

## Electronic Supplementary Information

# Multiple mode coupling in Cy3 molecules by impulsive coherent vibrational spectroscopy using a few-cycle laser pulse

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## 1. Experimental details of impulsive coherent vibrational spectroscopy

A schematic diagram of the impulsive coherent vibrational spectroscopy is shown in figure.S.1. It is composed of NOPA used as a light source<sup>1,2</sup>, a pump-probe setup and a data acquisition instrument as described as below.

### 1-1. NOPA

The pump source of this NOPA system was a commercially available regenerative amplifier (Spectra-Physics, Spitfire) that has a pulse duration of 50 fs, a center wavelength of 790 nm, a pulse repetition rate of 5 kHz, and an average output power of 800 mW. A small fraction of the fundamental was focused on to a 1-mm thick sapphire plate to generate white light continuum through a stable single filament. The second harmonic (SH) was generated in a 0.17mm thick BBO(type I,  $\theta = 29.2^\circ$ ) with 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. The amplified signal pulse after the double-pass NOPA with a spectrum extending from 1.69 -2.37eV was compressed with a pair of chirp mirrors and then with a prism pair, resulting in a pulse duration of 6.2fs, which is nearly Fourier transform(FT) limited. The pulse from the NOPA was split into two: the pump and probe pulses with energy of about 40 and 2nJ, respectively.

## 1-2. 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  $\text{mm}^{-1}$ , 500nm blazed ) was utilized to disperse the probe pulse and guide it to 128 avalanche photo detectors( Hamamatsu Photonics, S5343 ) by a 128 channel fiber bundle (FiberTech Optica). The four 32 channel lock-in amplifiers (Signal Recovery, 7210 ) were synchronized as a 128-channel lock-in amplifier system. The 128-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 1.5nm.. The pump-probe experiment was performed with a delay time step of 1 fs in the time range from -100 to 1100 fs.

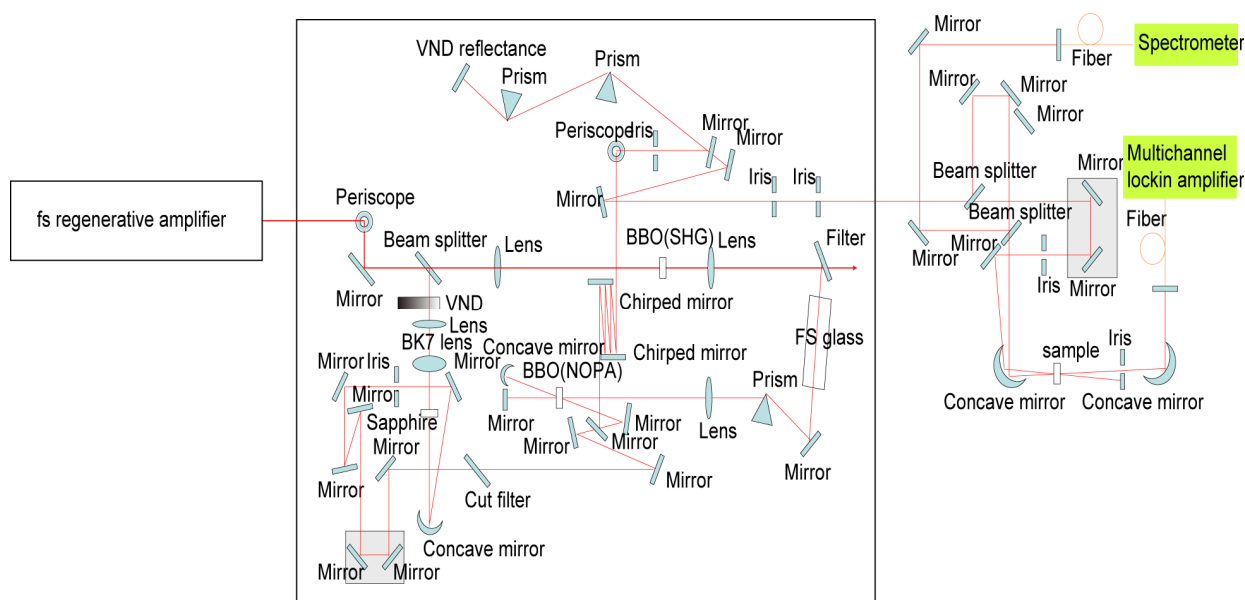


Fig.S1 Experimental apparatus

## 2. The pulse characterization and the influence to the pulse due to the sample

### 2.1. The pulse characterization

The pulse characterization has been done by the autocorrelation method by using the pump probe setup described in the figure.S1. A 5- $\mu\text{m}$ -thick BBO crystal ( $\theta = 31^\circ$ ) was placed on the sample holder. In order to precompensate the dispersion in the 1-mm thick front-wall of the quartz cell containing Cy3/water (0.11 mM), a 1-mm thick quartz plate is placed in front of BBO crystal during the characterization of NOPA pulse. The sum frequency of the pump and probe in the BBO crystal is measured as the auto-(cross-) correlation of the NOPA..

### 2.2 The simulation of the pulse propagation in the sample

As the pulse duration becomes ultrashort as in the preset experiment, we must take account of the effects of the pulse distortion during pulse propagation.

When incident pulse  $E(t, z) = E_0 \exp(-i\omega t - ikz)$  with amplitude of electronic field  $E_0$ , angular frequency  $\omega$  and propagation constant  $k$  propagate the material. The phase of incident pulse is modulated due to the dispersion and intensity decreases due to the absorption.

To consider the dispersion effect precisely, the propagation constant is expanded in Taylor series truncated with third order as follows.

$$k(\omega) \approx k_{\omega_0} + \left. \frac{\partial k}{\partial \omega} \right|_{\omega_0} (\omega - \omega_0) + \frac{1}{2} \left. \frac{\partial^2 k}{\partial \omega^2} \right|_{\omega_0} (\omega - \omega_0)^2 + \frac{1}{6} \left. \frac{\partial^3 k}{\partial \omega^3} \right|_{\omega_0} (\omega - \omega_0)^3 + \dots \quad (1)$$

where  $k_0^{(n)} \equiv \left. \frac{\partial^{(n)} k}{\partial \omega^{(n)}} \right|_{\omega_0}$  are described as

$$\begin{aligned} k_0' &= \frac{1}{c} \left( n + \omega \frac{dn}{d\omega} \right) \\ k_0'' &= \frac{1}{c} \left( 2 \frac{dn}{d\omega} + \omega \frac{d^2 n}{d\omega^2} \right) \\ k_0''' &= \frac{1}{c} \left( 3 \frac{d^2 n}{d\omega^2} + \omega \frac{d^3 n}{d\omega^3} \right) \end{aligned} \quad (2)$$

Here  $n$  and  $c$  are refractive index and velocity of light. In the calculation, we considered group-velocity dispersion (GVD)  $k_0''$ , and third-order dispersion(TOD)  $k_0'''$  as dispersion effects and included absorption effect. Thus pulse propagation is described as eq3.

$$\frac{\partial E}{\partial z} = \hat{D}E \quad (3)$$

$$\text{Where } \hat{D} = -\frac{ik_0''}{2} \frac{\partial^2}{\partial T^2} + \frac{k_0'''}{6} \frac{\partial^3}{\partial T^3} - \frac{\alpha}{2}$$

In the above equations, the dispersion effect and absorption of both solute ( Cy3 molecules ) and solvent(water) are included.

### 2.2.1 Solute's effect to the pulse propagation

Absorbance  $A = -\log_{10} I/I_0$  shown in figure 1 is related to the absorption coefficients  $\alpha$  as  $A' = -\ln I/I_0 = 0.434A = \alpha\ell$ . Here  $I_0$  and  $I$  means incident pulse and transmitted pulse of the sample cell with optical length  $\ell$ , respectively.

Because the relationship between absorption coefficients and extinction coefficients  $\kappa$  is described as  $\alpha = 2\omega\kappa/c$ , we can acquire the spectra of extinction coefficients of Cy3(Figure S2(a)). The spectra of difference refractive index from vacuum  $\Delta n \equiv n - 1$  (Figure S2(b)) can be acquired from Kramers-Kronig relations (eq(4)).<sup>3</sup>

$$\begin{aligned} \eta(\omega) - 1 &= \frac{2\omega}{\pi} P \int_0^{\infty} \frac{\omega' \kappa(\omega')}{\omega'^2 - \omega^2} d\omega' \\ \kappa(\omega') &= -\frac{2\omega}{\pi} P \int_0^{\infty} \frac{\eta(\omega) - 1}{\omega'^2 - \omega^2} d\omega' \end{aligned} \quad (4)$$

Because the refractive index change is quite small, we can consider that the refractive index of Cy3 is constant. Thus we do not need to include the dispersion but absorption effect of Cy3 molecules in the pulse propagation calculation.

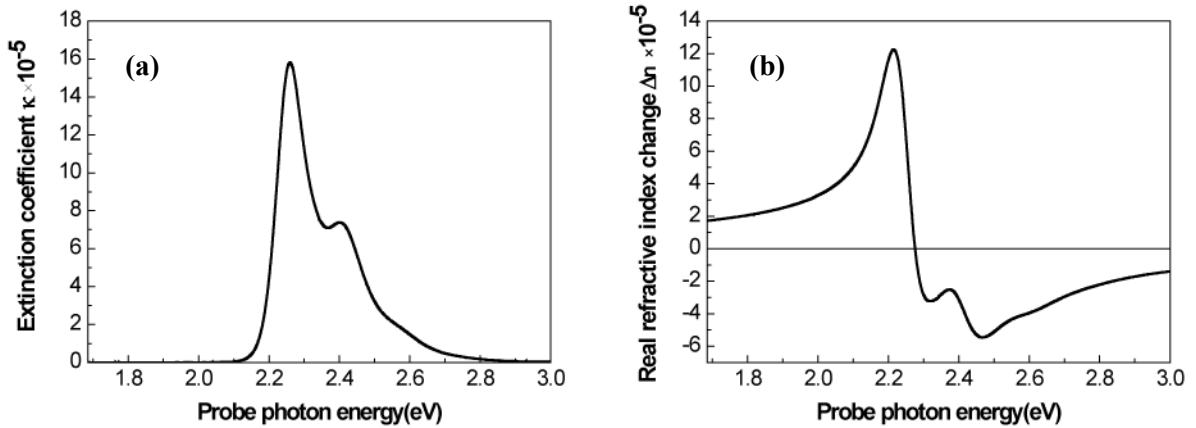


Fig.S2 (a) Extinction coefficients and (b)real refractive index change of Cy3 molecules

### 2.2.1 The effect of refractive index of solvent on the pulse shape depending on the pulse propagation distance

Because water is transparent in the visible region in this study, we must consider the dispersion effect. The reflective index of water is empirically written as below equation.<sup>4</sup>

$$n = 1.313242 + 15.7834/\lambda - 4832/\lambda^2 + 1.1455 \times 10^6/\lambda^3 \quad (5)$$

From the relation  $2\pi n_0/\lambda_0 = \omega_0 n_0/c = k_0$ , we can get GVD and TOD from refractive index of water. Each refractive index, GVD and TOD of water are shown in the figure. S3.

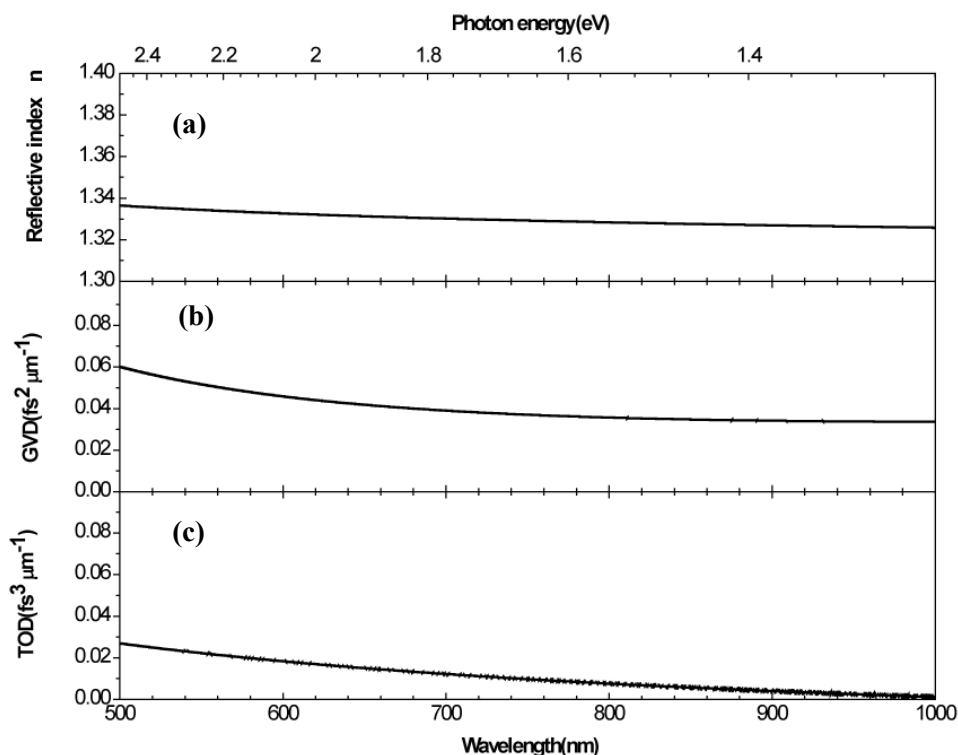


Fig.S3 (a)Refractive index, (b)GVD and (c)TOD of water

From the data of GVD and TOD of water and absorbance due to Cy3, we can calculate the pulse propagation of NOPA in the sample cell. The calculation has been done by split-step Fourier method with propagation distance from 0 to 1mm with 0.1mm step.<sup>5</sup> The result of both temporal and spectral change are shown in figure S4. The pulse broadens from 5.6 to 17.6 fs although the spectra does not change well. From these result we must take care of the material dispersion in the cell when we treat ultra short pulse. Because pump and probe pulses focus to the sample non-collinearly with the relative angle less than 3° and placed the center of sample cell relatively afterward of the focus point, the influence of pulse broadening of pump light is not critical to our experimental result.

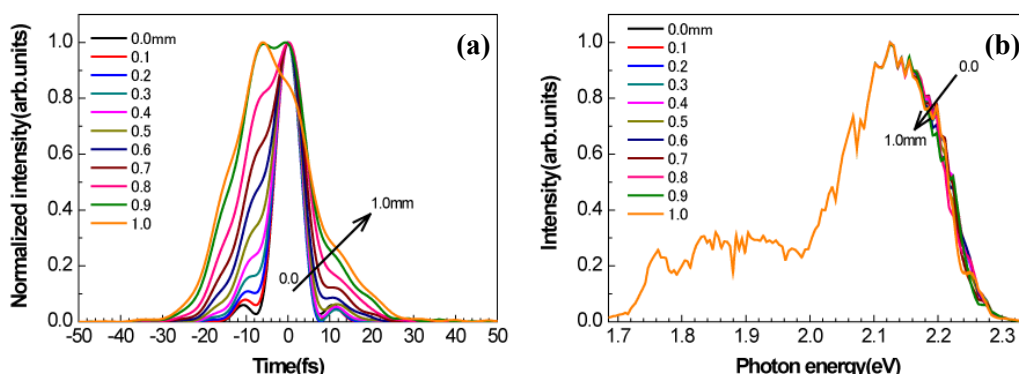


Fig.S4 The simulation result of (a)temporal and (b)spectral change due to pulse propagation in the sample

### 3. Electronic phase relaxation time

#### 3.1 The derivation of the electronic relaxation time from real-time vibrational spectroscopy

As described in ref.6, the  $\Delta A$  data in the negative time region is due to the electronic dephasing. According to it, the resultant data can be described as an exponential decay  $\Delta A(\omega, t) = A_0 \exp(-t/T_2)$ . The typical data is shown in figure3(A).

#### 3.2.The derivation of the electronic relaxation time from stationary absorption spectra

The absorption spectra can be described as follows.<sup>7</sup>

$$I(\omega) = C\omega \int_{-\infty}^{\infty} \exp(i\omega t) \langle \phi_0 | \phi(t) \rangle \exp(-\Gamma^2 t^2 + (iE_0 / \hbar)t) dt \quad (6)$$

Because inverse Fourier transformation of the stationary absorption spectra depicted in figure 3(c) shows the temporal separation between electronic and vibrational behaviour well, we can determine the electronic dephasing time by fitting the formula with inverse Fourier transformation of eq(6).

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