

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 coherent superposition of vibrational eigen states 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 this project, we study vibrational coherence in the condensed-phase molecules by using ultrashort optical pulses having a duration of ten ~ a few tens of femtoseconds.

VI-C-1 Excited-State Vibrational Coherence of Solution-Phase Molecules Observed in the Third-Order Optical Process Using Extremely Short Pulses

TAKEUCHI, Satoshi; FUJIYOSHI, Satoru¹;
TAHARA, Tahei²
(¹GUAS; ²IMS and RIKEN)

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Excited-state vibrational coherence of solution-phase polyatomic molecules was studied by two different time-domain spectroscopic methods. Raman-active low-frequency vibrations in the excited state of *trans*-stilbene were observed through transient impulsive stimulated Raman scattering spectroscopy. In transient absorption spectroscopy with a 40-fs resolution, a different vibrational mode of the same excited state was observed as a “beat” in the pump-induced absorption signal. We discussed the selection of the vibrational modes by noting the difference in the third-order optical processes relevant to the two spectroscopies. The vibrational coherence of a “reacting” excited state was also observed for ultrafast photodissociation of diphenylcyclopropenone.

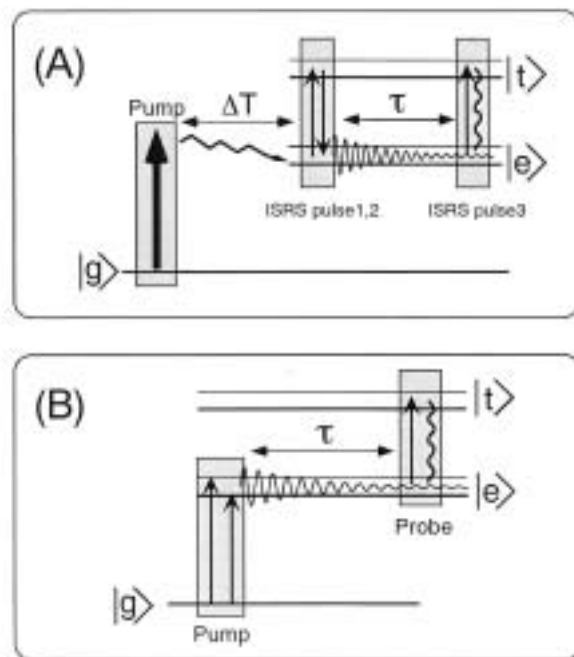


Figure 1. The third-order optical processes utilized to observe the excited-state vibrational coherence. (A) transient ISRS, (B) transient absorption.

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 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.

VI-D-1 Femtosecond/Picosecond Time-Resolved Spectroscopy of Trans-Azobenzene: Isomerization Mechanism Following $S_2(\pi\pi^*) \leftarrow S_0$ Photoexcitation

FUJINO, Tatsuya; ARZHANTSEV, Sergei, Yu.;
TAHARA, Tahei¹
(¹IMS and RIKEN)

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Photoisomerization dynamics and the electronic relaxation process of *trans*-azobenzene after the $S_2(\pi\pi^*) \leftarrow S_0$ photoexcitation were investigated in solution by femtosecond and picosecond time-resolved spectroscopy (UV-visible absorption, Raman, and fluorescence). Femtosecond time-resolved absorption spectroscopy was performed to observe the transient absorption of the S_2 and S_1 states. Immediately after photoexcitation, a very broad transient absorption peaked at 475 and 600 nm was observed. This transient absorption decayed rapidly within 0.5 ps, and this ultrafast component was attributed to the $S_n \leftarrow S_2(\pi\pi^*)$ absorption. After the decay of the S_2 state, a transient absorption showing peaks at 410 nm and 500 nm was observed, which was ascribable to the S_1 state. This transient absorption is similar to the $S_n \leftarrow S_1$ absorption that is observed after $S_1 \leftarrow S_0$ photoexcitation. Picosecond time-resolved Raman measurements were carried out to obtain information about the molecular structure of azobenzene in the S_1 state. The NN stretching frequency in the S_1 spectrum was determined with use of ¹⁵N-substituted azobenzene, and it was found that the NN stretching frequency in the S_1 state is very close to that in the S_0 state (1428 cm⁻¹ in the S_1 and 1440 cm⁻¹ in the S_0). This fact indicated that the NN bond retains a double bond character in the S_1 state. A good similarity was also found between the S_1 and S_0 Raman spectrum. The double bond nature of the NN bond as well as a good similarity between the S_1 and S_0 Raman spectra indicates that the observed S_1 state has a planar structure around the NN bond. The Raman data indicate that the observed S_1 state is not a twisted excited state that appears during the rotational isomerization, but the excited state that is populated during the $S_2 \rightarrow S_1 \rightarrow S_0$ relaxation process retaining a planar molecular structure. Anti-Stokes Raman measurements were performed to obtain information about the vibrational relaxation process. The anti-Stokes Raman spectra showed that the S_1 state was highly vibrationally excited. It was also observed that the hot bands due to the S_0 state appear after the decay of the S_1 state and that the S_0 hot bands disappear with a time constant of ~ 16 ps in hexane. Femtosecond time-resolved and steady-state fluorescence spectroscopy was performed and it revealed that the $S_2 \rightarrow$ 'planar' S_1 relaxation process is the major relaxation pathway following S_2 photoexcitation. The quantum yield of the $S_2 \rightarrow$ 'planar' S_1 electric relaxation was evaluated by comparing the intensity of the S_2 and S_1 fluorescence, and it was found to be almost unity. A series of time-resolved spectroscopy demonstrated that the S_2 rotational isomerization pathway, which had been believed so far, does not exist. It has been clarified that the isomerization occurs in the S_1 state after $S_2 \rightarrow S_1$

relaxation. Consequently, it is concluded that the isomerization of azobenzene takes place in the S_1 state by inversion in both cases of S_2 and S_1 photoexcitation.

VI-D-2 Ultrafast Fluorescence of the Chromophore of the Green Fluorescent Protein in Alcohol Solutions

MANDAL, Debabrata; TAHARA, Tahei¹;
WEBBER, N. M.²; MEECH, S. R.²
(¹IMS and RIKEN; ²Univ. East Anglia)

[*Chem. Phys. Lett.* **358**, 495 (2002)]

The ultrafast fluorescence dynamics of solutions of the chromophore responsible for emission from the Green Fluorescent Protein are measured by fluorescence up-conversion. Decays are non-exponential but well fit by a sum of two-exponentials. All decays have a prompt rise time. The two decay times are approximately independent of wavelength, but their weights are wavelength dependent, in a manner consistent with a spectral narrowing with time. The longer decay time has a weak dependence on medium viscosity.

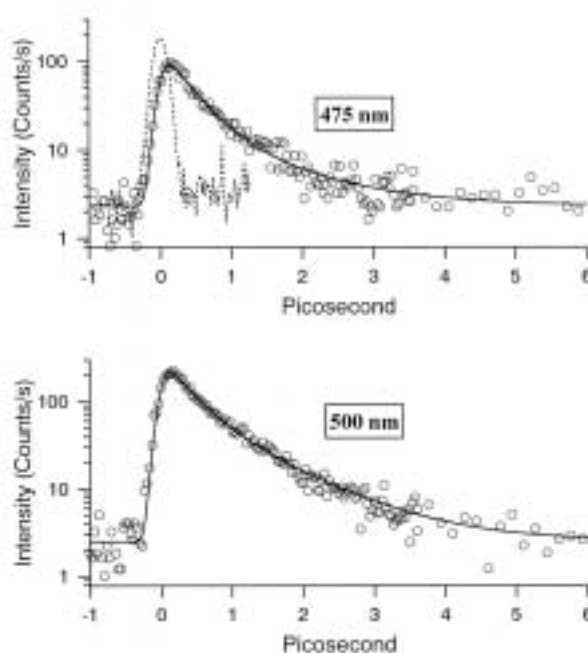


Figure 1. Fluorescence decay data for the anion of **I** in basic methanol, measured as a function of the emission wavelength. The data are fit to a sum of two exponential terms (solid line). Also shown in the 475 nm data is the instrument response function to illustrate time resolution.

VI-D-3 Femtosecond Study of Solvation Dynamics of DCM in Micelles

MANDAL, Debabrata; SOBHAN, Sen¹; TAHARA, Tahei²; BHATTACHARYYA, Kankan¹
(¹Indian Association Cultivation Sci.; ²IMS and RIKEN)

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Solvation dynamics of 4-(dicyanomethylene)-2-methyl-6-(p-dimethylamino-styryl) 4H-pyran (DCM) has been studied in neutral (triton X-100, TX) and cationic (cetyl trimethyl ammonium bromide, CTAB) micelles using femtosecond upconversion. Since DCM is insoluble in bulk water the observed solvation dynam-

ics reports the relaxation dynamics exclusively at the micellar interface. It is observed that the solvation dynamics in TX is slower than that in CTAB. The solvation dynamics is described by components of 2.1, 165 and 2050 ps for TX and 0.23, 6.5 (average 1.75 ps) and 350 ps for CTAB.

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.

VI-E-1 Picosecond Time-Resolved Raman Study of the Solvated Electron in Water

MIZUNO, Misao; TAHARA, Tahei¹
(¹IMS and RIKEN)

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Picosecond time-resolved Raman spectra of water were measured under the resonance condition with the electronic transition of the solvated electron. Transient Raman bands were observed in the OH bend and OH stretch regions in accordance with the generation of the solvated electron. The lifetime of the transient Raman bands were shortened by the addition of the electron scavenger, in exactly the same manner as the solvated electron absorption. It was concluded that the observed transient Raman bands are attributed to the water molecules that directly interact with the electron in the first solvation shell. The resonance enhancement factors were estimated as high as $\sim 10^5$ (the OH bend) and $\sim 10^3$ (the OH stretch) when the probe wavelength was tuned to the absorption maximum of the $s \rightarrow p$ transition of the solvated electron. This very high resonance enhancement indicated that the vibrational state of the solvating water molecules are strongly coupled with the electronic state of the electron, and that it is necessary to consider them together when we consider the vibronic state of the local solvation structure. The probe wavelength dependence of the transient Raman intensity was examined in a wide range from 410 nm to 800 nm. The obtained excitation profiles suggested that the $s \rightarrow$ conduction transition does not significantly contribute the resonance Raman enhancement. The polarized Raman measurement was also undertaken for the OH bend band. The non-zero depolarization ratio was observed, which implied that the nondegeneracy of the three sublevels in the excited p state can be observed in a time scale of the Raman

process. The OH bending and OH stretching frequencies of the solvating water molecule are red-shifted compared with the frequencies of the bulk water, indicating a structural change is induced by the strong interaction with the electron.

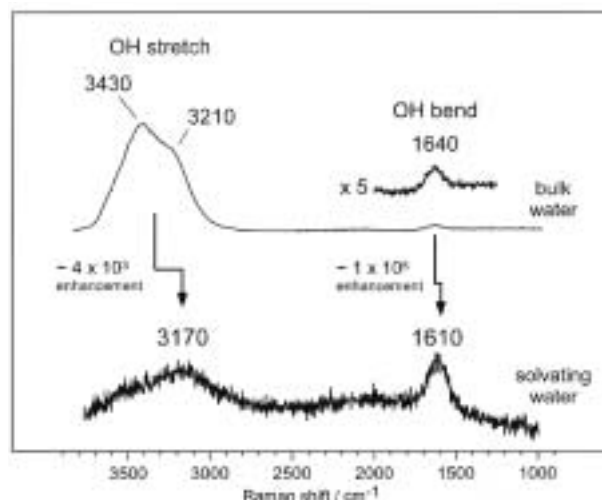


Figure 1. The non-resonance Raman spectrum of bulk water (top; 600 nm excitation) and the resonance Raman spectrum of the water molecules that solvate the electron (bottom; 620 nm excitation).

VI-E-2 Observation of Resonance Hyper-Raman Scattering from all-trans-Retinal

MIZUNO, Misao; HAMAGUCHI, Hiro-o¹;
TAHARA, Tahei²
(¹Univ. Tokyo; ²IMS and RIKEN)

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Hyper-Raman scattering of *all-trans*-retinal was measured for the first time in solution at room tempera-

ture. Under the two-photon resonance condition, the intensity of hyper-Raman scattering was so strong that it could be measured from a diluted solution at concentration as low as $1 \times 10^{-3} \text{ mol dm}^{-3}$. Hyper-Raman excitation profiles were examined in the excitation wavelength range from 770 nm to 840 nm ($\lambda_{\text{ex}}/2$: 385–420 nm). In this excitation range, the intensity of all the hyper-Raman bands monotonously increased with shortening excitation wavelength, and the hyper-Raman spectral feature was very similar to that of resonance Raman spectra excited with double the excitation energy ($\lambda_{\text{ex}}/2$). The resonance mechanism of hyper-Raman scattering was discussed and it was concluded that hyper-Raman scattering gains intensity enhancement from a two-photon resonance with the “ $^1\text{B}_u$ ” state, not with the “ $^1\text{A}_g$ ” state, through the Frank-Condon (the A term) mechanism.

Figure 1. The hyper-Raman excitation profiles of (a) 1579 cm^{-1} (the C=C stretch), (b) 1196 cm^{-1} (the C–C stretch), and (c) 1163 cm^{-1} (the C–C stretch). Black circles and solid lines indicate the intensity of resonance hyper-Raman (RHR) bands and one-photon absorption spectrum, respectively. The excitation profiles of each hyper-Raman band have been normalized by the hyper-Raman intensity measured at 770 nm.

