

## Excited-State Molecular Vibration Observed for a Probe Pulse Preceding the Pump Pulse by Real-Time Optical Spectroscopy

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It is shown experimentally that the absorbance change observed in the “negative” time range, where probe pulse precedes pump pulse in real-time vibrational spectroscopy is induced only by the excited-state wave-packet motion as theoretically expected. Coherent molecular vibration of a polymer in the excited state was observed in the real-time trace without the effect of wave-packet motion in the ground state, which usually makes it difficult to ascribe the signal either to the ground state or to the excited state.

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In pump-probe spectroscopy, the pump pulse perturbs the absorption spectrum of the medium, which is subsequently probed after a set time delay. This method assumes implicitly that the weak probe pulse does not induce any substantial excitation of the sample [1]. However, in the femtosecond regime difference absorption spectra cannot be directly interpreted as a change of the absorption spectrum because of coherence effects. These effects fall into two categories: one is “coherent coupling” due to the induced grating formed by temporally coincident pump and the probe in the sample [1–4], and the other is the “perturbed free polarization decay” generated by the probe and perturbed by a pump. In the present Letter, the coherent molecular vibration in the excited state in the “negative time” region, where the probe pulse precedes the pump, was observed and compared with the “positive time” data in the short “positive” delay time range after excitation.

Sample films of conjugated polymer, poly{[3-hexylthiophene-2,5-diyl]-[*p*-dimethylaminobenzylidenequinoidmethene]} (PHTDMABQ) were investigated at room temperature ( $298 \pm 1$  K) [5,6]. Using the 6.3 fs pulse, the pump induced absorbance change ( $\Delta A$ ) was measured at 128 different wavelengths from 515 to 716 nm [7,8].

Figures 1 and 2 show the traces of real-time molecular vibration probed at four different wavelengths from –200 fs to 1800 fs and near zero delay time, respectively. The negative time traces have periodic structures similar with positive delay traces as indicated by the delay-time figures attached to the peaks or valleys.

In the previous reports, the experimental results observed in the negative delay-time region were discussed in terms of perturbed free induction decay and coherent coupling [1–4,9–12]. The difference absorption spectrum was calculated for a two-level system and applied to mo-

lecular systems [13,14]. In the following we modified their treatment for the vibronic system, assuming only one mode is coupled to the excitation to the exciton state, but it can easily be extended to a multimode system.

In the rotating reference frame, the time evolution of the elements of the density matrix  $\rho$  for two-electronic state system, which interacts with pump ( $\mathbf{E}_{\text{pu}}(t)$ ) and probe ( $\mathbf{E}_{\text{pr}}(t)$ ) fields is described in Ref. [4] by

$$\dot{\rho}_{ba}(\mathbf{r}, t) = -\left(i\Omega + \frac{1}{T_2}\right)\rho_{ba}(\mathbf{r}, t) + \frac{i}{\hbar}V_{ba}(\mathbf{r}, t)N, \quad (1)$$

$$\begin{aligned} \dot{N} = & -\frac{N - N_0}{T_1} + \frac{2i}{\hbar}[V_{ba}^*(\mathbf{r}, t)\rho_{ba}(\mathbf{r}, t) \\ & - V_{ba}(\mathbf{r}, t)\rho_{ba}^*(\mathbf{r}, t)]. \end{aligned} \quad (2)$$

The interaction potential  $V_{ba}(\mathbf{r}, t)$  is given by [4]

$$V_{ba}(\mathbf{r}, t) = -\boldsymbol{\mu}[\mathbf{E}_{\text{pu}}(t)\exp(i\mathbf{k}_{\text{pu}}\mathbf{r}) + \mathbf{E}_{\text{pr}}(t)\exp(i\mathbf{k}_{\text{pr}}\mathbf{r})], \quad (3)$$

where  $\boldsymbol{\mu}$  is the transition dipole moment,  $T_1$  and  $T_2$  are the longitudinal and transverse electronic relaxation time, respectively, between state 1 and state 2;  $N = \rho_{bb}(\mathbf{r}, t) - \rho_{aa}(\mathbf{r}, t)$  is the population difference, and  $N_0 = [\rho_{bb}(\mathbf{r}, t) - \rho_{aa}(\mathbf{r}, t)]_0$  is the equilibrium population difference without the field;  $\Omega = \omega_{ba} - \omega_1$  is the detuning between the pump-field frequency  $\omega_1$  and the transition frequency  $\omega_{ba}$ .

Molecules composed of  $N$  atoms can have complicated vibronic absorption spectra due to the large number ( $3N - 6$ ) of vibrational modes and strong vibronic coupling. Because of the vibronic coupling, the signal described by Eq. (3) in Ref. [4] for the two-electronic state must be modified. In the following discussion, the system is considered to be composed of two electronic states, both

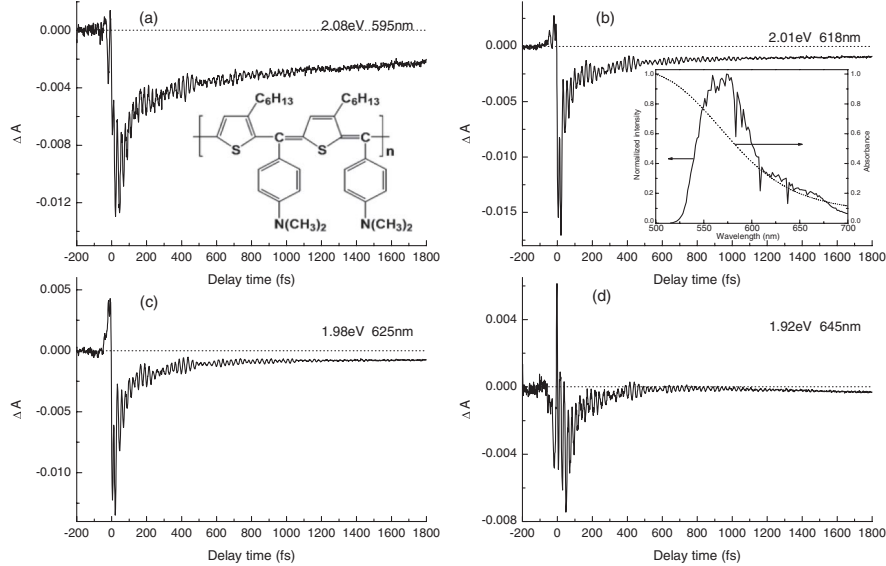


FIG. 1. The vibrational real-time spectra of difference absorption in the whole pump-probe delay time range from  $-200$  fs to  $1800$  fs at four typical probe photon energies of  $2.08$ ,  $2.01$ ,  $1.98$ , and  $1.92$  eV. The dotted lines show zero absorbance change ( $\Delta A$ ). The inset in (a) is the molecular structure of PHTDMABQ, and that in (b) is sample stationary absorption spectrum (dotted line) and laser spectrum (solid line).

coupled to the same vibrational mode with same frequency  $\omega_\nu$ , which is not thermally excited.

The macroscopic polarization  $\mathbf{P}_{\text{pr}}^{(3)}(t)$  in a molecular vibronic system propagating in the probe direction is given by

$$\begin{aligned} \mathbf{P}_{\text{pr}}^{(3)} = & N_0 F_2(t) \otimes \{ \mathbf{E}_{\text{pr}}(t) [F_1(t) \otimes (\mathbf{E}_{\text{pu}}(t) \mathbf{P}_{\text{pu}}^*(t) \\ & - \mathbf{E}_{\text{pu}}^*(t) \mathbf{P}_{\text{pu}}(t))] + \mathbf{E}_{\text{pu}}(t) [F_1(t) \otimes (\mathbf{E}_{\text{pr}}(t) \mathbf{P}_{\text{pr}}^*(t)) \\ & - \mathbf{E}_{\text{pr}}(t) [F_1(t) \otimes (\mathbf{E}_{\text{pu}}^*(t) \mathbf{P}_{\text{pr}}(t))] + \mathbf{E}_{\text{pr}}(t) \}, \end{aligned} \quad (4)$$

where

$$F_1(t) = F_2(t) = 0, \quad (t \leq 0) \quad (5)$$

$$F_1(t) = \frac{2i\mu}{\hbar} \exp(-t/T_1) \exp[-i(\omega_\nu t + \phi)], \quad (t \geq 0) \quad (6)$$

$$\begin{aligned} F_2(t) = & \frac{i\mu}{\hbar} \exp(-t/T_2^{\text{el}}) \exp(-i\Omega t) \exp(-t/T_2^{\text{vib}}) \\ & \times \exp[-i(\omega t + \phi)], \quad (t \geq 0) \end{aligned} \quad (7)$$

$$\phi = \arctan[(\omega - \omega_e + \omega_\nu)T_{\text{vib}}], \quad (8)$$

$$\mathbf{P}_x(t) = F_2(t) \otimes \mathbf{E}_x(t) \quad (x = \text{pu, pr}). \quad (9)$$

Here  $T_{\text{vib}}$  is the vibrational period, and  $T_2^{\text{el}}$  and  $T_2^{\text{vib}}$  are the electronic and vibrational dephasing times, respectively, and  $\omega_e$  is the frequency corresponding to the 0-0 transition energy from the ground state to the electronic excited state. The symbol  $\otimes$  denotes convolution.

The absorbance difference  $\Delta A(\omega)$  is then given by

$$\begin{aligned} \Delta A(\omega) \sim & -\text{Im} \left\{ \frac{f_2(\omega)}{e_{\text{pr}}(\omega)} \mathcal{F}[\mathbf{E}_{\text{pr}}(t) N_{\text{pu}}^{(2)}(t) \right. \\ & + \mathbf{E}_{\text{pu}}(t) [F_1(t) \otimes (\mathbf{E}_{\text{pr}}(t) \mathbf{P}_{\text{pu}}^*(t))] \\ & \left. - \mathbf{E}_{\text{pu}}(t) [F_1(t) \otimes (\mathbf{E}_{\text{pu}}^*(t) \mathbf{P}_{\text{pr}}(t))] \right\}. \end{aligned} \quad (10)$$

Here  $N_{\text{pu}}^{(2)}(t)$  is the population change induced by the pump field, which is modified phenomenologically corresponding to those in [4] and is given by

$$N_{\text{pu}}^{(2)}(t) = F_1(t) \otimes [\mathbf{E}_{\text{pu}}(t) \mathbf{P}_{\text{pu}}^*(t) - \text{c.c.}], \quad (11)$$

$f_2(\omega) = \mathcal{F}[F_2(t)]$  is the Fourier transform (FT) of  $F_2(t)$ .

The first (population) term in Eq. (10) appears only after the onset of pump [Eqs. (6) and (7)], contributing to the positive time region. The second (pump polarization coupling) term [Eq. (10)] is due to the coherent coupling between pump-field induced polarization and probe field appearing only when the probe and pump overlap.

The third (perturbed free polarization decay) term represents the case when the probe pulse comes earlier than the pump pulse, and there is no temporal overlap between them. The probe pulse generates electronic coherence in the sample with the duration of the electronic dephasing time. Then the intense pump field forms a grating  $[\mathbf{E}_{\text{pu}}^*(t) \mathbf{P}_{\text{pr}}(t)]$  term in Eq. (10), which interacts with another pump field to be diffracted into the probe direction, satisfying the causality. In the present case, vibronic coupling expected to be strong in the conjugated electron system is the origin of the electronic spectrum of the ground state. Therefore the polarization generated by the

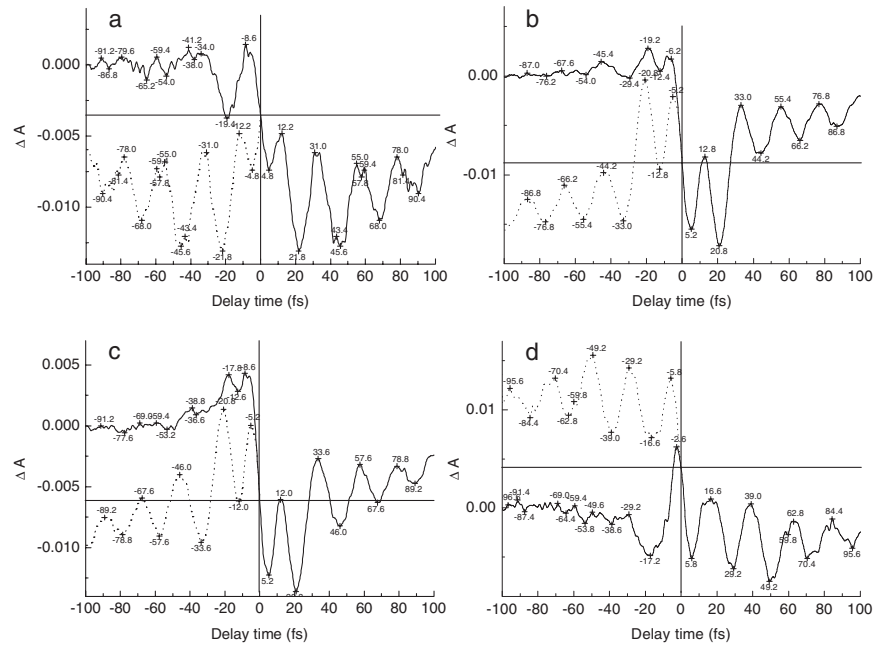


FIG. 2. The expanded real-time traces of corresponding near zero-delay time (in both negative and positive probe delay times) in Fig. 1. The solid lines show the original graphs. The dotted curves were obtained by inverting the real-time traces in the positive time region to the negative time with respect to the origin of the graph at point  $[t = 0, \Delta A(t = 0)]$  [except the curve in graph (a), which was obtained by mirror imaging at  $t = 0$ ].

probe pulse preceding to the pump pulse is not pure electronic transition but a vibronic transition. This is the origin of the observed signal of vibrational oscillation. Therefore, the induced polarization by the probe pulse  $P_{pr}(t)$  is the vibronic polarization associated with the transition between the ground vibrational level in the ground electronic state and the vibronically excited state. The wave-packet formation in the ground state requires the two fields of the pump pulse. Therefore, the third-term signal increases with delay time with the time constant of  $T_2^{el}$ , and disappears quickly at  $t = 0$  [4]. The “negative time” data provide the electronic dephasing time  $T_2^{el} = 12 \pm 1$  fs, which limits the precision of the vibrational frequency together with the vibrational dephasing time by the Fourier transformation.

Following the above discussion, let us discuss the experimental results of real-time spectra in both negative and positive time ranges.

Figures 3(a)–3(c) were calculated for different probe delay-time range at the probe wavelength of 618 nm. It is noticeable that the spectral shapes of the positive probe time ranges are substantially different from those of the negative time range even at the same probe wavelength. The FT power spectrum obtained for 200 to 1800 fs has peaks at 1111, 1184, 1343, 1461, 1514, and 1591  $\text{cm}^{-1}$ , which are high enough for the vibrational levels not to be populated at room temperature. In Figs. 3(b) and 3(c), there is almost no contribution of the most and the second most intense peaks at 1343 and 1111  $\text{cm}^{-1}$ , respectively. Instead, there are two peaks at  $1290 \pm 24$  and  $1530 \pm$

$23 \text{ cm}^{-1}$  for 0 to 200 fs region, and  $1245 \pm 19$  and  $1514 \pm 23 \text{ cm}^{-1}$  for  $-200$  to 0 fs range, respectively. The positions of the two corresponding peaks are close to each other for both peaks. Therefore the frequencies observed in Fig. 3(b) are attributed to the excited state. The frequency difference may be due to the small contribution of the ground-state modes existing only in the positive time range.

The instantaneous frequency of molecular vibration observed from 125 fs was analyzed by calculating a spectrogram, as shown in Fig. 4, at 2.01 eV (618 nm) by using a Blackman window of 240 fs FWHM (full width at half maximum). The dynamics of the amplitudes of 1290 and 1350  $\text{cm}^{-1}$  modes integrated with a 20  $\text{cm}^{-1}$  width were studied. The decay time constant of the former is about 160 fs, and the growth and the decay times of the latter were about 100 and 450 fs, respectively. This frequency shift could be explained in terms of the change in the electronic state associated with the geometrical relaxation from the free exciton to the exciton polaron [15]. The former decay time constant of 160 fs is overestimated because of the Blackman window of FWHM of 240 fs.

From the previous work on polydiacetylene [16], it is expected for the free exciton to decay into the nonthermal exciton polaron (self-trapped exciton) with vibrational mode of 1350  $\text{cm}^{-1}$  with  $\tau_1 = 80 \pm 20$  fs. The decay time is consistent with the growth time of about 100 fs of 1350  $\text{cm}^{-1}$  component. This is also close to the formation time of exciton polaron of  $\lesssim 100$  fs in several polydiacetylenes [16,17]. The mode frequencies of 1290 and

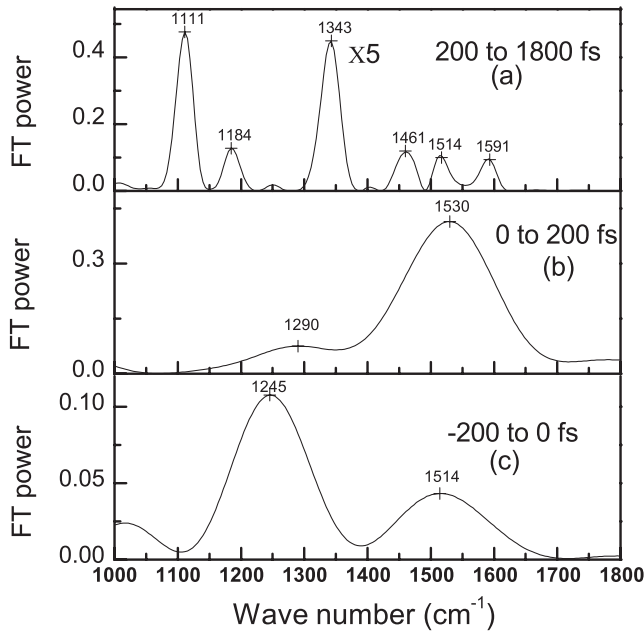


FIG. 3. The FT power spectra of real-time vibrational spectrum at 2.01 eV (618 nm).

1350  $\text{cm}^{-1}$  are then considered to be C-C bond stretching in the free exciton and the exciton polaron, respectively. As shown in Fig. 4, the frequency of the C-C stretching mode coupled to the exciton polaron is elevated to 1350  $\text{cm}^{-1}$  from that of free exciton (1290  $\text{cm}^{-1}$ ). The increase of coupled mode frequency by about 60  $\text{cm}^{-1}$  is due to the enhancement of the bond order by about 4.5% in the C-C bond in the polymer chain after geometrical relaxation from the “benzenoidlike” configuration to the “quinoidlike” one by  $\pi$ -electron delocalization associated with the formation of the exciton polaron. The coherent molecular vibration after the geometrical relaxation is considered to be a kind of reaction induced coherence [18,19].

In conclusion, it was shown that the real-time trace in negative time provided information about polarization

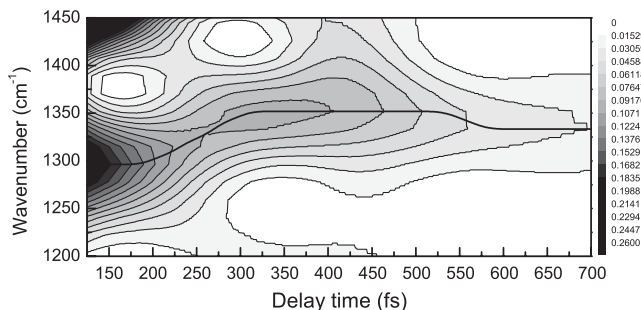


FIG. 4. The contour map of the two-dimension Fourier power spectra of vibrational components obtained by spectrogram calculation at 2.01 eV (618 nm). The solid line denotes the instantaneous Fourier power peak at each delay time.

modulated by molecular vibration in the excited state. The coherent molecular vibration was experimentally observed in the negative time range of the real-time trace of a polymer in the excited-state without the effect of wave-packet motion in the ground state. This “negative” time measurement is a powerful method for studying the excited-state dynamics using molecular structure information.

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