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Coherent wavepacket motion in an ultrafast electron transfer system monitored by femtosecond degenerate four-wave-mixing and pump–probe spectroscopy

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ABSTRACT

Coherent nuclear wavepacket motions were monitored by three types of femtosecond time-resolved spectroscopy, namely, transient absorption measurement utilizing white-light supercontinuum (WC-TA), degenerate four-wave-mixing (DFWM), and pump–probe (PP) measurements, for an ultrafast intermolecular electron transfer (ET) system with a dye molecule, oxazine 1 (Ox1), dissolved in an electron donating solvent, N,N-dimethylaniline (DMA). Vibrational frequencies of the wavepacket motion in the excited and in the ground states were 560–562 and 567–569 cm^{-1}, respectively, with only a few frequency difference of 5–9 cm^{-1}, which were clearly distinguishable by the highly accurate measurements. In DMA, the excited state wavepacket motion declined with time constant of 160–240 fs which is somewhat longer than that of the ultrafast ET; 60–80 fs.

1. Introduction

Chemical reaction is a process that transforms the molecular structure of a compound into another, thus, certain molecular motions are considered to be involved in a specific reaction. For a simple two atomic molecule, it is easy to imagine that the stretching of a covalent bond between the atoms is coupled to a photodissociation reaction. In the case of sodium iodide, Zewail and coworkers have observed by femtosecond ultrafast spectroscopy that the photoproduct, sodium and iodine atoms, are produced stepwise each time when the molecule is stretched [1,2]. However, in the case of more complex chemical reaction of polyatomic molecules, it becomes difficult to identify the molecular motion involved.

In the case of electron transfer (ET), the particle in motion is an electron, thus simply thinking, it may seem that it is independent from the motion of atoms and molecules. However, solvent reorganization (solvation) is considered to be the driving force of ET in polar solvents because the charge or electric dipole is significantly stabilized by the polarization induced by solvation [3–8]. Moreover, when electron moves from one molecular orbital to another, molecular structure could also change as a consequence of the change in bonding ability. Therefore, the motion of solvent molecules and/or intramolecular atoms which are much heavier than an electron could be the rate limit factor for ET. In relation with the ET theory of Marcus [5,9], the effect of solvation upon ET have been studied extensively [6–8], while the effect of intramolecular nuclear motion remains mostly unexplored. It is considered that asymmetric bell-shaped energy gap dependence of ET arises from the contribution of vibrational levels in the product state [10,11], however, specific vibration involved in ET is yet to be identified.

From the view point of dynamics, intramolecular nuclear organization is considered to exceed the solvation process and induces ultrafast ET. One of such well studied system is a dye dissolved in neat electron donating solvents [12–17]. Because the electron acceptor is always surrounded by donors, the ET occurs for the most favorable pair without any molecular diffusion. By femtosecond ultrafast spectroscopies, this system is reported to exhibit ET with time constant of <100 fs [18,19] which is even shorter than the usual picosecond vibrational dephasing time. Especially, coherent nuclear wavepacket motions have been reported for oxazine 1 (Ox1) in N,N-dimethylaniline (DMA) by Zinth and coworkers

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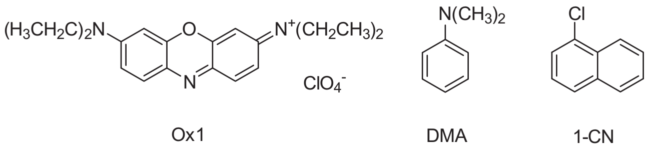

Fig. 1. The molecular structures of oxazine 1 (Ox1), N,N-dimethylaniline (DMA), and 1-chloronaphthalene (1-CN).

[19–21], the structures of which are shown in Fig. 1. However, the vibrational frequencies of the wavepackets did not change considerably upon photoexcitation nor ET, i.e., 562 and 567 cm^{-1} for the excited and ground states, respectively, and they were overlapped in a wide range of probe wavelengths. Thus, the time behavior of the wavepacket motion during the course of ET is not yet fully evaluated.

Recently, we have also started to investigate the details of the wavepacket motion in Ox1/DMA system by means of degenerate four-wave-mixing (DFWM) spectroscopy [22], and in the present article, two types of femtosecond pulse laser spectroscopies [23–27], namely transient absorption utilizing white-light supercontinuum (WC-TA) and pump–probe (PP) techniques, are also been applied to extract the behavior of wavepacket motions. WC-TA spectroscopy can simultaneously monitor the entire visible range of 400–800 nm, although, higher S/N ratio and time-resolution can be attained by DFWM and PP spectroscopies carried out at a single wavelength. Background-free three-pulse DFWM can also coherently control wavepacket motions [28,29] and, it is reported that coherent vibrations can be selectively switched from that in the ground state to that in the excited state in the case of neat iodine vapor [30,31]. Tuning the pump and probe wavelengths will also enable access to the details of the wavepacket dynamics. It would be an interesting task to distinguish the wavepackets of Ox1 with similar frequencies in multiple electronic states and extract the real time behavior of the one involved in the ET process by combination of these spectroscopies.

2. Experimental methods

Setup for ultrafast measurements have been reported previously [32,33], although the laser system was replaced by non-collinear optical parametric amplifier (TOPAS-White, Light Conversion) pumped by regenerative amplified Ti: sapphire laser (Solstice or Tsunami with Spitfire, Spectra Physics). For WC-TA measurement, pulse centered at ca. 660 nm generated from TOPAS-White and white-light supercontinuum generated from a 1 mm glass plate were utilized and the polarization was set at magic angle. The signal and the reference pulses were detected with multichannel diode array systems (PMA-10, Hamamatsu) and sent to a personal computer for further analysis. Spectra were calibrated for group velocity dispersion by optical Kerr measurement between the pump pulse and the white-light continuum. The energy of the pump pulse measured at the sample position was ca. 10 nJ and the size of the laser beam was ca. 0.15 mm at the focusing point. The fwhm of the pump pulse was determined to be ca. 18 fs while that of the supercontinuum depends on the wavelength. Consequently, the time resolution of the apparatus depends on the wavelength and it was ca. 30 fs around 650 nm while it stretches to 45 fs around 450 nm.

For degenerate four-wave-mixing (DFWM) measurement, pulses generated at wavelengths centered at ca. 620 nm or 660 nm were divided into three beams by reflective neutral density (ND) filters. There are two variable time delays that can be controlled for DFWM measurement, i.e., the interval between the first and the second pulse, t_{12} and that between the first and the third pulse, t_{13}. In the present case, t_{12} was set at certain values such as −13, 0, and 13 fs and t_{13} was scanned. The pulse duration and pulse energies measured at the sample position were 12–14 fs and 4–7 nJ, respectively, and the size of the laser beam was ca. 0.1 mm at the focusing point. For PP measurement, only two of the three pulses were utilized and the energy of the probe pulse was reduced to ca. 0.5 nJ by a variable ND filter. The signals were measured by photodiodes with lock-in amplifiers (EG&G Princeton Applied Research, Model 5210).

Oxazine 1 (Ox1) was purchased from Exciton Chemicals, N,N-dimethylaniline (DMA) and 1-chloronaphthalene (1-CN) were from Aldrich (redistilled, 99.5%+) and Tokyo Chemical Industry (EP, >97.0%), respectively, and used without further purification. Absorption and fluorescence spectra were measured by Hitachi U-3500 spectrophotometer and F850 spectrofluorometer, respectively.

3. Results and discussion

3.1. Steady state electronic spectra

The absorption spectra of Ox1 in DMA and in an inert solvent, 1-CN, are shown in Fig. 2a. Because the polarity of 1-CN is similar to that of DMA, i.e., the values of normalize empirical parameter of solvent polarity are 0.19 and 0.22, respectively [34], the absorption maximum is located at similar wavelength of ca. 658 nm without any solvatochromic shift. It can be also seen that the spectrum in DMA is significantly broader than that in 1-CN, although no additional new band is detectable, which indicates that the solute and solvent are forming a weak charge transfer (CT) complex [35]. The fluorescence of Ox1/DMA was undetectable due to the quenching induced by the ultrafast excited state ET [15], thus, only the fluorescence spectrum of Ox1/1-CN is presented in Fig. 2a. The fluorescence quantum yields of Ox1 in ethanol and 1,2-dichloroethane are reported to be 0.11 and 0.44, respectively [36]. From these values, we estimate that that in 1-CN to be ca. 0.49. The

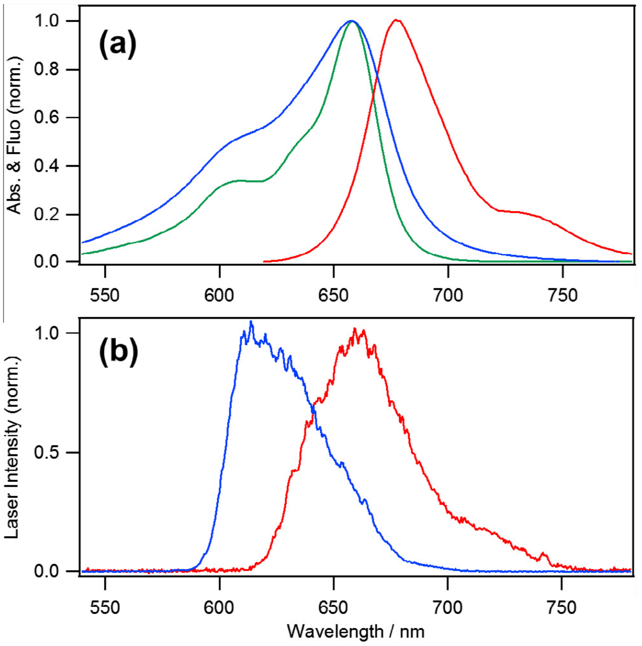

Fig. 2. (a) The absorption spectra of Ox1 in 1-CN (green curve) and DMA (blue curve) and fluorescence spectrum in 1-CN (red curve). (b) Laser spectrum centered at ca. 620 nm (blue curve) and 660 nm (red curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)