VI-C Observation of Vibrational Coherence (Wavepacket Motion) in Solution-Phase Molecules Using Ultrashort Pulses

With recent remarkable improvements of ultrashort-pulse lasers, we are now able to generate an optical pulse shorter than a few tens of femtoseconds. Owing to its ultrashort duration and broad frequency bandwidth, the ultrashort pulse can excite a molecule 'impulsively' to generate a coherence superposition of a number of vibrational state either in the excited state or in the ground state. This vibrationally coherent state evolves in time, which is called wavepacket motion. The observation and control of the wavepacket motion is one of the most interesting topics in modern spectroscopy. In past years, we have generated ultrashort optical pulses whose duration is ten ~ a few tens of femtoseconds by utilizing several nonlinear optical methods. In this year, we constructed experimental setups using these ultrashort pulses, and performed time-resolved measurements to observe vibrational coherence (wavepacket motion) in the excited state and the ground state.

VI-C-1 Observation of Vibrational Coherence of S_1 *trans*-Stilbene in Solution by 40-fs-Resolved Absorption Spectroscopy

TAKEUCHI, Satoshi; TAHARA, Tahei

[*Chem. Phys. Lett.* **326**, 430 (2000)]

Recent remarkable advance in laser technology has made it possible to generate an optical pulse shorter than a few tens of femtoseconds. Owing to its ultrashort duration and broad energy bandwidth, the ultrashort pulse can excite a molecule into a coherent superposition of a number of vibrational states. The coherent properties of the prepared state and its time evolution have been receiving much attention in relation to the exploration of a possible role of the vibrational coherence in photochemical processes.

In this project trying to examine the mechanism for the excited-state vibrational coherence, we carried out time-resolved absorption measurements for trans-stilbene in solution with use of a setup based on 10-fs pulses (Figure 1). We measured a temporal behavior of the $S_n \leftarrow S_1$ absorption signal around 640 nm following the 320-nm excitation with a time-resolution as good as 40 fs (Figure 2). In the obtained data, an underdumped oscillation due to the S_1 vibrational coherence was observed in the early times. The Fourier-transform analysis showed that the S_1 in-plane deformation mode (ν_{25}, 200 cm^{-1}) predominantly gives rise to the oscillatory signal. We considered the mechanism for this mode-specificity, and found that the amplitude of the vibrational coherence signal can be related to the $S_n \leftarrow S_1$ resonance-Raman activities of the S_1 vibronic levels and their Franck-Condon activities in the $S_1 \leftarrow S_0$ excitation process. With reference to the reported S_1 vibrational spectra, we evaluated the relative amplitude of the ν_{25} component against that of the ν_{24} mode (285 cm^{-1}) that appears strongly in the S_1 Raman spectra, and obtained the ratio consistent with the experimental data. It was concluded that the substantial contribution of the ν_{25} mode in the pump-probe data results from significant displacements among the S_0, S_1, and S_n potentials along the corresponding vibrational coordinate.

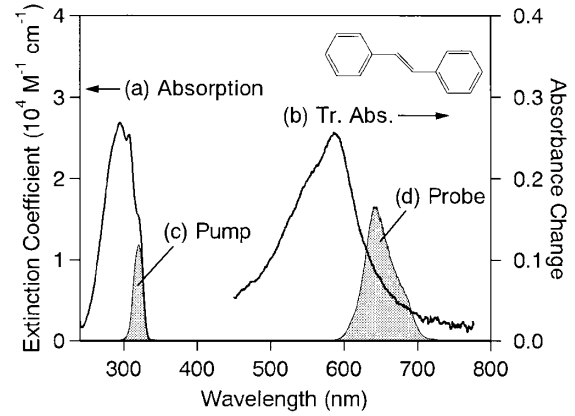

Figure 1. Spectral properties of *trans*-stilbene in the S_0 and S_1 states. (a) Steady-state absorption spectrum of *trans*-stilbene in heptane. (b) $S_n \leftarrow S_1$ transient absorption spectrum of *trans*-stilbene in heptane measured at 1 ps after 267-nm photoexcitation. Spectra of the pump (c) and the probe (d) pulses used in the 40-fs-resolved absorption measurements are also shown.

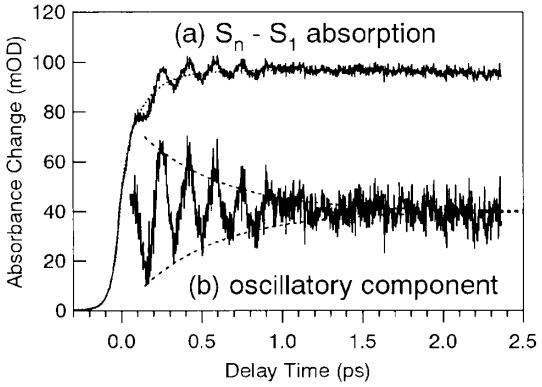

Figure 2. Time-resolved absorption signal of *trans*-stilbene in heptane (10^{-2} M). (a) Temporal behavior of the $S_n \leftarrow S_1$ absorption (640 nm) measured with excitation at the reddest edge of the ground-state absorption (320 nm). (b) Oscillatory component depicted in a magnified scale.

VI-C-2 Generation of Two Independently-Tunable Pulses for Extremely-Fast Pump-Probe Absorption Spectroscopy

TAKEUCHI, Satoshi; TAHARA, Tahei

Time-resolved absorption spectroscopy using ultrashort pump and probe pulses has been widely employed for the studies of the dynamical properties of

photoexcited molecules. With increasing progresses in laser technology, the time-resolution of these measurements has also been improved drastically, which gives us a chance to even observe new phenomena occurring within a few tens of femtoseconds. In order to achieve such a good time-resolution in molecular spectroscopy, we previously reported the construction of a time-resolved absorption spectrometer utilizing 10-fs pulses generated from a high-power optical parametric amplifier (OPA). In this setup, the second harmonic of the 10-fs pulse was used as a pump pulse in the uv region, while the 10-fs fundamental pulse in the visible region was used as a probe pulse. Consequently, the pump wavelength changed with the tuning of the probe wavelength. This restriction placed on the combination of the pump and probe wavelengths has so far limited the applicability of this spectrometer. Although we successfully applied the spectrometer to the observation of the vibrational coherence of S_1 *trans*-stilbene,[1)] it is apparently highly desirable that the pump and probe wavelengths can be tuned *independently* in the pump-probe measurements. For this purpose, we modified the previous apparatus by adding another low-power OPA with a single-pass amplification scheme (Figure 1). In this modified setup, the entire output of the high-power OPA (10–20 fs, 10 μJ, 1 kHz) is frequency-doubled to generate the pump pulse (≈ 0.3 μJ) tunable in the range of 250–375 nm. On the other hand, the output of the low-power OPA in the visible region (500–750 nm) is used as a probe and a reference pulse that are tunable independently of the pump wavelength. The time-resolution of this apparatus is typically *ca.* 40 fs, as evaluated by the FWHM of a cross-correlation trace between the two pulses. The independent tunability as well as the good time-resolution achieved in this spectrometer is highly suitable to extremely-fast molecular spectroscopy. Making the most use of these advantages, we are now investigating the coherent properties of molecules during ultrafast chemical reactions.

Reference

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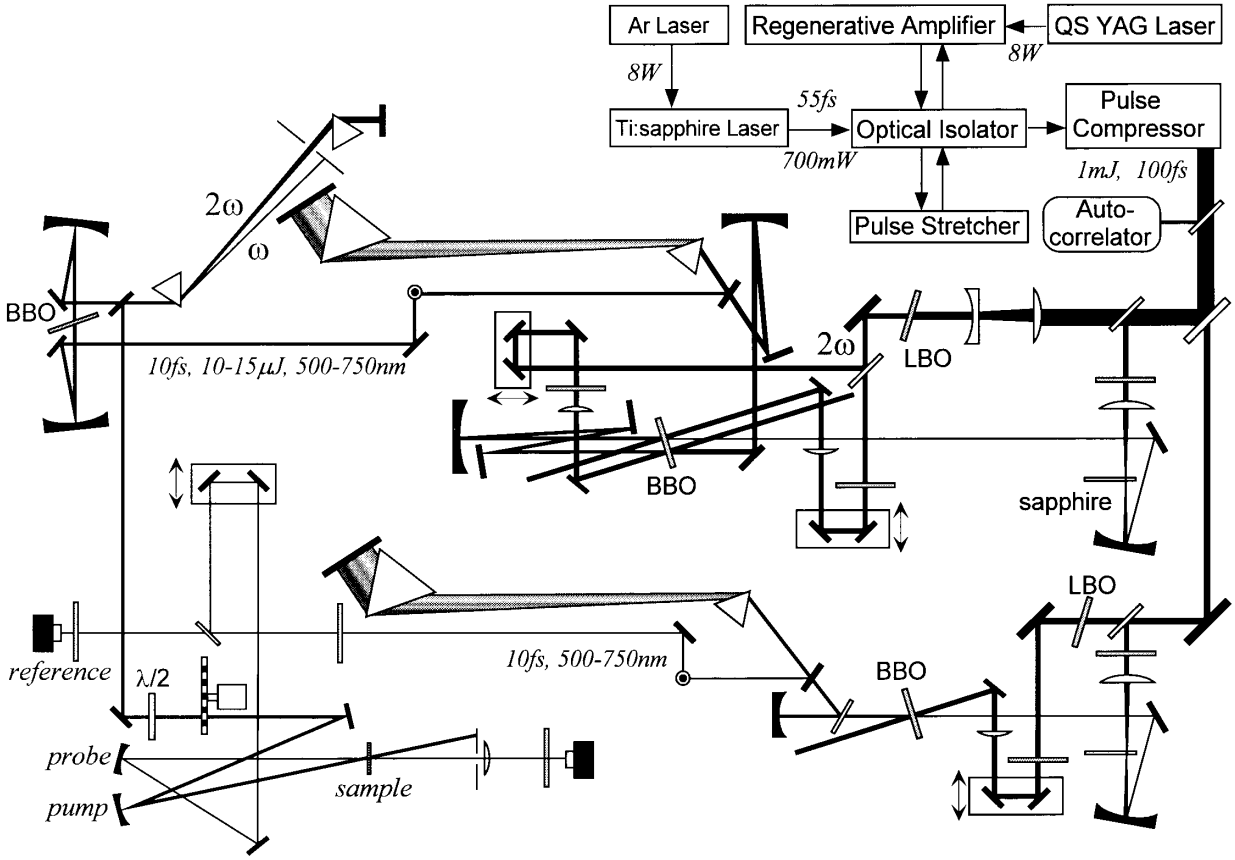

Figure 1. Experimental apparatus of the extremely-fast time-resolved absorption spectrometer using independently-tunable pump and probe pulses.

VI-C-3 Measurement of Impulsive Stimulated Raman Scattering Using Ultra-Short Pulses Generated by a Krypton Gas-Filled Hollow Fiber

FUJIYOSHI, Satoru[1]; TAKEUCHI, Satoshi; TAHARA, Tahei
([1]GUAS)

Impulsive stimulated Raman scattering (ISRS) spectroscopy is one of the third-order nonlinear spectroscopy suitable to the study of the low-frequency molecular vibrations. The frequency region to which this technique is sensitive depends on the duration of the pulse used in the measurements. Therefore, we need to use short pulses in order to obtain the information about the molecular vibrations in the wide frequency region.

We generated ultra-short pulses (τ ~ 35 fs, 800 nm) by using a Kr gas-filled hollow fiber (the autocorrelation is shown in inset of Figure 1) and applied it to the ISRS measurement. The homodyne ISRS signal obtained from liquid CS_2 is shown in figure 1. In addition to the electric response (sharp peak around 0 ps) and nuclear response (collective motion, broad peak around 0.2 ps), a beating signal with a period of 51 fs can be recognized. This beating signal corresponds to the intramolecular vibration at 655 cm^{-1}, which becomes observable with use of optical pulses as short as 35 fs.

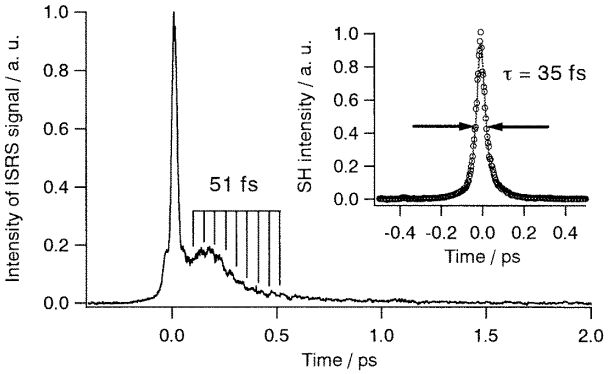

Figure 1. Impulsive stimulated Raman scattering signal of liquid CS_2. Inset: The autocorrelation of ultra short pulses that are used in this measurement.

VI-C-4 Construction of an Apparatus for Optical Heterodyne Detected Impulsive Stimulated Raman Scattering Measurement Using a Phase Mask

FUJIYOSHI, Satoru[1]; TAKEUCHI, Satoshi; TAHARA, Tahei
([1]GUAS)

Femtosecond optical heterodyne detected impulsive stimulated Raman scattering (OHD-ISRS) spectroscopy is one of the time-domain spectroscopies that can afford information about the low-frequency molecular vibrations. In order to achieve stable heterodyne detection, the relative optical phase between the signal light and the local oscillator (LO) light needs to be accurately controlled. We previously reported OHD-ISRS measurements, in which the phase control was attained by active adjustment of the optical path length.[1)] Recently, a diffractive optics (phase mask) was reported to be applicable in this spectroscopy, which does not require active path-length stabilization[2,3)] and hence facilitate heterodyne detection. We constructed an apparatus with use of the phase mask and the diagram is shown in Figure 1a.

In this apparatus, the visible femtosecond pulse is first divided into two pluses. Each pulse is diffracted into two first-order pulses. The first pair is used as pump pulses and the second pair is used as probe and LO pulses. Figure 1b shows OHD-ISRS signal obtained from liquid carbon tetrachloride with this setup using 75-fs femtosecond pulses (700 nm). The relative phase between the signal light and the LO light was kept stable over a span of one hour even without any active feed back.

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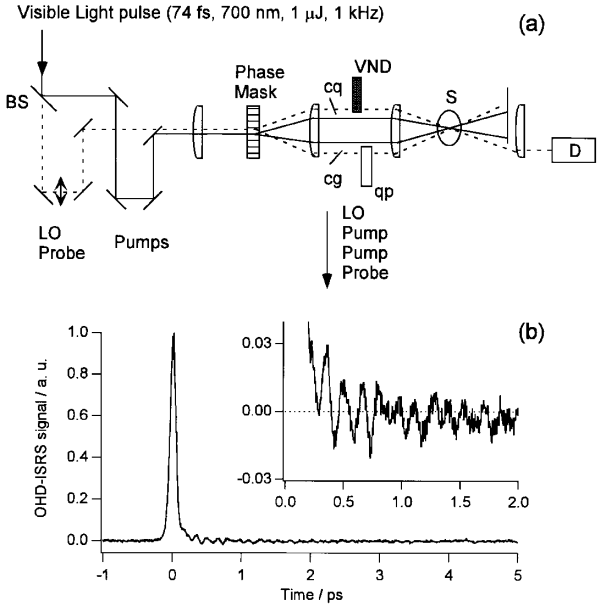

Figure 1. (a) Constructed apparatus of an OHD-ISRS measurement. (b) Optical heterodyne detected impulsive stimulated Raman scattering signal of liquid carbon tetrachloride measured using a phase mask. Inset: The signal in the early time region is depicted in a magnified scale.

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 taking place in the femtosecond time region. In this project, we study primary photochemical/physical processes in the condensed phase by time-resolved fluorescence and absorption spectroscopy with a few hundreds femtoseconds time-resolution. 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 the "well-known" ground state and the excited state in question. Thus time-resolved fluorescence spectroscopy can afford unique information not only about the dynamics but also other properties of the excited singlet states such as their energies and oscillator strengths. On the other hand, however, time-resolved absorption spectroscopy is considered

to be more versatile because it can detect not only fluorescent excited singlet states but also other "dark" transients. In this year, we investigated the ultrafast dynamics of excited-state proton transfer of anthaquinone derivatives, isomerization of azobenzene, and relaxation of the S_2 state of zinc(II) porphyrins, with use of these time-resolved electronic spectroscopy. In addition, we started construction of a new setup for femtosecond time-resolved infrared spectroscopy.

VI-D-1 Ultrafast Excited-State Proton Transfer Dynamics of 1,8-dihydroxyanthraquinone (chrysazin) Studied by Femtosecond Time-Resolved Fluorescence Spectroscopy

ARZHANTSEV, Sergei; TAHARA, Tahei

[*Chem. Phys. Lett.* **330**, 83 (2000)]

The steady-state fluorescence spectrum of 1,8-dihydroxyanthraquinone (crysazin) shows very large Stokes shift and dual bands emission. This fluorescence feature indicates that a marked geometry change takes places in the excited state. The steady-state fluorescence has been considered as an evidence of the proton transfer reaction across the intramolecular hydrogen bond in the excited state. Femtosecond time-resolved fluorescence intensities of crysazin in hexane have been measured at room temperature for a wide visible wavelength region (470–670 nm) using up-conversion method. Time-resolved fluorescence spectra were reconstructed after deconvolution taking account of the finite instrumental response. The time-resolved fluorescence spectra are presented in Figure 1. The following three points can be noted from these spectra: (1) Both parts in a dual fluorescence (the blue part and the red part) exist even at the time origin. The relative intensity of the blue part is high immediately after photoexcitation, compared with that in the steady-state fluorescence. (2) The fluorescence intensity of the blue part decreases and that of the red part increases in a few picoseconds. (3) After 5 ps, the fluorescence does not show any significant spectral change and it is very similar to the steady-state fluorescence spectrum. The fluorescence intensity decreases monotonously at all the observed wavelengths.

Almost instantaneously appearance of both of the "normal-form type" fluorescence and the "tautomeric-form type" fluorescence indicates that a barrierless excited-state proton transfer occurs in the time scale of several tens of femtoseconds, reflecting delocalization of the excited-state wavefunction. We assign the fluorescence dynamics in a few picosecond time scale to an additional proton translocation reflecting the intramolecular vibrational relaxation.

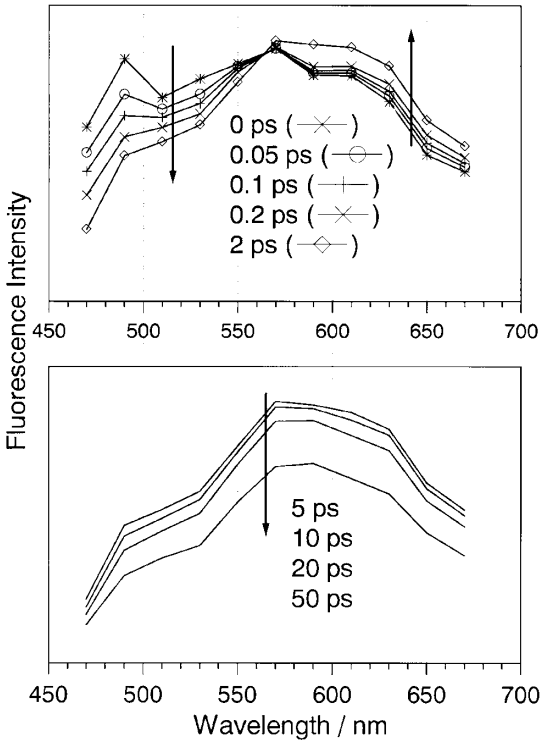

Figure 1. Reconstructed time-resolved fluorescence spectra of chrysazin. The spectra in the early time region are presented in the top panel. The spectra after 5 ps are presented in the bottom panel.

VI-D-2 Femtosecond Dynamics of Photoexcited *trans*-Azobenzene Observed by Time-Resolved Fluorescence Up-Conversion Spectroscopy

FUJINO, Tatsuya; ARZHANTSEV, Sergei; TAHARA, Tahei

The femtosecond time-resolved fluorescence spectroscopy was applied to study the photochemistry of *trans*-azobenzene. The excitation wavelength (280 nm, third harmonic pulses of a Ti:saphhire oscillator) in the present experiments corresponds to the blue side of the $S_2(\pi\pi^*) \leftarrow S_0$ absorption ($\varepsilon_{280} \approx 10000$ mol^{-1} dm^3 cm^{-1}), and the molecules were initially photoexcited to the $S_2(\pi\pi^*)$ state. The femtosecond time-resolved fluorescence signals were measured in the wavelength region from 340 to 680 nm using the up-conversion method. The fluorescence decays obtained from a hexane solution (5.0×10^{-3} mol dm^{-3}) at four different wavelengths are shown in Figure 1. These data clearly shows that the temporal behavior of the fluorescence signals varies with the change of fluorescence wavelength. The fluorescence decay at 440 nm looks quite similar to the cross-correlation trace, indicating that the lifetime of the major portion of the fluorescence is shorter than the time resolution. This rapid decay was also dominant in the near-ultraviolet region (340~420

nm). The second fluorescence component becomes noticeable in the fluorescence decay at longer wavelength. In the signals at 560 and 620 nm, the intensity of the second component becomes comparable to that of the first rapid component. A global fitting was performed for the quantitative analysis of the observed decays, and it was clarified that the fluorescence consists of two decay components having lifetimes of ~ 110 and ~ 500 fs. The spectral analysis referring to the steady state fluorescence spectrum clarified that the two fluorescence components exhibit spectra with intensity maxima at ~ 400 and ~ 650 nm. Since these spectra are good mirror images of the $S_2 \leftarrow S_0$, and the $S_1 \leftarrow S_0$ bands in the absorption, they were assignable to the fluorescence from the S_2 and S_1 states, which have planar structure around the central NN bond.

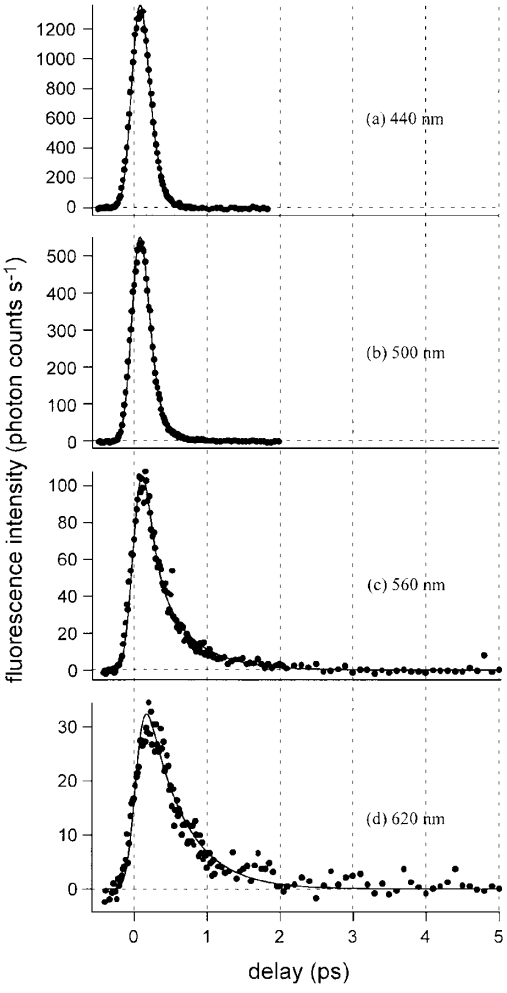

Figure 1. Time-resolved fluorescence of trans-azobenzene in hexane solution (5.0×10^{-3} mol dm^{-3}) at 440 nm (a), 500 nm (b), 560 nm (c), and 620 nm (d). The dots are experimental data and the solid curves are the results of fitting analysis.

VI-D-3 S_2 Emission of a Series of Zinc(II) Porphyrins Studied by Femtosecond Fluorescence Spectroscopy

ASANO-SOMEDA, Motoko[1]; ARZHANTSEV, Sergei; TAHARA, Tahei
([1]Tokyo Inst. Tech.)

Fluorescence from the second electronically excited singlet state (S_2 emission) has been observed for various metalloporphyrins even under the steady-state condition. Zinc(II) porphyrin is one of the typical metalloporphyrins and exhibits S_2 emission. However, quantum yields of S_2 emission largely depend on the porphyrin peripheral substituents, and in some of zinc(II) porphyrins, no steady-state S_2-emission could have been detected. To elucidate what controls the S_2 emission intensity and the radiationless transitions from the S_2 state, we have performed time-resolved fluorescence study for a series of zinc(II) porphyrins, which involves "non-S_2-emissive" porphyrins. For all six compounds, S_2 emission was successfully detected by using up-conversion method. The decay rates of the S_2 emission were coincident with the rise rates of the S_1 emission, and the observed S_2 lifetimes vary from 2 ps to 70 fs depending upon the peripheral substituents. There is no clear correlation between the S_2 lifetimes and S_2–S_1 energy gaps or transition dipole moments of the S_2 state. However, the S_2 lifetime strongly correlates with the intensity ratio of the Q(0,0) and Q(1,0) absorption bands. This leads to a suggestion that a substle difference in the electronic structure of the porphyrin π-system, which is sensitive to the peripheal substituents, remarkably affects the $S_2 \rightarrow S_1$ internal conversion rate.

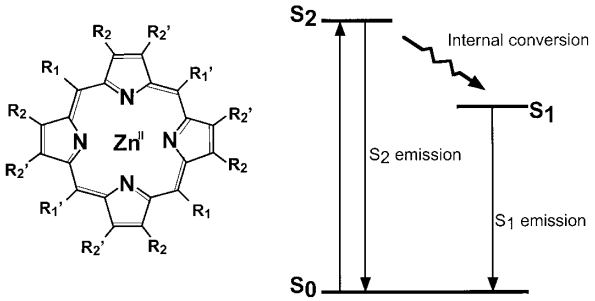

Figure 1. Molecular structure and schematic diagram of the relaxation processes of zinc(II) porphyrin.

VI-D-4 Construction of Femtosecond IR-IR Pump-Probe Spectrometer

FUJINO, Tatsuya; TAHARA, Tahei

An apparatus for femtosecond IR-IR pump-probe measurements was constructed. The setup is based on a regeneratively amplified output of a Ti:sapphire laser that delivers 100 fs pulses of ~ 0.7 mJ at a repetition rate of 1 kHz. These pulses are used to pump a commercial optical parametric generation and amplification (OPG/OPA) system operating with a BBO crystal. The differential frequency between the signal and idler pulses was generated by a $AgGaS_2$ crystal, and it is used as a frequency-tunable infrared source (3~12 μm, ~ 3 μJ). A long-wave pass (> 2500 nm) filter and a Ge filter are used to separate the mid-infrared pulses from the signal and idler. A beam splitter divides the infrared pulse into two parts. The intense pulse was used to excite the fraction of molecules, and the weak one was utilized to probe the induced transmission change. Both pulses are focused on a sample by a CaF_2 lens (focal

length 150 mm), and the sample-transmitted probe (signal) energy as well as the pulse-to-pulse fluctuation (reference) of the probe are measured with the two HgCdTe detectors. The data from the signal and reference detectors are used to determine the IR transmission with (T) and without the pump (T_0) pulse. The normalized pump-induced transmission change, $\Delta T/T_0 = T/T_0 - 1$, is determined as a function of delay time between the pump and probe pulse.

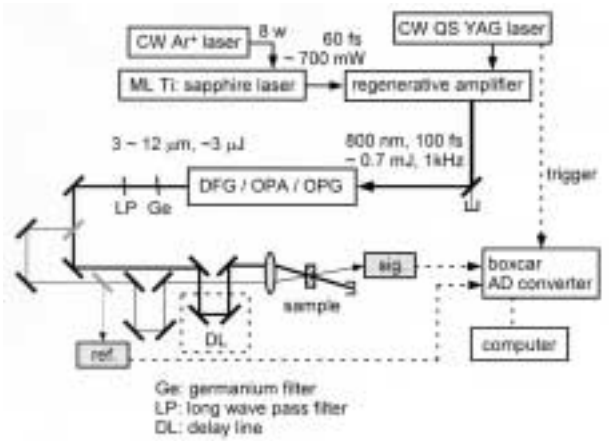

Figure 1. Apparatus for the femtosecond IR-IR pump-probe measurements.

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 chemical reactions. It often affords detailed information about the molecular structure of short-lived intermediates, 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 lower than one picosecond because of the limitation of the uncertainty principle. In this sense, picosecond measurements are the best compromise between the energy resolution and time resolution for time-resolved frequency-domain vibrational spectroscopy. In this project, we study photochemical processes and short-lived transient species by using picosecond time-resolved Raman spectroscopy. In this year, we studied the picosecond dynamics of the excited state of several fundamental aromatic compounds. In addition, we found that strong hyper-Raman scattering was observed from *all-trans* retinal when amplified picosecond pulses were used for excitation. We obtained information about the low-lying excited singlet states of this molecule from the data of the hyper Raman excitation profile.

VI-E-1 Observation of Picosecond Time-Resolved Raman Spectra of *p*-Nitroaniline

FUJINO, Tatsuya; TAHARA, Tahei

P-nitroaniline is a prototypical molecule that shows intramolecular charge-transfer (CT) with photo-excitation. Because of its simple structure with an electron donor group ($–NH_2$) and an acceptor group ($–NO_2$), *p*-nitroaniline has a variety of photochemical properties associated with the CT excited state. Time-resolved Raman spectroscopy was performed to study the picosecond dynamics of this CT state in solutions. In this experiment, the excitation pulse (390 nm) was the second harmonics of the regeneratively amplified output of a Ti:sapphire laser. The first Stokes pulse (465 nm, for the water solutions) of H_2 Raman shifter or second Stokes pulse (509 nm, for the toluene solution) of D_2 Raman shifter excited by 390-nm pulse was used as probe. Transient Raman spectra of *p*-nitroaniline in toluene solution are shown in Figure1. The Raman bands assignable to the T_1 state appeared with the time constant of several tens picosecond after the excitation whereas the S_1 Raman band was not observed. The lifetime of T_1 state was estimated at ~ 5 ns by measuring the decay of the transient Raman bands. In water solution, on the other hand, transient Raman bands assignable to the S_1 state were observed with its lifetime of ~ 10 ps whereas T_1 Raman band was not observed. These results indicated that the lifetime of S_1 (CT) state and the intersystem crossing rate to the T_1 (CT) state are strongly affected by the change of the solvent polarity.

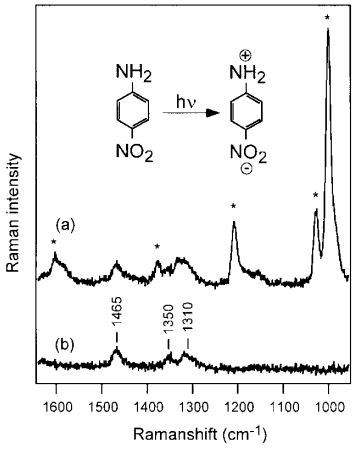

Figure 1. Picosecond time-resolved Raman spectra of *p*-nitroaniline in toluene solution (1.5×10^{-2} mol dm^{-3}) at the delay time of 50 ps. Transient spectra (b) was obtained after the subtraction of the solvent (*) and the ground state signals from (a).

VI-E-2 Femtosecond and Picosecond Time-Resolved Spectra of 5-Dibenzosuberenone

UEDA, Atsuhiro[1]; FUJINO, Tatsuya; MIZUNO, Misao; TAHARA, Tahei; TAKAHASHI, Hiroaki[1]
([1]Waseda Univ.)

Femtosecond time-resolved absorption and picosecond time-resolved resonance Raman spectra of 5-dibenzosuberenone were measured. It was observed in the time-resolved absorption spectra that the S_1 state decayed in a few picoseconds after excitation, while the T_1 state became prominent with time changing in band shape. In the picosecond time-resolved Raman spectra, a Raman band at 1490 cm^{-1} was observed immediately after excitation, which was assigned to the S_1 state. Several Raman bands assignable to the T_1 state were also observed to increase in intensity with time. In addition, a T_1 Raman band exhibited a frequency upshift from 1498 to 1517 cm^{-1}. The observed frequency shift was considered to be caused by the vibrational cooling process in the T_1 state, and it was detectable thanks to the very rapid intersystem crossing.

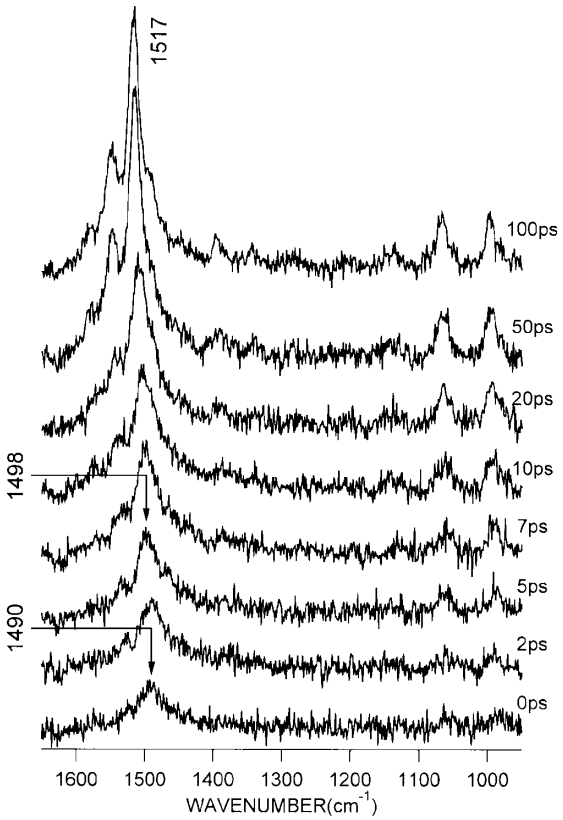

Figure 1. Picosecond time-resolved resonance Raman spectra of 5-dibenzosuberenone in acetonitrile.

VI-E-3 Resonance Hyper-Raman Scattering of *all-trans* Retinal from a Diluted Solution: Excitation Profile and Energy Levels of the Low-Lying Excited Singlet States

MIZUNO, Misao; HAMAGUCHI, Hiro-o[1]; TAHARA, Tahei
([1]Univ. Tokyo)

Strong hyper-Raman scattering of *all-trans* retinal was observed from a diluted solution under the resonance condition by using picosecond amplified Ti:sapphire laser pulses for excitation. Figure 1a shows resonance hyper-Raman (RHR) spectra of *all-trans* retinal in cyclohexane excited at every 10 nm from 770 nm to 840 nm. The concentration of the sample solution is only 1×10^{-3} mol dm^{-3}, which is much lower than the concentration in typical RHR measurements (~ 1 mol dm^{-3}).[1)] This implies that the intensity of RHR scattering from *all-trans* retinal is very high. The RHR intensity increases with shortening of the excitation wavelength whereas the spectral pattern does not change significantly. In *all-trans* retinal, there exist three low-lying excited singlet states, that is, the ^1B_u, ^1A_g and $^1n\pi^*$ states. The hyper-Raman resonance enhancement is considered to predominantly arise from two-photon resonance with the ^1A_g state, and hence, RHR intensity is expected to be the maximum when double the excitation photon energy matches the energy of the ^1A_g state. Figure 2 shows the RHR excitation profile of the intensity of the 1575 cm^{-1} band. The slope of the RHR excitation profile is close to that of the one-photon $^1B_u \leftarrow S_0$ absorption band (broken line in Figure 2), which indicates that the energy separation between the ^1A_g state and the ^1B_u state is small. In addition, the spectral pattern of the RHR spectrum is very similar to that of resonance Raman spectrum that is observed with half wavelength of RHR excitation (Figure 1b). It suggests that the resonance mechanism of RHR scattering of *all-trans* retinal is attributed to the A-term of the vibronic theory[2)] and that Franck-Condon factor between the S_0 state and the ^1A_g state resembles that between the S_0 state and the ^1B_u state.

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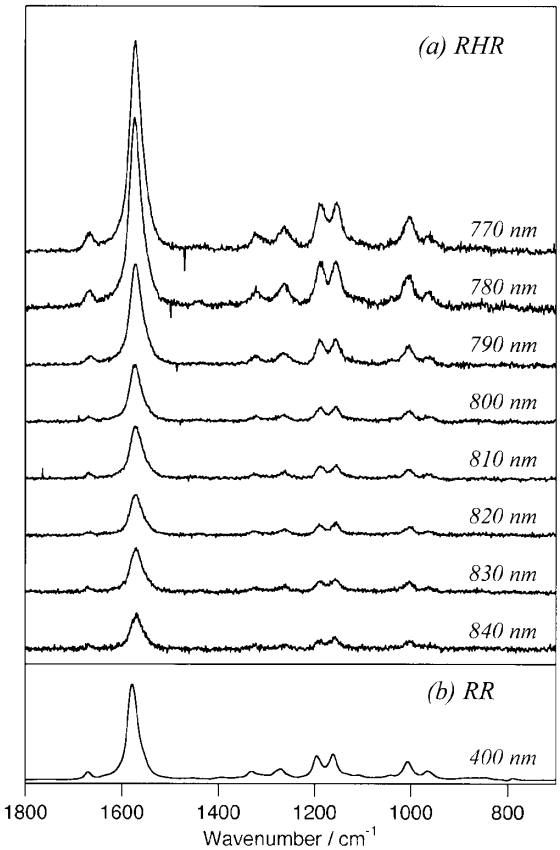

Figure 1. (a) Resonance hyper-Raman (RHR) and (b) resonance Raman (RR) spectra of *all-trans* retinal in cyclohexane (1×10^{-3} mol dm^{-3}).

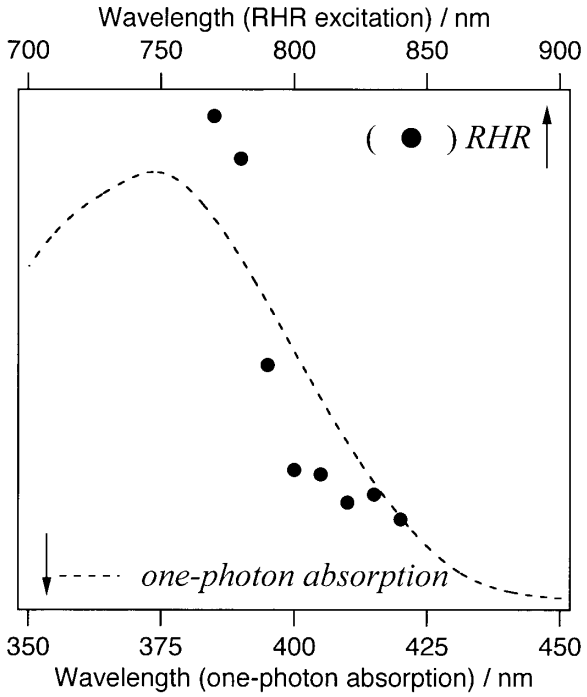

Figure 2. Excitation profile of the 1575 cm^{-1} of the RHR band. The black circles indicate RHR band intensities. Broken line shows absorption spectrum of *all-trans* retinal in cyclohexane.