1 Femtosecond degenerate four-wave-mixing measurements
2 of coherent intramolecular vibrations in an ultrafast
3 electron transfer system

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1

2 **Abstract**

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

13

14 **Keywords**

15 ultrafast spectroscopy; electron transfer; coherent nuclear wavepacket motion;
16 degenerate four-wave-mixing

17

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 also contribute in ET.[10] In order to include the effect of nuclear

1 reorganization into such a model, nested type of energy potentials are introduced, *i.e.*,
2 potential energy surface of solvation must be considered for each vibrational level.[20,
3 21] Therefore, in this model, several crossing points appear between the vibrational
4 levels of reactant and product states and the reaction proceeds through the crossing
5 points with the largest electronic coupling. It is considered that the vibrational levels of
6 the product state contribute to ET in the Marcus inverted region and affect the
7 bell-shaped energy gap dependence to be asymmetric. However, while the influence of
8 solvation dynamics upon ET has been studied extensively, the effect of intramolecular
9 nuclear motion remains mostly unexplored. It is considered that, because intramolecular
10 nuclear reorganization can occur much faster than solvent reorganization,
11 intramolecular degrees of freedom is expected to induce ET much faster than solvation
12 dynamics.[10, 22, 23] However, involvement of specific vibration in ET is not yet
13 investigated thoroughly.

14 Femtosecond nonlinear spectroscopies, such as degenerate four-wave-mixing
15 (DFWM) and pump-probe (PP) techniques, are useful techniques to investigate the
16 effect of intramolecular contributions because it can induce and monitor coherent
17 nuclear wavepacket motions when the laser pulse duration is sufficiently short.[24]
18 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 a 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 Figure 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.

pulse. The signal was measured by photodiodes 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 Figure 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]

Insert **Figure 2** here.

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 coworkers 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 ± 13 fs, are shown in Figure 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 Figure 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

1 amplitude is weaker, it seems that the oscillation endure longer than those at either $t_{12}=$
2 0 fs or 13 fs. By a least-squares-fitting, the dephasing time for the strongest vibrational
3 mode at 562 cm^{-1} is obtained to be 1.3 ps at $t_{12}= 13\text{ fs}$ and 1.5 ps at $t_{12}= 0\text{ fs}$ while it is
4 $2.8\pm0.1\text{ ps}$ at $t_{12}= -13\text{ fs}$.

5 **Insert Figure 3 here.**

6 These two effects are due to photon echo type of signal appearing at positive
7 value of t_{12} . At least eight double sided Feynman diagrams are necessary to describe the
8 time-evolution of the density matrix element involved in DFWM process.[23] The
9 photon echo type rephasing diagrams only appear when $t_{12} > 0$ and no rephasing takes
10 place for $t_{12} < 0$. Therefore the spike in the signal and the faster vibrational dephasing
11 time at $t_{12} \geq 0$ are due to the difference in time evolution of the density matrix element.

12 3-3. DFWM signal of Ox1/DMA

13 On the other hand, DFWM signals of Ox1 in DMA shown in Figure 4a initially exhibit
14 ultrafast decay which is independent of the value of t_{12} and the amplitude of the
15 oscillation is significantly weaker than that of Ox1/1-CN. The signal could be fitted
16 reasonably with oscillating components, two decay components and a rise. The time
17 constants (relative intensity) for the decays and rise are $59 \pm 1\text{ fs}$ (0.60), $1.8 \pm 0.2\text{ ps}$

(0.40), and 1.0 ± 0.2 ps (-0.16), respectively. The fastest and the longest decay correspond to the ET and the back ET processes, respectively,[32, 33] while the 1.0 ps rise component is presumably due to the conformational relaxation in the CT state which has never been reported. Because DFWM is a back-ground-free homodyne measurement, two fold of the longest time constant, ca. 3.6 ps, agrees with the previously reported value of 3.8 ps for the back ET.[32] On the other hand, two fold of the shortest time constant, ca. 120 fs, is somewhat longer than the reported values of 30-80 fs.[32, 33] It should be considered that the longer decaying components could serve as a local oscillator for the faster components which enables the heterodyne detection (cross term between the two components can be detected as the diffracted light intensity). Therefore, the directly obtained value of 60 fs is closer to the actual time constant for the ET.

Insert **Figure 4** here.

It can be seen from the oscillatory part of the signal (Figure 4b), obtained by subtracting the decay components, that the vibrational dephasing is accelerated by the ultrafast decay. The time constant for the dephasing is about 440 ± 20 fs for the 570 cm^{-2} mode which is significantly longer than that obtained for the decay caused by the ET. If

the oscillation originates from the excited state, it seems as if the oscillation is not diminished instantaneously by the ET but somewhat extends into the product state.

Fourier transformed spectra of the oscillations (normalized) in 1-CN and DMA are shown in Figure 5a and 5b, respectively. Real parts of the spectrum is represented because it connote initial phase information, *i.e.*, cosine function appear as a Lorentzian-shape band in the spectrum while $\pi/2$ shifted sine function appears as a derivative of that and π shifted function will appear as a negative band. As can be seen from Figure 5, all the bands have positive peaks without derivative-type shape, thus the initial phase of the vibration must be all similar. The band at 562 cm^{-1} is the dominant mode in 1-CN and it is slightly shifted to a higher frequency of 570 cm^{-1} in DMA. The bands in 1-CN are very sharp due to the long dephasing time, while the bands in DMA do not resemble Lorentzian but they rather look as if a sharp band is located on top of a broader background. It may be a combination of two vibrations with similar frequencies but with shorter and longer dephasing times. Thus, fitting was carried out utilizing a cosine function multiplied by double exponential functions and the dephasing times (relative intensity) for the band at 570 cm^{-1} in DMA ($t_{12}=0\text{ fs}$) were obtained to be $240 \pm 40\text{ fs}$ (0.80) and $1.2 \pm 0.2\text{ ps}$ (0.20). This result indicates that the oscillations can be arising from multiple electronic states.

1 with the probe beam being the stable local oscillator. Therefore, PP signal should be
2 more straight forward to interpret and the measurement was carried out.

3 As shown in Figure 6, while the PP signal of Ox1/1-CN strongly vibrates,
4 ultrafast decay and reduction of the vibrational amplitude can be observed in the signal
5 for Ox1/DMA. This result indicates that the reduction of the vibrational amplitude is not
6 just a reflection of an ultrafast decay in the local oscillator but it represents actual
7 diminishment of the vibration caused by the ET. The time constants (relative intensities)
8 of the decay components are 81 ± 2 fs (0.34), 560 ± 30 fs (-0.13), and 3.2 ps (0.66) for
9 Ox1/DMA where the shortest and the longest time constants are in agreement with the
10 previously reported values for the ET and back ET.[32, 33]

11 Insert **Figure 6** here.

12 The oscillatory part of the signal obtained by subtracting the decay components
13 are shown in Figure 7a. Interestingly, the vibration of Ox1/DMA initially dephases very
14 rapidly with a time constant of 160 ± 40 fs, which was obtained by a simple
15 least-squares-fitting with a fixed frequency of 562 cm^{-1} in the range of <500 fs, while
16 the disappeared vibration seems to reappear and endure for >3 ps. Real parts of the
17 Fourier transformed spectra of the vibrations are shown in Figure 7b. The major band in

1 1-CN is located at 561 cm^{-1} which is consistent with that obtained by DFWM
2 measurement. Interestingly, negative band appears at 567 cm^{-1} in DMA. Note that the
3 band shape is not a derivative of a Lorentzian but it looks rather like a sharp negative
4 band overlapped on top of a broader positive band. It is plausible that the long-lasting
5 vibration in the ground state and the fast decaying vibration in the excited state are
6 out-of-phase by π . The higher frequency observed for Ox1 in DMA compared to that in
7 1-CN supports this conclusion.

8 Insert **Figure 7** here.

9 10 **4. Conclusions**

11 By means of femtosecond degenerate four-wave-mixing and pump-probe spectroscopy,
12 the excited state vibration at 562 cm^{-1} for Ox1 was observed as a coherent nuclear
13 wavepacket motion in an inert solvent, 1-CN. On the other hand, ultrafast electron
14 transfer in DMA with time constant of $<100\text{ fs}$ diminished the excited state vibration.
15 The remaining weak vibration with slightly higher frequency of $567\text{-}570\text{ cm}^{-1}$ was
16 assigned to that in the ground state. It is demonstrated that, by these ultrafast

1 spectroscopies, it is capable to separate vibrations arising from different electronic states
2 even though the frequency difference is minor.

3 In the present experiment, the laser wavelength is only limited to ca. 620 ± 25
4 nm, thus, to be rigorous, the entire spectral range must be scanned carefully to
5 understand the details of the relation between intramolecular vibrations and ET which
6 will be our future project.

7 **5. Acknowledgement**

9 YN was supported by Research for Embryonic Science and Technology (PRESTO),
10 Japan Science and Technology Agency (JST). HM was supported by a Grant-in-Aid for
11 Scientific Research (23245004) from the Ministry of Education, Culture, Sports,
12 Science and Technology (MEXT), Japan.

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Figure Captions

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

Figure 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).

Figure 3. (a) Femtosecond DFWM signal of Ox1 in 1-CN. DFWM excited at 620 nm with t_{12} set at -13, 0, and +13 fs. (b) Oscillatory part (normalized) of the DFWM signal obtained by subtracting the decay components from the signal.

Figure 4. (a) Femtosecond DFWM signal of Ox1 in DMA. DFWM excited at 620 nm with t_{12} set at -13, 0, and +13 fs. (b) Oscillatory part (normalized) of the DFWM signal obtained by subtracting the decay components from the signal.

Figure 5. Real parts (normalized) of the Fourier transformed spectra of the oscillations of DFWM signals of Ox1 in (a) 1-CN and (b) DMA.

Figure 6. Femtosecond pump-probe (PP) signals (normalized) of Ox1 in 1-CN and DMA.

Figure 7. (a) Oscillatory part (normalized) of the PP signal obtained by subtracting the decay components from the signal. (b) Real parts (normalized) of the Fourier transformed spectra of the oscillations in the PP signal of Ox1 in 1-CN and DMA.

Figure 1

Ox1

DMA

1-CN

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7