Observation of Coherent Nuclear Motion in the Photoinduced Ring-Opening Reaction of Diphenylcyclopropenone

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When the time-resolution in time-resolved spectroscopy exceeds the period of molecular vibrations, we have a chance to observe the nuclear motions in real time. Thanks to recent progresses in short-pulse lasers, the observation of such a coherent nuclear dynamics becomes possible even during fast chemical reactions. Here, we report on our time-resolved absorption study of the coherent vibrational dynamics in the reaction of diphenylcyclopropenone (DPCP). This molecule has a highly strained three-membered ring structure. It is known that photoexcitation of DPCP causes a dissociation of the carbonyl group, giving rise to diphenylacetylene (DPA) as a product. From our sub-picosecond transient absorption measurements, we concluded that this ring-opening reaction starts from the S2 state of DPCP, generating the product DPA in the electronically excited (S2) state. In order to examine the nuclear dynamics during the reaction, we carried out time-resolved absorption measurements with a time resolution as good as 60–70 fs. Figure 1 depicts a temporal behavior of the absorption from the S2 DPCP, the precursor of the reaction. The precursor absorption decays with a 0.2-ps time constant as the reaction proceeds, which is followed by a residual absorption decay (9 ps) due to the reaction product (S2 DPA). In addition to this reaction dynamics, we found a weak but significant oscillatory modulation superposed on the decay of the precursor absorption. This modulation arises from the vibrational coherence created by the photoexcitation. The modulation period (110 fs) corresponds to a vibrational frequency of ca. 300 cm⁻¹. We concluded that the DPCP exhibits a coherent nuclear motion having the 300-cm⁻¹ frequency during the ring-opening reaction.

Construction of Transient Resonance Impulsive Stimulated Raman Scattering Spectrometer

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Time-resolved spectroscopic study of the low-frequency intra- and inter-molecular vibrations is very important to understand the structure and function of short-lived species such as reaction intermediates. However, observation of low-frequency vibrations by time-resolved frequency-domain Raman spectroscopy is extremely difficult, because a strong Rayleigh scattering often disturbs the measurements. In contrast, it is known that the Rayleigh scattering is readily separated in time-domain Raman methods such as the impulsive stimulated Raman scattering (ISRS) spectroscopy. So far, this ISRS method has been utilized to observe Raman-active low-frequency vibrations of molecular liquids in the ground state. It is highly expected that the ISRS method can also be applied to the observation of
the low-frequency vibrations of transient species. Here, we report our experimental setup constructed for the ISRS spectroscopy of transient species ("transient resonance ISRS").

Figure 1 shows the apparatus used for the transient resonance ISRS measurements. The light source is a Ti:sapphire regenerative amplifier system. The output of this amplifier (800 nm, ~0.1 ps) is divided into two parts. One portion is converted to the third harmonic at 267 nm (~0.5 ps). It is used as a pump pulse, and is focused to the sample jet to generate transient species. Another portion is converted to a visible pulse (600 nm, ~0.04 ps) in an optical parametric amplifier and subsequent frequency doubling. This visible pulse is used for the ISRS process. It is tunable in the 600–800 nm region for best resonance to the absorption of the transient species. The pulse duration of the visible pulse can be as short as 40 fs after the prism compensator. The visible pulse is divided into three, and is focused to the photoexcited portion of the sample jet with a standard BOXCARs geometry. The signal light that is diffracted in the phase matching direction is detected by a photodiode.

VI-C-3 Observation of the Low-Frequency Vibration of S1 Trans-Stilbene in Solution Using Transient Resonance Impulsive Stimulated Raman Scattering Method

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Recently, we have developed a novel spectrometer for the detection of impulsive stimulated Raman scattering (ISRS) from transient species. By using this transient resonance ISRS method, we measured the low-frequency vibration of excited-state polyatomic molecules in solution, for the first time. The ISRS signals obtained from trans-stilbene in ethanol are shown in Figure 1. Before photoexcitation (~20 ps), only a weak signal corresponding to the non-resonant electronic response of the solvent was observed (broken line). After photoexcitation (20 ps), in contrast, the intensity of the ISRS signal was strongly enhanced (solid line). The probe wavelength of the ISRS process is in resonance with the $S_0 \leftrightarrow S_1$ transient absorption, so that the enhanced ISRS signal is attributed to $S_1$ trans-stilbene. The observed ISRS signal of $S_1$ trans-stilbene consists of a sharp peak, an oscillatory component, and a slowly decaying component. The frequency of the oscillatory component was determined to be 290 cm$^{-1}$ by Fourier analysis, and it is equal to the frequency of an $S_1$ in-plane bending mode (ν24) that has been observed in time-resolved frequency-domain Raman spectroscopy.1) The present measurement successfully demonstrated a high potential of the transient resonance ISRS spectroscopy for the study of low-frequency vibrations of polyatomic molecules in the excited state.

Reference

VI-D Studies of Primary Photochemical/physical Processes Using Femtosecond Electronic Spectroscopy

Ultrafast spectroscopy is playing an essential role in elucidation of photochemical reactions. Thanks to the recent advance in laser technology, we are now able to examine the dynamics of chemical reactions that take place in the femtosecond time region. In this project, we study primary photochemical/physical processes of the condensed-phase molecules using time-resolved fluorescence and absorption spectroscopy whose time-resolution is a few hundreds femtoseconds. Time-resolved fluorescence and absorption spectroscopy are complimentary to each other. The advantage of fluorescence spectroscopy lies in the fact that fluorescence originates from the transition between...
VI-D-1 Femtosecond Time-Resolved Fluorescence Study of Excited-State Intramolecular Proton Transfer in Hydroxy Derivatives of Anthraquinone

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The proton transfer is one of the most fundamental reactions and plays crucial roles in many processes in chemistry. Anthraquinone is an excellent nucleus for the study of excited state intramolecular proton transfer since the availability of many –OH and –NH₂ derivatives and the diversity of positions for substitution. In this study, we chose four α-hydroxy derivatives of anthraquinone: 1-hydroxyanthraquinone (1-HAQ), 1,4-, 1,5-, and 1,8-dihydroxyanthraquinones (DHAQ) to investigate the influence of the second hydroxyl group on photochemistry of molecules.

The steady-state fluorescence spectra of 1-HAQ, 1,5- and 1,8-DHAQs show very large Stokes shift and dual character of emission that is considered as an evidence of the proton transfer reaction in the excited state. In contrast, the fluorescence of 1,4-DHAQ is close to mirror image of absorption. There is no evidence of proton transfer reaction in the excited state.

Femtosecond time-resolved fluorescence intensities of all four molecules in hexane were measured at room temperature for a wide visible wavelength region using up-conversion method. Time-resolved fluorescence spectra were reconstructed after deconvolution taking account of the finite instrumental response. The reconstructed time-resolved fluorescence spectra are presented in Figure 1. We observed the following dynamics for molecules that show dual fluorescence. (1) Both parts of dual fluorescence exist at the time origin. (2) The intensity of short wavelength fluorescence is compatible with intensity of long wavelength fluorescence at the time origin in contrast to the steady-state spectrum. (3) All three molecules show the decrease of short wavelength fluorescence and simultaneous rise of long wavelength fluorescence in the time scale up to 10 ps. (4) In addition, 1-HAQ and 1,5-DHAQ molecules exhibit very fast decay of short wavelength fluorescence intensity in the time scale of 50 fs.

In the case of molecule that shows mirror image type fluorescence (1,4-DHAQ), we found the following dynamics. (1) The spectral changes in the time scale up to 2 ps are similar to spectral changes observed for molecules that exhibit excited state proton transfer. (2) In the time scale from 2 ps up to 50 ps the fluorescence shows the increasing intensity of short wavelength part of the spectrum.

We concluded that proton transfer in α-hydroxy derivatives of anthraquinone is barrierless type of reaction and it occurs in a time scale of several tens of femtoseconds, reflecting delocalization of the excited-state wavefunctions. We assigned the fluorescence dynamics in a few picosecond time scale to an additional proton translocation reflecting the intramolecular vibrational relaxation. It is shown that the excited-state dynamics is affected by position of the second hydroxyl group.

Figure 1. The reconstructed time-resolved fluorescence spectra of hydroxy derivatives of anthraquinone.
VI-D-2 Steady-State and Femtosecond Time-Resolved Fluorescence Study of Trans-Azobenzene with S2(ππ*) ← S0 Photoexcitation

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Femtosecond time-resolved fluorescence spectroscopy was performed to study the photochemistry of trans-azobenzene. Azobenzene in hexane was initially photoexcited to the S2(ππ*) state by 280-nm light (560 pJ, 230 fs, 82 MHz) and the time-resolved fluorescence was measured in the wavelength region from 340 to 680 nm by the up-conversion method. The observed fluorescence exhibited double exponential decay and the lifetimes were determined as ~110 and ~500 fs. The spectral analysis of the two fluorescence components showed that their intensity maxima are located at ~400 and ~650 nm. Since they showed good mirror images of the S2 ← S0 and the S1 ← S0 absorption bands, we assigned them to the fluorescence from the S2 and S1 states, respectively, which have planar structure around the central NN bond. The quantum yield of the S2 → ‘planar’ S1 electronic relaxation was evaluated by comparing the S2 and S1 fluorescence intensities, and it was found to be almost unity. It implies that almost all molecules photoexcited to the S2(ππ*) state are relaxed to the ‘planar’ S1(ππ*) state. The present time-resolved fluorescence study clarified that the isomerization pathway starting directly from the S2(ππ*) state does not exist. It was also indicated that the isomerization mechanism of azobenzene is the inversion isomerization occurring in the S1 state, regardless of difference in photoexcitation conditions.

Figure 1. The absorption spectrum (left) and the steady-state fluorescence spectrum obtained with the 280-nm excitation (right). The fluorescence intensity is represented as the photon number intensity in the frequency space. In the fluorescence spectrum, open circles and open triangles represent the S2 and S1 fluorescence components, respectively. The wavenumber region from 22000 to 12000 cm⁻¹ is expanded in the inset.

VI-D-3 A New Insight into the Relaxation Mechanisms of trans-Azobenzene Following the S2(ππ*) ← S0 Photoexcitation: Rotational Deactivation Process from the Vibrationally Excited S1(ππ*) State

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It is known that the quantum yield of trans → cis photoisomerization of azobenzene depends on the excitation wavelength: the S2 excitation gives almost the half value (~0.1) of the S1 excitation (~0.2). The photoisomerization mechanism of azobenzene has been discussed on the basis of the isomerization quantum yield, and it has been considered that the photoisomerization after the S2 excitation proceeds differently (rotation) from that after the S1 excitation (inversion). However, our recent spectroscopic studies clarified that S2 azobenzene is exclusively relaxed to the ‘planar’ S1 state, and hence rotational isomerization pathway from the S2 state was ruled out. Since it is now clear that the isomerization of azobenzene occurs in the S1 state regardless of the difference in initial photoexcitation, we need to reconsider the implication of the difference in the isomerization quantum yield between S2 and S1 excitation.

After the rapid decay of the S2 state (~0.11 ps), a considerable amount of photoexcitation energy is localized in the S1 state in the form of the vibrational excess energy, because vibrational cooling process occurs in a much longer time scale (several tens picosecond). Therefore, a significant difference between S2 and S1 excitation is the vibrational excess energy in the S1 state that appears after photoexcitation. The S1 state produced after S2 excitation is highly vibrationally excited (hot) compared to the S1 state generated by direct S1 excitation. Thus, the low isomerization quantum yield of S2 excitation is attributable to the low isomerization efficiency of the vibrationally excited S1 state. It indicates that another relaxation channel exists especially in the vibrationally excited S1 state.

It was reported that the isomerization quantum yields obtained with S2 and S1 excitation become the same (~0.2) when the rotational motion of azobenzene is prohibited by chemical modification.13 This result suggests that the relaxation channel in the vibrationally excited S1 state is blocked by the chemical modification. In other words, the relaxation channel, which we propose for the vibrationally excited S1 state, is related to the rotational coordinate, although this channel does not produce the cis isomer but generates only trans S0 azobenzene.

Reference
Dynamic of Photoinduced Ring-Opening Reaction of Diphenylcyclopropenone Studied by Sub-Picosecond Transient Absorption Spectroscopy

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Since the first synthesis of cyclopropenone derivatives, the aromaticity, stability, and reactivity of their three-membered ring structure have been attracting much interest. Diphenylcyclopropenone (DPCP) is one of the molecules having such a highly strained structure. It is known that photoexcitation of DPCP causes a dissociation of the carbonyl group, giving rise to diphenylacetylene (DPA) as a product (Figure 1). This ring-opening reaction has been studied in solution by picosecond absorption spectroscopy, and it was found that the excited state of DPA is formed by the $S_2$ excitation of DPCP. However, the ring-opening dynamics itself was not clarified so far because of the low time resolution of the reported measurements (several tens of picoseconds). In this project, we carried out transient absorption measurements with a better (sub-picosecond) time-resolution to elucidate the ultrafast reaction dynamics.

Figure 2 shows transient absorption spectra of DPCP in cyclohexane measured with the $S_2$ excitation at 267 nm. For comparison, we also plot transient absorption spectra obtained by direct photoexcitation of DPA. It is readily found from this comparison that the DPCP spectra become very similar to the DPA spectra in the delay time region later than 30 ps. This spectral similarity assures that the photoexcitation of DPCP leads to the excited state of DPA. The broad peak around 430 nm recognized in the 30–60 ps time range is due to the $S_1$ state of DPA generated by the reaction, which then relaxes to the $T_1$ state ($\lambda_{\text{max}} = 410$ nm) at later delay times. In the early time region, by contrast, the DPCP spectra are significantly different from the DPA spectra. A strong band is observed around 480 nm just after photoexcitation, which is not seen in the DPA spectra. From its instantaneous rise and fast decay (0.2 ps), we assigned the 480-nm band to the initially-populated $S_2$ state of DPCP, the precursor of the reaction. This precursor band at 480 nm becomes noticeable only with the good time resolution in the present study. After the fast disappearance of the 480-nm band, the DPCP spectra exhibit a broad feature extending over the entire visible region, which also looks different from the DPA spectra. We tentatively assigned this broad feature to the $S_2$ DPA generated right after the reaction. The spectral difference seen in the 1–10 ps time range might be due to a reaction-induced structural change of the product DPA in the $S_2$ state. We conclude that the ring-opening reaction starts from the $S_2$ DPCP with a 0.2-ps time constant, giving rise to the $S_2$-like DPA.
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7-Azaindole dimer is a prototypical system showing the proton transfer reaction in the excited state. It is one of the ideal systems where we can examine the mechanism of the double proton transfer. An important question about the double proton transfer is whether the two protons are translocated in the concerted way or the step-wise way. These two reaction mechanisms have been the subject of intensive debates on the reaction of the 7-azaindole dimer.

Experimentally, it has been confirmed that there exist two components (0.2 ps and 1.1 ps) in the precursor dynamics of the reaction. However, as illustrated in Figure 1, these two components were assigned differently in the discussion that supports each mechanism. In the argument for the concerted mechanism, the 0.2-ps component was assigned to the $S_2 \rightarrow S_1$ electronic relaxation before the reaction and the 1.1-ps component to the actual translocation of the two protons from the $S_1$ state. On the other hand, in the argument supporting the step-wise mechanism, the 0.2-ps and the 1.1-ps components were assigned to the first and the second proton transfer, respectively. In other words, the two components were attributed to the formation and disappearance of the intermediate in which only one proton is transferred. Therefore, the assignment of the 0.2-ps component is the key to know which mechanism is correct.

In this project, we examined an excitation-wavelength dependence of the ultraviolet fluorescence dynamics. The experiment for the excitation-wavelength dependence is crucial to distinguish the two mechanisms. If the concerted mechanism is relevant, the change of the excitation-wavelength alters the initial population ratio of the $S_2$ and $S_1$ states, so that the relative amplitude of the 0.2-ps and 1.1-ps components should change with the excitation-wavelength. In the case of the step-wise mechanism, on the contrary, the relative amplitude of the two components is expected to be constant irrespective of the excitation wavelength, since they correspond to two successive proton-transfer steps. Figure 2 shows fluorescence decays of the dimer excited state(s) (reaction precursor) measured with six excitation wavelengths. It is clear that the precursor dynamics shows a significant excitation-wavelength dependence. In fact, the 0.2-ps component becomes smaller as the excitation wavelength gets longer. Finally, the 0.2-ps component almost vanishes when the dimer is excited at 313 nm, i.e., the red-edge of the dimer absorption. These experimental data are inconsistent with the step-wise mechanism, and deny the existence of the reaction intermediate. We concluded that the proton transfer in solution starts from the $S_1$ state in the concerted manner with a time constant of 1.1 ps.

Figure 1. Two reaction mechanisms proposed for the double proton transfer of 7-azaindole dimer.

Figure 2. Logarithmic plot of the fluorescence decay of the dimer excited state(s) (reaction precursor) measured with six excitation wavelengths. The dotted straight line drawn for each data corresponds to a 1.1-ps single-exponential decay.
VI-E Studies of Photochemical Reactions Using Picosecond Time-Resolved Vibrational Spectroscopy

Time-resolved vibrational spectroscopy is a very powerful tool for the study of short-lived transient species. It often affords detailed information about the molecular structure of transients, which is not obtainable with time-resolved electronic spectroscopy. However, for molecules in the condensed phase, we need energy resolution as high as 10 cm$^{-1}$ in order to obtain well-resolved vibrational spectra. This energy resolution is compatible only with time-resolution slower than one picosecond because of the limitation of the uncertainty principle. In this sense, picosecond measurements are the best compromise between energy resolution and time resolution for time-resolved frequency-domain vibrational spectroscopy. In this project, we study photochemical processes and/or short-lived transient species by using picosecond time-resolved Raman spectroscopy. In this year, we studied the solvated electron in water and found a novel resonance Raman enhancement due to the water molecules solvating electrons. For instrumentation, we constructed a new apparatus to perform time-resolved Raman measurements in the near-infrared region. We also demonstrated a new method for temporal fluorescence rejection in Raman spectroscopy and achieved the highest rejection efficiency at the moment.

VI-E-1 Novel Resonance Raman Enhancement of Local Structure around Solvated Electrons in Water

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The solvated electron is the most important basic anionic species in solutions. The absorption maximum of the solvated electron in water is located around 720 nm. This absorption is assigned to the \(s \rightarrow p\) electronic transition of the solvated electron. We measured picosecond time-resolved Raman spectra under the resonance condition with this electronic transition for the first time.

In the experiment, the output of picosecond Ti:sapphire regenerative amplifier was used as the light source for time-resolved Raman measurements. The third harmonic (267 nm) was used to generate solvated electrons. The fundamental pulse (800 nm) was utilized to probe Raman scattering under the condition resonant with the \(s \rightarrow p\) transition of the solvated electron. Figure 1 shows picosecond time-resolved resonance Raman spectra of an indole aqueous solution. Indole is used as the electron seed molecule. A strong transient Raman band appears around 1610 cm$^{-1}$ in accordance with the generation of the solvated electron, while only the weak OH-bend Raman band of bulk water can be observed before the pump pulse irradiation. This transient Raman band is attributable to the vibration of the solvating water molecules that strongly interact with the solvated electron in the first solvation shell. The mechanism of this resonance Raman enhancement was also discussed on the basis of the vibronic theory.

VI-E-2 Construction of A Near-Infrared Time-Resolved Raman Spectrometer

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Picosecond time-resolved resonance Raman spectroscopy is a very important tool to study the molecular structure of short-lived transient species appearing in photochemical reactions. In order to take advantage of resonance intensity enhancement, the wavelength of the probe light is required to be resonant with the absorption of the transient species. As for the time-resolved Raman measurements in the visible
region, the instrumentation has been already established for both the light source and the detector, and a large number of experiments have been performed. Some important transient species, however, show absorption in the near-infrared region, and near-infrared Raman measurements are needed to study these transients. Therefore, we constructed a new apparatus for near-infrared picosecond time-resolved resonance Raman spectroscopy. The second or third harmonics of the regeneratively amplified output of a picosecond Ti:sapphire laser are used to photoexcite the sample, and the fundamental pulse is used for the probe. Raman scattering is detected by a liquid nitrogen cooled InGaAs multi-channel detector that has sensitivity for the near-infrared light. Figure 1 shows a Raman spectrum of a water-acetonitrile mixture probed by 800 nm, which was measured using the constructed apparatus. We are now able to perform picosecond time-resolved Raman measurement for transient species that shows transient absorption in the near-infrared region.

![Diagram](a)

**Figure 1.** (a) Apparatus for the near-infrared time-resolved Raman spectroscopy. (b) Raman spectrum of a water-acetonitrile (4:1) mixture measured by an InGaAs detector. (probe wavelength 800 nm; laser energy 10 µJ; repetition rate 1 kHz)

VI-E-3 Temporal Fluorescence Rejection in Raman Spectroscopy by the Application of Femtosecond Upconversion Technique

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Temporal fluorescence rejection is a well known and effective method for detecting weak Raman scattering from fluorescent samples. In this method, the temporal response of an ultrafast detection system acts as a “time-gate” to selectively detect the Raman signal, rejecting the longer-lived fluorescence. The efficiency of rejection is proportional to the ratio of fluorescence lifetime and the gating-time. Several techniques have been developed for this purpose, ranging from the use of ultrafast streak camera to applying nonlinear optical effects. But so far, the highest time resolution achieved has been a few picoseconds, using optical Kerr gating technique. We have developed a new method of temporal fluorescence rejection based on femtosecond upconversion. Second harmonic pulses (460 nm) from a Ti:Sapphire oscillator (Tsunami, Spectra Physics) are used to optically excite a solution of acetonitrile containing coumarin 153, a fluorophore with an intense fluorescence having a lifetime of several nanoseconds. The emission from the solution is monitored temporally by the upconversion method using the laser fundamental at 920 nm as the gate pulse. The temporal response of the apparatus is 170 fs, which was given by the fwhm of the cross correlation signal of the gate pulse and the Raman scattering from the neat solvent. Using such a short response time automatically enhances the rejection efficiency by over 1 order of magnitude compared with the previous works.

Excitation at 460 nm causes the Raman lines of acetonitrile to fall within the frequency range of coumarin 153 fluorescence, where they are undetectable in steady-state measurements. However, in the upconversion traces, the Raman response is found to strongly dominate the initial part of the signal at certain emission frequencies (Figure 1). The time resolved emission spectra (TRES) reconstructed from the decays at different emission frequencies clearly exhibit two prominent peaks at \( \approx 2250 \text{ cm}^{-1} \) and \( \approx 2900 \text{ cm}^{-1} \) which appear at early delay times (Figure 2a). At slightly later times the peaks vanish, leaving only the fluorescence background (Figure 2b). Comparing the TRES with the Raman spectrum of pure acetonitrile (Figure 2c) recorded with cw excitation, the peaks are assigned to the C–N and C–H stretch Raman bands of acetonitrile respectively. It is noted, however, that both the peaks in the TRES are broadened by almost 200 cm\(^{-1}\). This band broadening results from the inevitable loss of frequency resolution inherent in femtosecond measurements. Nevertheless, our results show that femtosecond upconversion is an efficient solution to the problem of temporal fluorescence rejection in Raman spectroscopy. Additionally, by applying the shortest time-gate for this problem so far, we have achieved an upper limit in the rejection efficiency.
Figure 1. Time-resolved emission of coumarin 153 in acetonitrile at different emission frequencies.

Figure 2. Reconstructed time-resolved emission spectra of coumarin 153 in acetonitrile at different time-delays (time res. 160 fs): a) 50 fs, b) 500 fs, c) Raman spectra of neat acetonitrile (measured with cw excitation).