

Molecular Spectroscopy Laboratory
Chief Scientist: Tahei Tahara (D.Sci.)



(0) Research field

CPR Subcommittee: Chemistry

Keywords: Ultrafast spectroscopy, Interface-selective nonlinear spectroscopy, Single molecule spectroscopy

(1) Long-term goal of laboratory and research background

Spectroscopy is the “eyes” of modern science, and hence it plays essential roles in a variety of fields covering physics, chemistry, engineering, and biology. We develop and utilize the most advanced spectroscopy for studying complex molecular systems. To elucidate a variety of phenomena occurring in the complex systems, we need to clarify their electronic and vibrational states, the response of surroundings, and the fluctuation and dissipation of energy behind them. Based on this view, we carry out fundamental research of molecular science using the most advanced linear/nonlinear spectroscopic methods with the most suitable time- and space-resolution for the problems. Currently, we are carrying out the following projects: (1) Study of ultrafast dynamics using advanced time-resolved spectroscopy; (2) Study of soft interfaces using novel interface-selective nonlinear spectroscopy; (3) Study of structural dynamics of biomolecules and development of new single molecule spectroscopy.

(2) Current research activities (FY2020) and plan (until Mar. 2025)

In the ultrafast spectroscopy project, we demonstrated the ultrafast, photo-induced polarization switching in the crystal of the [CrCo] dinuclear complex by ultrafast pump-probe spectroscopy in the visible region. Our data clearly showed that the photo-induced polarization switching is an ultrafast process occurring with a time constant of 280 fs, demonstrating itself as the fastest polarization switching material realized using the metastable state. Interestingly, the pump-probe data revealed the pronounced appearance of coherent nuclear wavepacket motion with a frequency as low as 22 cm^{-1} , which is attributable to a lattice vibration. We also investigated the excited-state dynamics of the [Pt(CN)₄]²⁻ oligomers formed with metallophilic interaction in solution. Time-resolved absorption spectra exhibited complicated dynamics including the intersystem crossing of the trimer and tetramer coexisting in the solution. Clear oscillations of transient absorption were observed in the first few picoseconds, and the frequency vs detected-wavelength 2D analysis revealed that the observed 135-cm^{-1} and 65-cm^{-1} oscillations arise from the Pt-Pt stretch vibrations of the S₁ trimer and S₁ tetramer, respectively. Moreover, we performed time-domain Raman measurements of trans-1,2-bis(4-pyridyl)ethylene (BPE) adsorbed on gold nanoparticle assemblies (GNAs) with impulsive stimulated Raman spectroscopy using sub-8-fs pulses. We observed coherent nuclear wavepacket motion of BPE on GNAs with drastic enhancement as high as 10^5 - 10^6 through the surface plasmon resonance. This demonstration of surface-enhanced impulsive stimulated Raman spectroscopy (SE-ISRS) provides a firm technical basis for femtosecond time-resolved SE-ISRS experiments to track ultrafast dynamics of the adsorbates. In the coming years, we will realize time-resolved SE-ISRS experiments and develop a new method for ultrafast spectroscopy to reveal the potential energy surface of the reactive systems, aiming at clarifying the ultrafast dynamics of complex molecules in various environments and the relevant mechanisms that realize their functions.

In the interface-selective nonlinear spectroscopy project, we achieved breakthrough discoveries using

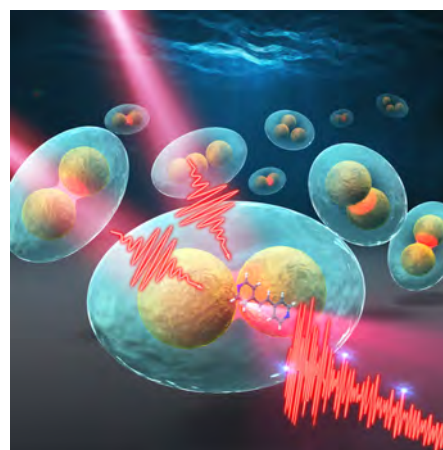


Fig. 1 Time-domain measurement of the surface-enhanced Raman signal by ISRS.

time-resolved (TR-) heterodyne-detected vibrational sum-frequency generation (HD-VSFG) spectroscopy developed at RIKEN. First, vibrational TR-HD-VSFG measurements of water at the air/water interface revealed that vibrational relaxation of non-hydrogen bonded OH (free OH) of water at the topmost water surface is not affected by isotopic dilution. This indicates that the relaxation of free OH proceeds via diffusive rotation of free OH. Second, photochemical reaction dynamics of phenol at the aqueous solution surface was successfully measured by UV-excited TR-HD-VSFG. It was revealed that the photo-deprotonation reaction of phenol at the interface proceeds more than 10^4 times faster than that in the bulk aqueous phase. This demonstrated that the reaction dynamics at interfaces can be drastically different from those in bulk. Furthermore, we applied HD-VSFG for studying a buried polymer/water interface and clarified the structure of polymer and water at the interface. In addition, we developed the fundamental understanding of quadrupole contributions in the second-order nonlinear spectroscopy. In the coming years, we will elucidate the ultrafast vibrational dynamics at the air/water interface using 2D HD-VSFG spectroscopy that we have developed recently. Furthermore, we will study properties of buried material interfaces such as the oxide/water interface, polymer/water interface, and electrode/electrolytes interface to clarify fundamental molecular processes occurring at materials interfaces.

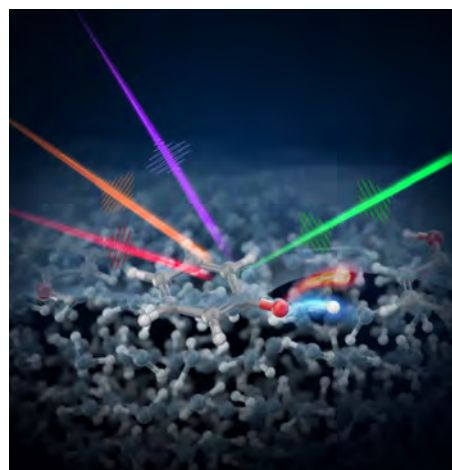


Fig. 2 Photochemical reaction dynamics at an interface studied by TR-HD-VSFG.

In the single-molecule spectroscopy project, we are developing new methods of single-molecule fluorescence spectroscopy for elucidating conformational heterogeneity and dynamics of biopolymers. In this year, we developed two-color two-dimensional fluorescence lifetime correlation spectroscopy (2-color 2D FLCS). In the previous 2D FLCS, we label a target biopolymer with a FRET pair and measure only the donor fluorescence lifetime to obtain the structural information. In contrast, 2-color 2D FLCS also utilizes the acceptor fluorescence to enhance the sensitivity to a high-FRET species in which the donor fluorescence is relatively weak. We applied 2-color 2D FLCS to FRET-labeled RNA/DNA oligonucleotides having analogous hairpin-forming sequences and analyzed the dynamics with the help of the filtered FCS method. As a result, it was found that the dissociation rate of the hairpin structure of RNA is an order-of-magnitude slower than that of DNA, while their hairpin-forming rates are comparable. This result was ascribed to the different duplex structures of RNA and DNA. In the coming years, we will continue the development of new sensitive single-molecule spectroscopic methods and apply them to important problems of biomolecular dynamics such as heterogeneity, hierarchy, and cooperativity.

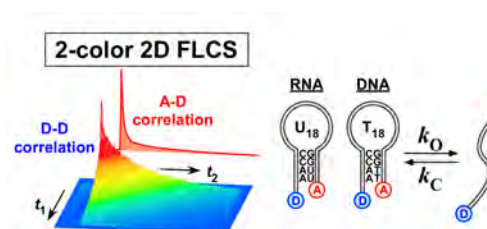


Fig.3 Measurement of conformational dynamics of biopolymers using 2-color 2D FLCS. Reprinted with permission from J. Phys. Chem. B 124, 10674-10681 (2020). Copyright 2020 American Chemical Society.

(3) Members

(Chief Scientist)

Tahei Tahara

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Kunihiko Ishii, Satoshi Nihonyanagi

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as of March, 2021

(Special Postdoctoral Researcher)

Korenobu Matsuzaki

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Tsukasa Takanashi, Wooseok Heo

(Contract Researcher)

Feng Wei

(Postdoctoral Researcher)

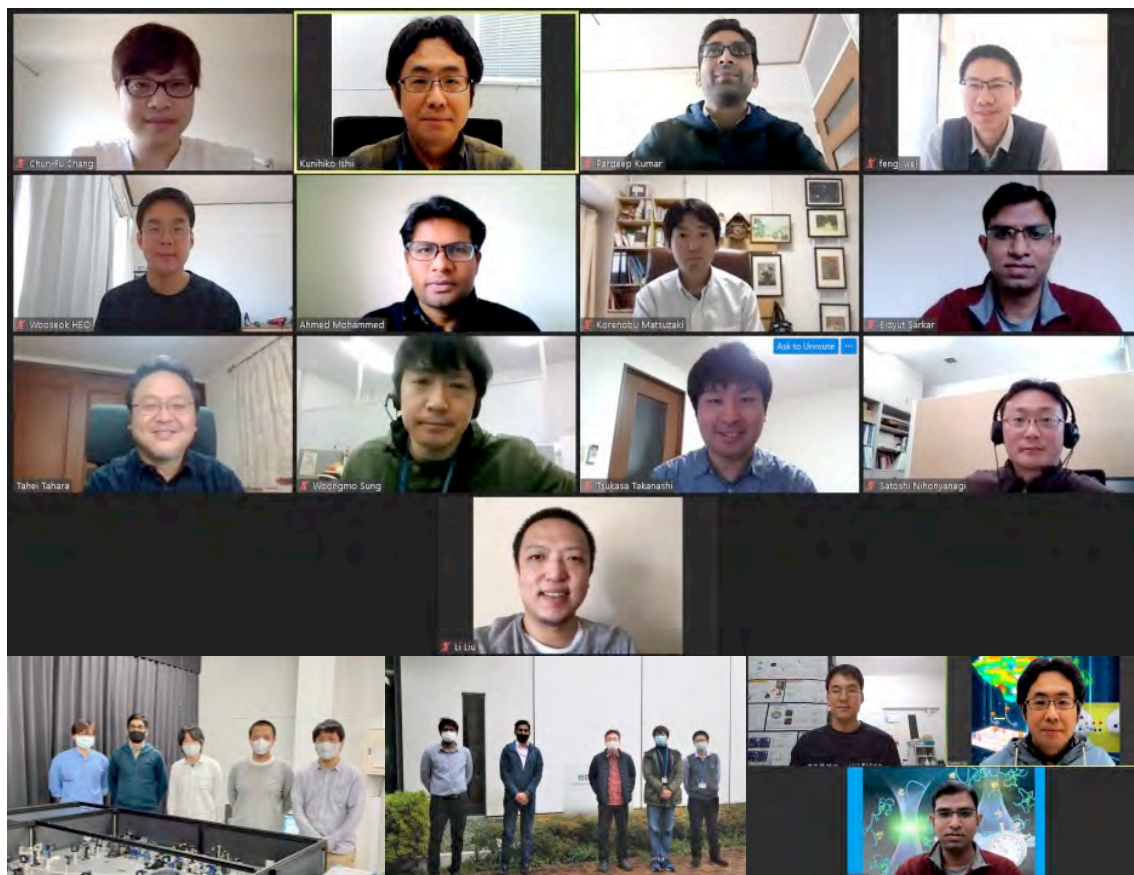
Bidyut Sarkar, Woongmo Sung, Li Liu
Pardeep Kumar, Chun-Fu Chang

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(4) Representative research achievements

1. “Femtosecond Polarization Switching in the Crystal of a [CrCo] Dinuclear Complex”, H. Kuramochi, G. Aoyama, H. Okajima, A. Sakamoto, S. Kanegawa, O. Sato, S. Takeuchi, T. Tahara, **Angew. Chem. Int. Ed.** 59, 15865-15869 (2020).
2. “Coherent vibration and femtosecond dynamics of the platinum complex oligomers upon intermolecular bond formation in the excited state”, M. Iwamura, A. Fukui, K. Nozaki, H. Kuramochi, S. Takeuchi, T. Tahara, **Angew. Chem. Int. Ed.** 59, 23154-23161 (2020).
3. “Reorientation-induced relaxation of free OH at the air/water interface revealed by ultrafast heterodyne-detected nonlinear spectroscopy”, K. Inoue, M. Ahmed, S. Nihonyanagi, T. Tahara, **Nat. Commun.** 11, 5344/1-7 (2020).
4. “The photochemical reaction of phenol becomes ultrafast at the air–water interface”, R. Kusaka, S. Nihonyanagi, T. Tahara, **Nat. Chem.** 13, 306-311 (2021).
5. “Microsecond equilibrium dynamics of hairpin-forming oligonucleotides quantified by two-color two-dimensional fluorescence lifetime correlation spectroscopy”, C. Cheng, K. Ishii, T. Tahara, **J. Phys. Chem. B** 124, 10673-10681 (2020).

Supplementary**Laboratory Homepage**

https://www.riken.jp/en/research/labs/chief/mol_spectro/index.html

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