

# Femtosecond degenerate four-wave-mixing measurements of coherent intramolecular vibrations in an ultrafast electron transfer system<sup>☆</sup>



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## ABSTRACT

Femtosecond degenerate four-wave-mixing (DFWM) spectroscopy was carried out to investigate the behavior of coherent wavepacket motion in an ultrafast intermolecular electron transfer (ET) system which consists of a dye molecule, oxazine 1 (Ox1), in an electron donating solvent, *N,N*-dimethylaniline (DMA). Due to the ultrafast ET in DMA with time constant of ca. 59–81 fs, acceleration of the vibrational dephasing for the excited state mode at 562 cm<sup>-1</sup> was observed by the DFWM measurement and confirmed by pump-probe (PP) spectroscopy. Interestingly, the dephasing time of the excited state mode in DMA is in the order of 160–240 fs, which is significantly longer than the time constant of ET, which indicates that the oscillation is not diminished instantaneously by the ET but somewhat persists into the product state.

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## 1. Introduction

Photoinduced electron transfer (ET) is one of the most important fundamental processes in chemical reaction which is related to light-energy conversion [1–3]. Simply thinking, it may seem that dynamics of ET is independent from the motion of atoms and molecules because the particle in motion is an electron. However, in the case of ET in polar solvents, solvent reorganization (solvation) is considered to be the driving force because the charge or electric dipole produced by the reaction are stabilized by solvation [4–6]. Ordinary salt, sodium chloride, easily dissolves in water and dissociates into sodium cation and chloride anion because of the solvation. Therefore, in the fundamental theoretical model of ET in solution developed by Marcus [7–10], the reaction coordinate is described by two parabolic curves that represent polarization induced by the solvent for the reactant and product states. In

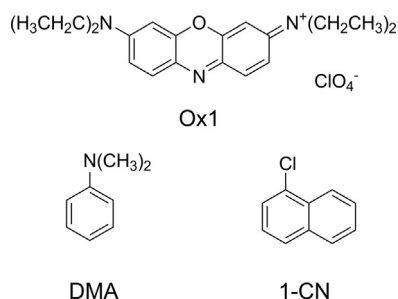
this model, the reaction rate depends on the energy gap [11–13], the coupling between the two states [14–16], and the fluctuating motion of solvent molecules [17–19].

Moreover, when an electron moves from one molecular orbital to another, molecular structure could also change as a consequence of the change in bonding ability. Therefore, not only the motion of solvent molecules but also intramolecular nuclear reorganization could contribute in ET [10]. In order to include the effect of nuclear reorganization into such a model, nested type of energy potentials are introduced, i.e., potential energy surface of solvation must be considered for each vibrational level [20,21]. Therefore, in this model, several crossing points appear between the vibrational levels of reactant and product states, and the reaction proceeds through the crossing points with the largest electronic coupling. It is considered that the vibrational levels of the product state contribute to ET in the Marcus inverted region and affect the bell-shaped energy gap dependence to be asymmetric. However, while the influence of solvation dynamics upon ET has been studied extensively, the effect of intramolecular nuclear motion remains mostly unexplored. It is considered that because intramolecular nuclear reorganization can occur much faster than solvent reorganization, intramolecular degrees of freedom is expected to induce ET much faster than solvation dynamics [10,22,23]. However, involvement of specific vibration in ET is not yet investigated thoroughly.

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

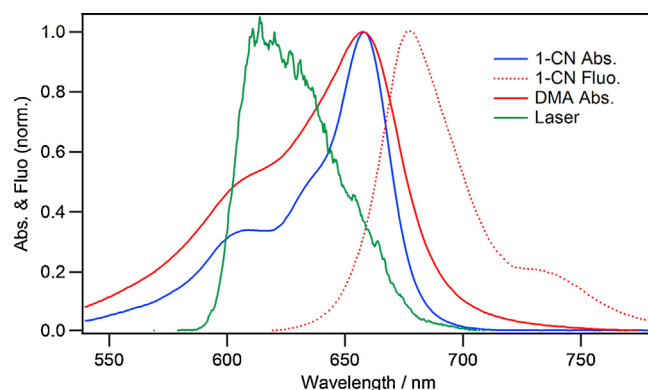
Femtosecond nonlinear spectroscopies, such as degenerate four-wave-mixing (DFWM) and pump-probe (PP) techniques, are useful techniques to investigate the effect of intramolecular contributions because it can induce and monitor coherent nuclear wavepacket motions when the laser pulse duration is sufficiently short [24]. Especially, three-pulse DFWM is applied to study solvation dynamics [25] and intramolecular vibrations [26]. DFWM can also enhance or suppress certain wavepacket motions by controlling the delay between the two pump pulses [27,28] and, in the case of neat iodine vapor, it is reported that observation of coherent vibrations can be selectively switched from that in the ground state to that in the excited state [29]. Therefore, DFWM can be a powerful tool to study the role of coherent vibration in chemical reactions.

The problem is that the vibrational dephasing of general organic molecules is in the picosecond time range which is quite short, although, it can be overcome by utilizing an ultrafast ET system. The system we have chosen is dye dissolved in an electron donating solvent, in the present case, oxazine 1 (Ox1) in *N,N*-dimethylaniline (DMA), the structures of which are shown in Fig. 1. Because the electron acceptor is dissolved in a donor solvent, the ET occurs without any molecular diffusion. By femtosecond ultrafast spectroscopies, this system is reported to exhibit ET with time constant of <100 fs which is faster than the general vibrational dephasing [30–33]. The rate of ET is also much faster than the diffusive solvation process that occurs in the picosecond range [4], suggesting the involvement of ultrafast intramolecular nuclear reorganization. Therefore, we have applied femtosecond DFWM and PP measurements to elucidate the role of coherent vibrations in ultrafast ET.

## 2. Experimental methods

Setup for DFWM measurement has been reported previously [27,34–36], although the laser system was replaced by non-collinear optical parametric amplifier (TOPAS-White, Light Conversion) pumped by regenerative amplified Ti: sapphire laser (Solstice, Spectra Physics). The pulses generated at wavelengths centered at ca. 620 nm were divided into three beams by reflective ND filters and the pulse duration and pulse energies measured at the sample position were 12–14 fs and 4–7 nJ, respectively.

In DFWM measurement, the first two pulses are the pump pulses that generate an interference pattern in the sample, and the third probe pulse is diffracted into directions that satisfy the phase matching condition. There are two variable time delays that can be controlled, 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,  $t_{12}$  is set at certain values and  $t_{13}$  is scanned. For the pump-probe (PP) measurement, one of the three pulses was blocked and the energy of another was reduced to 1/10 by a variable ND filter and utilized as the probe pulse while the remaining one was utilized as the pump pulse. The signal was measured by photodiodes



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

with lock-in amplifiers (EG&G Princeton Applied Research, Model 5210).

Ox1, DMA, and 1-chloronaphthalene (1-CN) were purchased from Exciton Chemicals, 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 absorption and fluorescence spectra

The absorption spectra of Ox1 in 1-CN and DMA, fluorescence spectrum of Ox1 in 1-CN, and the laser spectrum are shown in Fig. 2. The fluorescence of Ox1 in DMA was undetectable due to the quenching induced by the ultrafast excited state ET. 1-CN is an inert solvent with polarity similar to that of DMA, hence the absorption maximum is located at similar wavelength of ca. 658 nm without any solvatochromic shift. It can be 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 could be forming a weak charge transfer (CT) complex [37].

The laser spectrum was chosen to be centered at a wavelength of ca. 620 nm which is located at the blue side of the absorption maximum. Zinth and co-workers have reported that the excited state absorption of Ox1 is overlapped with that of the ground state in the range of <640 nm [32]. Thus, it is expected that the excited state vibrational motion could be detectable at this excitation wavelength.

### 3.2. DFWM signal of Ox1/1-CN

The DFWM signal of Ox1 in inert solvent, 1-CN, with the values of  $t_{12}$  set at 0 and  $\pm 13$  fs, are shown in Fig. 3a. When  $t_{12}$  is tuned to positive delay ( $t_{12} = 13$  fs), a spike appears near the time origin and the spike dominates the signal with further increasing the delay (not shown). In Fig. 3b, oscillatory part of the signal is shown which was obtained by subtracting the decay components (in this case it is nearly constant because ET does not occur in this solvent) from the signal. The oscillations could be generated either in the excited state by Franck-Condon transition and/or in the ground state by stimulated resonance Raman process. At a negative delay of  $t_{12} = -13$  fs, although the amplitude is weaker, it seems that the oscillation endure longer than those at either  $t_{12} = 0$  fs or 13 fs. By

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