

Kinetic isotope effect on the proton-transfer in indigo carmine

Izumi Iwakura^{a,b}, Atsushi Yabushita^c, Takayoshi Kobayashi^{b,c,d,e,*}

^a JSPS Research Fellow, 8 Ichibancho, Chiyoda-ku, Tokyo 102-8472, Japan

^b Department of Applied Physics and Chemistry and Institute for Laser Science, University of Electro-Communications, 1-5-1 Chofugaoka, Chofu, Tokyo 182-8585, Japan

^c Department of Electrophysics, National Chiao-Tung University, Hsinchu 300, Taiwan

^d ICORP, JST, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

^e Institute of Laser Engineering, Osaka University, 2-6 Yamada-oka, Suita, Osaka 565-0971, Japan

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ABSTRACT

We have found that photo-excited indigo carmine causes stepwise proton transfer to generate mono-alcohol intermediate, which immediately returns to the parent molecule [I. Iwakura, A. Yabushita, T. Kobayashi, Chem. Lett. 38 (2009) 1020]. The kinetic isotope effect in the proton transfer of this system has been studied by direct observation of the real-time molecular vibrational amplitude during the reaction including the transition state using a sub-5-fs laser pulse. The k_a^H/k_a^D ratio for the proton transfer after photo-excitation is observed to be 1.5 ± 0.1 .

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1. Introduction

Kinetic isotope effects (KIEs), usually defined by the ratio of reaction rates between compounds with and without an isotopic label, have been used to clarify the mechanisms of many reactions, such as proton transfer [1–4], Claisen rearrangement [5–10], Diels–Alder reaction [11,12], and osmium oxidation [13].

However, it is difficult to accurately estimate the reaction rates. The method of pump–probe measurement is based on the time-dependent molecular vibrations including their frequencies and phases, which directly provide information on structural changes. Therefore, it presents a crucial clue for clarification of the reaction mechanism behind the observed KIE.

In the present work, pump–probe signals have been obtained using a sub-5-fs laser pulse to observe real-time molecular vibrational frequency, which has enabled observation of the structural changes during the chemical reactions for direct estimation of KIE.

We have chosen indigo carmine for our sample. We confirmed in our previous work [14] that the stepwise proton transfer took place in this molecule after photo-excitation and that a mono-alcohol intermediate was generated. However, this intermediate was found to revert immediately to the parent molecule because this mono-alcohol species is unstable (Fig. 1). The present sub-5-fs study has enabled us to work on the KIE by this proton transfer without accumulation of the product.

2. Experimental

Indigo carmine in saturated anhydrous methanol solution (purity >99.8%, <0.005% water, Sigma Aldrich) and methanol-*d* solution (>99.5 atom% D, Sigma Aldrich) (Fig. 2a) were selected as samples to identify the KIE in the proton transfer process in the excited state using the real-time vibrational spectroscopy, because indigo carmine has high enough solubilities in these solvents and methanol has no molecular vibrational signal in the frequency range examined in this study. A cell with an optical path length of 1 mm was used to contain the sample solution.

Pump–probe experiment using sub-5-fs laser pulses (Fig. 2b) [15], which extended from 525 to 725 nm, was performed to identify the KIE. Sub-5-fs pulses were generated by compressing the output from a non-collinear optical parametric amplifier (NOPA) seeded by a white-light continuum. The output of the sub-5-fs pulsed beam was split into two beams for pump-and-probe pulses. The pump source of the NOPA was a regenerative amplifier (Spectra-Physics, model Spitfire) with pulse duration of 100 fs, central wavelength of 790 nm, and repetition rate of 5 kHz.

Fig. 2c shows the intensity autocorrelation trace of the pulse after compression by using a BK7-prism pair with a 37 cm slant length between the two prisms. A fit assuming a Gaussian function yielded a pulse width of 7.25 fs. The experiments were performed at pump and probe pulse intensities of 2580 and 480 GW cm⁻², respectively. The focal areas of the pump and probe laser pulses were 100 and 75 μm², respectively. The polarizations of the pump and probe pulses were parallel to each other. All measurements were performed at 295 ± 1 K.

The time-resolved difference transmittance ΔT in the spectral range extending from 525 to 725 nm was simultaneously measured using a multi-channel lock-in amplifier coupled to a

* Corresponding author. Address: Department of Applied Physics and Chemistry and Institute for Laser Science, University of Electro-Communications, 1-5-1 Chofugaoka, Chofu, Tokyo 182-8585, Japan. Fax: +81 3 5841 4165.

E-mail addresses: kobayashi@ils.ucc.ac.jp, nakajima@ils.ucc.ac.jp (T. Kobayashi).

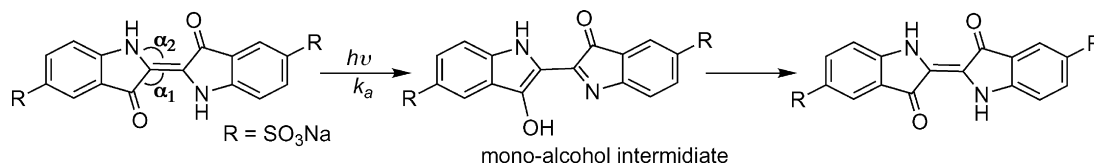


Fig. 1. Proton-transfer process in a photo-excited indigo carmine molecule (R = SO₃Na).

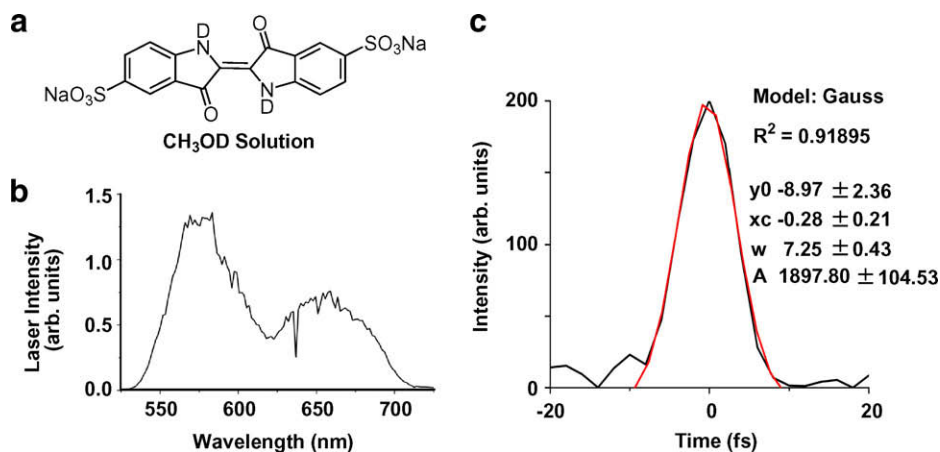


Fig. 2. (a) Molecular structures of deuterated indigo carmine. (b) Sub-5-fs laser spectrum. (c) Intensity autocorrelation trace (black line) after pulse compression. A fit assuming a Gaussian function yields a pulse width of 7.25 fs (red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

polychromator (300 grooves/mm, blazed at 500 nm), which was utilized to disperse the probe pulse and guide it to avalanche photodiodes via a 128-channel fiber bundle. The spectral resolution of the total system was ~ 1.57 nm. The transmitted probe spectrum after the sample without injection of the pump was recorded by averaging 50 000 laser shots. The transmission difference of the probe was accumulated every 3000 shots under excitation from the pump pulse.

3. Results and discussion

3.1. Pump–probe experimental results

Fig. 3 shows the traces of absorbance change, $\Delta A(\omega)$, for deuterated indigo carmine; see Ref. [14] for the $\Delta A(\omega)$ spectra of the non-deuterated system. The positive $\Delta A(\omega)$ in the range longer than 705 nm is dominated by the induced absorption from the lowest excited state. Therefore, the real-time vibrational frequency of the excited molecule can be observed with a minimum contribution of the ground-state wavepacket in this spectral range, if the modulation due to the refractive index induced by the ground-state wavepacket is small.

3.2. Spectrogram analysis

Fig. 4 shows a spectrogram [16] obtained by a sliding-window Fourier transform around 720 nm with a Blackman window function of full width at half maximum (FWHM) of 120 fs:

$$S(\omega, \tau) = \int_0^\infty S(t)g(t - \tau) \exp(-i\omega t) dt, \quad (1)$$

$$g(t) = 0.42 - 0.5 \cos(2\pi t/T) + 0.08 \cos(4\pi t/T),$$

where T is the gate width of the Blackman window function.

The spectrogram was calculated after applying a high-pass filter to the signal, because slow modulation on the signal (slower than several tens of fs) is caused by fluctuation of laser power instead of molecular vibration. The obtained spectrogram clarifies the change in the instantaneous frequency and the intensity of the vibrational modes during the proton transfer reaction of photo-excited indigo carmine.

Observation of the vibrational coherence after some relaxation or reaction processes may sound hardly understandable. According to the discussions in Refs. [17–20], however, the transfer of vibrational coherence and even the creation of coherence by a chemical reaction account for the modulation of transition probability observed in an electronic curve crossing process [17]. The modulation of transition probability is thought to be due to the motion of a wavepacket composed of coherent superposition of vibrational eigenstates with different quanta. The bare electronic coupling [17] and diabatic vibrational frequency have comparable magnitudes causing considerable interfusion of non-resonant diabatic states. Therefore, the vibrational coherence can be transferred into the product via an electronic curve crossing process under sufficiently strong electronic coupling [18–20]. Champion et al. showed experimentally the coherence generated by dissociation.

A peak around 1700 cm⁻¹, due to the C=O stretching mode ($\nu_{C=O}$) of the reactant [21–23], appeared just after the excitation. Both of the samples, with and without deuteration, showed that a new peak appeared around 1250 cm⁻¹ after photo-excitation, reflecting the formation of the mono-alcohol intermediate [24,25]. These results agree well with the fact that the Raman frequencies of the C–O stretching modes (ν_{C-O}) of C₆H₅OH and C₆H₅OD have the same value, 1250 cm⁻¹ [26]. As for indigo carmine, the peak of 1250 cm⁻¹ appeared around 270 fs delay time, while it appeared around 410 fs for deuterated indigo carmine.

Peaks near 3450 cm⁻¹ (Fig. 4a) and 2380 cm⁻¹ (Fig. 4b) appeared just after photo-excitation and were assigned to the N–H

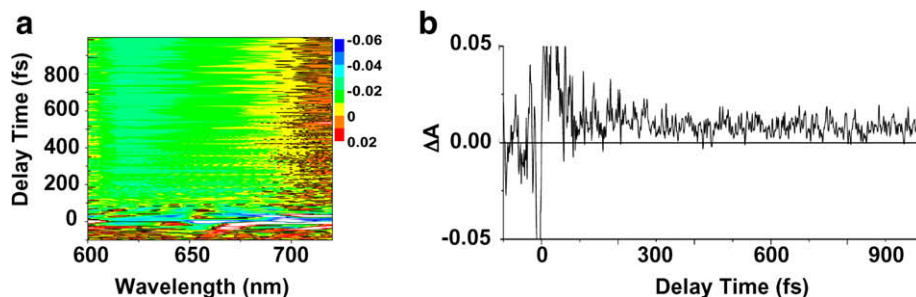


Fig. 3. (a) A two-dimensional display of the absorbance change on the probe delay time and the wavelength following the sub-5-fs pulse excitation of deuterated indigo carmine. (b) Dependence of absorbance change on the probe delay time at 720 nm.

stretching (ν_{N-H}) [22,23] and N–D stretching (ν_{N-D}) [23] modes, respectively. The frequency of ν_{N-D} is lower by a factor of $\sim(2)^{1/2}$ than that of non-deuterated indigo carmine. The frequencies of ν_{N-H} and ν_{N-D} showed a gradual red shift, and another peak appeared around 3200 and 2250 cm^{-1} at ~ 270 and ~ 410 fs, respectively. These peaks located at 3200 and 2250 cm^{-1} are assignable to the O–H (ν_{O-H}) and O–D (ν_{O-D}) stretching modes [27–30], respectively, because these new peaks appeared at nearly the same time as $\nu_{C=O}$.

3.3. Reaction rates

We analyzed the data to read the probe delay time when the intensities of the $\nu_{C=O}$, $\nu_{C=O}$, ν_{O-H} (ν_{O-D}) and ν_{N-H} (ν_{N-D}) modes show their peak values. Their delay times were 320, 340, 340 and 330 fs, respectively, and 490, 510, 510, and 520 fs for the corresponding deuterated sample. Therefore, the reaction times in the non-deuterated (deuterated) samples were calculated to be 330 ± 10 (500 ± 13) fs. The latter value gives the reaction rate in deuterated indigo carmine as $(2.0 \pm 0.1) \times 10^{12} \text{ s}^{-1}$ in contrast with $(3.0 \pm 0.1) \times 10^{12} \text{ s}^{-1}$ in the non-deuterated system. The primary KIE obtained from the experimental results predicts that

the proton-transfer rate in the deuterated system is 44% slower than that in the non-deuteride system. The corresponding rate ratio (k_a^H/k_a^D) between H and D ranges widely from 1.15 (in the early transition state) to several hundred (in the late transition state) [31,32]. Photo-excitation of indigo carmine is expected to proceed through an early transition state due to strong hydrogen bonding, and the observed k_a^H/k_a^D ratio, 1.5, exceeds that for the early transition state. This is due to the increase in k_a^H , indicating that the proton transfer takes place via the tunnel mechanism.

Fig. 3a shows that $\nu_{C=O}$ is gradually red shifted from 1700 to 1250 cm^{-1} . On the other hand, Fig. 3b shows that the frequency of $\nu_{C=O}$ is red shifted from 1700 to $\sim 1500 \text{ cm}^{-1}$, followed by a blue shift to $\sim 1600 \text{ cm}^{-1}$, and then a red shift to $\sim 1250 \text{ cm}^{-1}$. This slow oscillatory modulation of the $\nu_{C=O}$ frequency observed for the deuterated system is considered to be induced by the modulation of instantaneous frequency of $\nu_{C=O}$ by low-frequency modes. These low-frequency modes are probably coupled to those related to C=C, such as the scissoring modes of $C^I=C^1-C^2$ (α_1) and $C^I=C^1-N$ (α_2) associated with the deuteron transfer. The mechanism of the mode coupling inducing the modulation can be explained as follows.

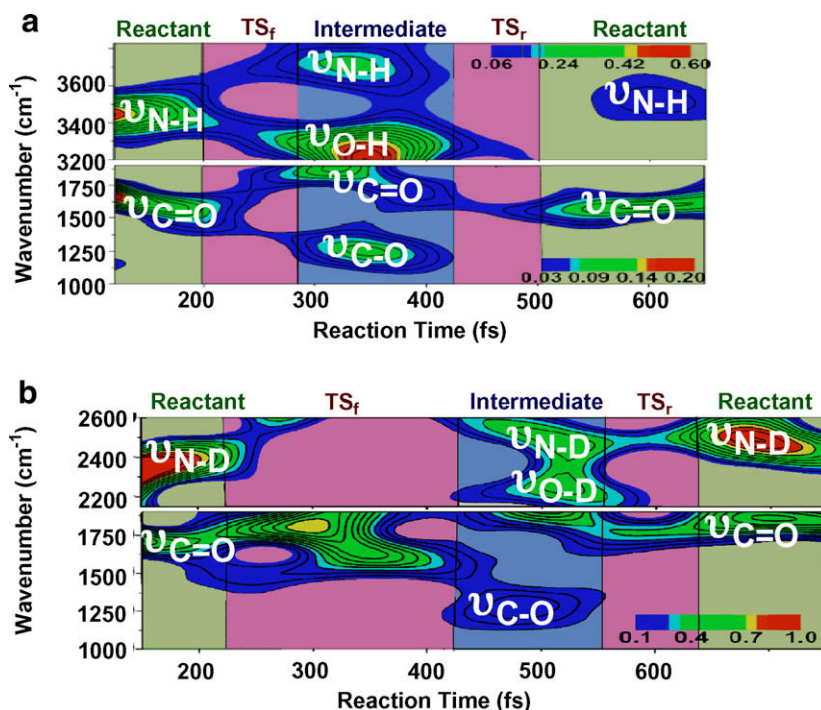


Fig. 4. Spectrogram of real-time vibrational modulation of the absorbance change with a Blackman window function of FWHM of 120 fs (a) in indigo carmine shown in Ref. [14] and (b) in deuterated indigo carmine obtained in this work.

In the first deuteron transfer, the distance between N–D and C=O decreases for the deuteron to be transferred to the acceptor. In association with these processes, the $C^1=C^1-C^2$ and $C^1=C^1-N$ bond angles are expected to decrease and increase, respectively, with decrease in the carbon–carbon bond order changing from $C^1=C^1$ to C^1-C^1 . These changes in the bond angles in turn trigger the scissoring modes of $C^1=C^1-C^2$ and $C^1=C^1-N$. On the other hand, the oscillatory feature of $\nu_{C=O}$ has not been observed in the non-deuterated sample. It is probably caused by a much faster proton-transfer rate than the period of molecular vibrations.

In the deuterated system, the transition state of the recovery process (TS_r) of indigo carmine has shorter duration time than that of the mono-alcohol generation (TS_f). This difference may be ascribed to that in their energetics as follows: The mono-alcohol system is unstable and the activation energy to generate indigo carmine (TS_r) is lower than that to generate the mono-alcohol (TS_f). Moreover, the reaction pathways of the two processes are not simply the reversal from forward to backward along the same reaction coordinate space. It is because the reactant of the forward reaction (i.e., deuterated indigo carmine just after photo-excitation) is different from the product of the backward reaction (the product after the deuteron transfer). In the non-deuterated system, the intensity of ν_{N-H} has not been observed to decrease around 600 fs. It is because the ν_{N-H} mode of 8-fs period is hardly detectable by using the sub-5-fs pulse as the intensity of this mode is weakened by decoherence.

4. Conclusion

KIE has been observed directly in the reaction dynamics revealed by real-time vibrational spectroscopy using a sub-5-fs pulse, which has enabled us to measure the vibrational response directly and accurately. Direct observation of real-time vibrational spectroscopy using an ultrashort pulse has been proved to be a new powerful method for studies of KIE.

Acknowledgments

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