4)

and

$$\frac{\Delta T_B(\omega,\tau)}{I(\omega)} \propto \omega_e \exp\left(-\frac{\tau}{T_4}\right) \frac{\Omega' \sin(\omega_v \tau) + \gamma_2 \cos(\omega_v \tau)}{\Omega'^2 + \gamma_2^2},$$
(5)

respectively, where  $I(\omega)$  is the incident spectral intensity of the probe pulse,  $\gamma_2 \equiv 1/T_2$ ,  $\Omega \equiv \omega - \omega_e + \omega_v$ , and  $\Omega' \equiv \omega - \omega_e$ . Real-time spectral changes of the probe pulse are presented for both NL processes A and B. The signals are modulated around  $\Delta T=0$  and do not contribute so much to the integrated spectral change throughout the delay time so that it is difficult to observe this process by other spectroscopies. The spectral width and the vibrational dephasing time in Eqs. (4) and (5) are determined by the electronic dephasing time  $T_2$ and the vibrational dephasing time  $T_4$ , respectively. Using this principle, the electronic dephasing time and the vibrational dephasing time are distinguishable from each other. Because of the advantage of the real-time measurement, this calculation also demonstrates the dependence of the phase of the periodic modulation on the probe wavelength. The difference of the phases reaches  $\pi$  between the higher-energy region  $(|\Omega| \ge \gamma_2, \Omega > 0)$  and the lower-energy region  $(|\Omega|$  $\gg \gamma_2, \Omega < 0$ ). This is an appropriate criterion for the identification of the ground-state dynamics and separation of the cause of the vibration in such a spectrally resolved real-time experiment [8,17,18]. The details of the phase dependence of the experimental results will be discussed later.



FIG. 4. The laser spectrum and the absorption spectrum of PDA-4BCMU.

#### **III. EXPERIMENT**

The sample is a cast film of red-phase PDA-4BCMU on a CaF<sub>2</sub> substrate. PDAs have strong absorption due to the  $1 {}^{1}B_{\mu}$  exciton in the visible wavelength range and are characterized by strong coupling between electronic excitation and vibrational modes along the quasi-one-dimensional main chain [19-21]. Therefore this coupling leads to prominent phonon sidebands of the typical stretching modes of double and triple bonds of carbon atoms in the absorption spectrum with energies about 1500 and 2100 cm<sup>-1</sup>, respectively. The phonon sidebands are well separated from the zero-phonon band so that we can excite the 0-0 transition and the 1-0 transition without exciting the 0-1 transition. The laser pulse for the pump and probe is produced by a noncollinear optical parametric amplifier seeded by white-light continuum [22,23] with a pulse compressor. The source laser of this system is a commercially supplied regenerative chirpedpulse amplifier (Clark-MXR, CPA1000) seeded by a frequency-doubled fiber laser oscillator (IMRA, Femtolite). The pulse duration, central wavelength, repetition rate, and power of the output of this amplifier are 120 fs, 790 nm, 1 kHz, and 400 mW, respectively. The laser developed in our group has a spectrum extending from 500 to 800 nm which could lead to a pulse duration of 4 fs [24,25]. However, in the present experiment the high-energy spectral component (500-550 nm) was filtered out to prevent the excitation of the 0-1 transition of PDA-4BCMU by inserting a block at a compressor consisted of a grating, a concave mirror, and a flexible mirror. The details of our 4-fs laser system are described in [25]. Figure 4 shows the absorption spectrum of PDA-4BCMU and the laser spectrum after removing the higher-energy spectral components. The energy and intensity of the pump pulse at the sample were about 40 nJ and  $0.18 \text{ GW/cm}^2$ , respectively, and those of the probe pulse were about a quarter of those for the pump. Normalized transmittance changes were measured at pump-probe delay times from -100 to 900 fs with steps of 1 fs.

In order to detect the weak pump-probe signal at many probed wavelengths, we applied the multichannel lock-in



FIG. 5. Schematic of the multichannel lock-in amplifier with a pump-probe measurement system. APDs, avalanche photodiodes; PC, personal computer for data acquisition.

amplifier shown in Fig. 5 to time-resolved spectroscopy. The multichannel lock-in amplifier was specially designed for the purpose of detecting low-intensity signals at many probed wavelengths simultaneously over the whole probe spectrum. Although multichannel detection of pump-probe signals has already been realized by a photodiode array or a charged-coupled device (CCD), they are less sensitive to low-level signals buried in a large background, resulting in lower signal-to-noise ratio than in lock-in detection. Multichannel

lock-in detection is a natural solution to use all the information in the probe and to avoid various experimental instabilities, such as sample degradation and laser instability. In this experiment signals spectrally resolved by a polychromator (JASCO, M25-TP) at 128 wavelengths from 540 to 740 nm were detected by avalanche photodiodes and lock-in amplified with a reference from an optical chopper modulating the pump pulse at 210 Hz.

### **IV. RESULTS AND DISCUSSION**

Several typical examples of normalized-transmittance changes at six wavelengths are shown in Fig. 6(a). The power spectra of the Fourier transform (FT) of the acquired signals at each probe wavelength are shown in Fig. 6(b) with a high-pass filter of cutoff frequency 333 cm<sup>-1</sup>. Positive photoinduced transmittance changes especially found at 571 and 603 nm can be attributed to the bleaching of the groundstate population. At the other probed wavelengths, where neither bleaching nor photoinduced absorption is clearly observed, periodic modulations around  $\Delta T/T=0$  are found as predicted by Eq. (4). In Fig. 6(b), two prominent vibrational modes are found in the FT power spectra around 1500 and 2100 cm<sup>-1</sup>. They can be attributed to the stretching modes of carbon-carbon double and triple bonds in the PDA main



FIG. 6. Normalized transmittance changes  $(\Delta T/T)$  (a) of the probe pulse as a function of the pump-probe delay time at six probed wavelengths and FT power spectra (b) of the oscillating components in the delay-time trace of the corresponding transmittance changes.



FIG. 7. FT power spectra of the periodic components of the pump-probe signal over the probed wavelength. *x*, *y*, and *z* axes correspond to probed wavelength (nm), FT frequency  $(cm^{-1})$ , and FT power, respectively.

chain [26]. The relative intensities of C=C and C≡C stretching are changing gradually with the probe wavelength from 603 to 682 nm. In order to analyze this probewavelength dependence in more detail, the FT power spectra at all probed wavelengths are calculated in Fig. 7. In this figure, two broad signals are found around 570 and 625 nm for the 1516 cm<sup>-1</sup> mode, and two more signals are found around 570 and 665 nm for the 2089 cm<sup>-1</sup> mode. This figure clearly shows the dependence of the power spectrum of periodic oscillations on the probe wavelength, which was indicated in Eq. (4), as the periodically modulated signal appears at  $\hbar\omega = \hbar\omega_e - \hbar\omega_v$ . That is, for the NL process A, the modulated signals by different vibrational modes of  $\omega_{v1}$  and  $\omega_{v2}$ appear below the absorption energy  $\omega_e$  at  $\omega_e - \omega_{v1}$  and  $\omega_e$  $-\omega_{v2}$ , respectively. In Fig. 7, the intense FT power of the 1516 cm<sup>-1</sup> mode is found at 625 nm and that of the 2089 cm<sup>-1</sup> mode is found at 665 nm due to the NL process A. In the NL process B, on the other hand, the nonlinear polarization has the same angular frequency as that of the absorbed probe pulse  $\omega_{e}$ . In Fig. 7, the two peaks at 1516 and 2089 cm<sup>-1</sup> appear around the same wavelength of 570 nm due to NL process B. In the two-dimensional diagram of Fig. 7, the spectral width of the signal (nm, horizontal axis) is related to the electronic dephasing time  $T_2$  between  $|e\rangle$  and  $|g_{\nu}\rangle$ , and the signal width as a function of frequency (cm<sup>-1</sup>, vertical axis) reflects the vibrational dephasing time  $T_4$ . This is one of the advantages of the two-dimensional diagram in impulsive Raman spectroscopy, in which the electronic and vibrational dephasing times appear separately along the two different axes. This vibrational dephasing time  $T_4$  (fs) and the spectral width D (PHz) (full width at half maximum) measured by stationary Raman scattering are expected to have the relationship  $T_4=2/D$ . In Fig. 7, the width is larger than  $2/T_4$  since vibrational signals are obtained by Fourier transform over a limited time range, shorter than the vibrational decay time. It should be noted that stationary resonant Raman scattering uses a narrow bandwidth laser, while impulsive Raman scattering uses ultrashort laser pulses with a wide bandwidth, which lead to exciting inhomogeneously



FIG. 8. The FT power spectra: two extracted spectra from Fig. 7 around 1516 cm<sup>-1</sup> (dotted line) and 2089 cm<sup>-1</sup> (dashed line), two modified spectra of which each wavelength is shifted toward higher energy by the vibrational energy [1516 cm<sup>-1</sup> (bold dotted line) and 2089 cm<sup>-1</sup> (bold dashed line)] from the spectra above, and the absorbed laser spectrum of the sample (solid line).

broadened transitions of a sample. The latter could result in the simultaneous excitation of different vibrational frequencies of the same mode because of electronic and/or vibrational inhomogeneity. This broadening is expected to cause a shorter dephasing time of a oscillation by destructive interference among inhomogeneous groups.

The probed spectral width along the horizontal axis corresponds to the electronic dephasing time of the 1-0 transition. This method provides only a way to determine the spectral width of the 1-0 transition in the NL process A. Similarly, the 0-0 transition can be determined by this method in principle, but it is difficult to determine accurately the spectral width of the 0-0 transition from the present data because of the insufficient spectrum of the probe laser at its edge.

In Fig. 8, two FT power spectra are extracted from Fig. 7 and are compared with the absorbed probe spectrum. In this figure three groups of spectra are shown. The first one is composed of two FT power spectra as a function of wavelength, extracted at  $1516 \text{ cm}^{-1}$  (dotted line) and 2089 cm<sup>-1</sup> (dashed line). The second one is the shifted FT power spectra, which are obtained by shifting the extracted spectra by  $1516 \text{ cm}^{-1}$  (bold dotted line) and at 2089 cm<sup>-1</sup> (bold dashed line). The third one is the normalized spectrum of absorbed laser intensity, which is calculated from the spectra of the sample absorption and the laser. This figure shows reasonable agreement between the absorbed laser spectrum and the shifted spectra, demonstrating that the ground-state vibrations appear in the real-time pump-probe signals even below the fundamental absorption edge.

In order to investigate the real-time dynamics of the ground state in the pump-probe experiment, we applied linear prediction-singular value decomposition (LP-SVD) [27] and determined the phases of the real-time data that is expected to be probe-wavelength dependent. The phase of a dumped oscillation is defined with the delay time  $\tau$ , the de-



FIG. 9. Phases of the periodic oscillation  $(1516 \text{ cm}^{-1})$  at t = 0 fs and the fitted result using Eq. (7).

cay time constant  $\tau_0$ , the angular frequency of the vibration  $\omega_v$ , and the optical angular frequency  $\omega$  as

$$\Delta T(\tau, \omega_v, \omega) = A(\omega_v, \omega) \exp\left(-\frac{\tau}{\tau_0(\omega_v, \omega)}\right) \cos[\omega_v \tau + \phi(\omega_v, \omega)].$$
(6)

The wavelength dependence of the phase  $\phi(\omega_v, \omega)$  for the 1516 cm<sup>-1</sup> mode is plotted in Fig. 9. The phases at higher energy  $(|\Omega| \ge \gamma_2, \Omega > 0)$  and at lower energy  $(|\Omega| \ge \gamma_2, \Omega < 0)$  are approximately  $\pi/2$  and  $-\pi/2$ , respectively. In order to determine the center energy  $(\hbar \omega_e - \hbar \omega_v)$  of the periodic signal described in Eq. (4) and the dephasing time  $T_2$ , we fitted this phase dependence of the 1516 cm<sup>-1</sup> mode  $(\omega_v = 1516 \text{ cm}^{-1})$  on  $\omega$  by

$$\phi(\omega_v = 1516 \text{ cm}^{-1}, \omega) = \arctan\left(\frac{(\omega - \omega_e + \omega_v)}{\gamma_2}\right) + \psi$$
 (7)

with the three parameters  $\omega_e - \omega_v$ ,  $\gamma_2$ , and  $\psi$ . The obtained center wavelength, the dephasing time, and the phase offset are  $(\omega_e - \omega_v)/(2\pi) = 475 \pm 2$  THz,  $T_2 = 17.5$  fs (corresponding to 57 THz), and  $\psi = 0.25 \pm 0.09$  rad, respectively. The center wavelength  $(=\hbar \omega_e)$  of the excitation range was calculated as 576 nm (adding the vibrational energy to 475 THz), which corresponds to the center wavelength of the absorbed probe spectrum. The electronic transverse dephasing time in PDAs has been determined to be a few tens of femtoseconds [28,29]. The result calculated above did not include any inhomogeneous broadening and if the inhomogeneity is taken into consideration, the transverse dephasing time will be longer. The phase offset of 0.25 rad indicates a delay-time offset of 0.9 fs.

## V. SUMMARY

In this paper we have demonstrated the spectrally resolved real-time observation of impulsive resonant Raman scattering. The theoretical calculation and the results allowed us to observe the probe-pulse spectral modulation by the vibrations and two nonlinear processes among many other processes.

The experiment in the present paper showed that the ground-state dynamics occurs at an energy far below the absorption energy where the pump-probe signal would be influenced by the excited-state dynamics. This effect is often confused with the excited-state vibrations in induced absorption. If a periodic oscillation could not be explained by the ground-state dynamics, the oscillation would represent the excited-state dynamics, which is expected to mediate conformational changes and photochemical reactions.

We have also presented the two-dimensional diagram as a function of both optical and vibrational frequencies. This two-dimensional Fourier-transformed electronic-vibrational resonance spectroscopy is quite suitable for the detection of both resonance frequency and homogeneous broadening. In conventional one-dimensional absorption and emission spectroscopies of medium size molecules, vibrational structures do not necessarily show up clearly because of the complicated features caused by the spectral broadening. A twodimensional diagram resolved the overlapping vibrational spectra to each vibrational mode as shown in Fig. 7. The spectral widths show vibrational and electronic dephasing times separately on two axes, although the data should be carefully analyzed if the sample has inhomogeneous broadening.

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