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. Based on this view, we carry out fundamental research 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 (FY2019) and plan (until Mar. 2025)

In the ultrafast spectroscopy project, we investigated the Au-Au bond formation process in the trimer of a gold (I) complex using time-resolved impulsive stimulated Raman spectroscopy (TR-ISRS) which is time-domain Raman spectroscopy developed at RIKEN. Dicyanoaurate(I) complexes [$Au(CN)_2^-$] are loosely associated in solutions, while strong chemical bonds are formed between gold atoms in the excited state upon photoexcitaion. This system provides us with an opportunity to investigate ultrafast dynamics relevant to chemical bond formation, which is extremely difficult to be studied compared to unimolecular reactions such as photodissociation and photoisomerization. We examined the dynamics of the trimer, and clarified that the Au-Au distance is shortened within 200 fs and then the geometrical change gradually proceeds from a bent to linear structure on a few ps time scale. This study resolves recent controversy on this process. In addition, we extended TR-ISRS to 5^{th} order time-domain Raman measurements that can reveal anharmonicity of the potential energy surface. We also studied the primary process of the photocycle of the most prototypical photoreceptor protein, bacteriorhodopsin, by extending femtosecond stimulated Raman spectroscopy (FSRS) to the deep UV region. We found that the change of the protein moiety takes place before the isomerization process of the retinal chromophore. This observation significantly changes the present understanding about the photocycle because the isomerization of the retinal chromophore has been believed to be the first event that triggers all the following processes. In the coming years, we will develop a new method for ultrafast spectroscopy to reveal the potential energy surface of the reactive systems and clarify the ultrafast reaction dynamics of complex molecules as well as the relevant mechanism behind.

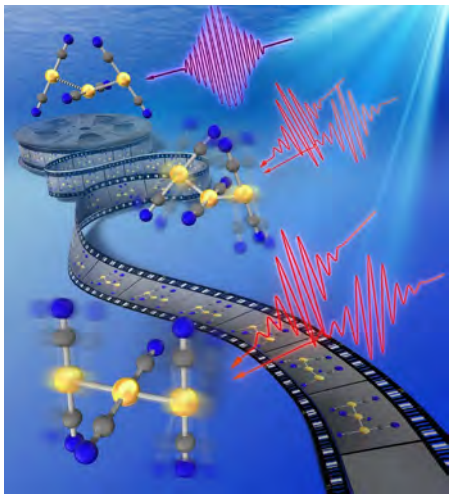

Fig. 1 Au-Au bond formation process of the trimer of a gold compes stucy studied by TR-ISRS

In the interface-selective nonlinear spectroscopy project, we succeeded in clarifying the structure of electrode/electrolyte interface by realizing electrochemical heterodyne-detected vibrational sum-frequency generation (HD-VSFG) spectroscopy. HD-VSFG is powerful interface-selective nonlinear spectroscopy developed at RIKEN, which enables direct

measurements of the phase and amplitude of the nonlinear optical signal generated at the interface. We newly developed an in-situ phase calibration method and realized observation of potential dependent structure of the electrode/electrolyte interface including up/down orientation of solvent molecules with HD-VSFG measurements. We also developed fundamental understanding of the quadrupolar mechanism, which is an unconventional mechanism of VSFG, as well as the effect of Fresnel factor on VSFG spectra. Furthermore, we applied HD-VSFG for studying properties of interfaces between organo-lead- halide perovskite and various materials, and found that organic cations have a preferential orientation at the hole-transporter/perovskite interface. We also discovered unique water structure at a negatively charged hydrophobic interface by two-dimensional HD-VSFG that is an extension of infrared-excited femtosecond time-resolved HD-VSFG. In the coming years, we will try to realize the ultimate time-resolution of 2D HD-VSFG measurements and elucidate the ultrafast vibrational dynamics at the air/water interface, and also investigate photochemical reactions at the water surface by UV-excited time-resolved HD-VSFG. Furthermore, we will study structure and dynamics of complex buried interfaces such as polymer/water and electrode/electrolytes interfaces to clarify fundamental molecular processes occurring at materials interfaces.

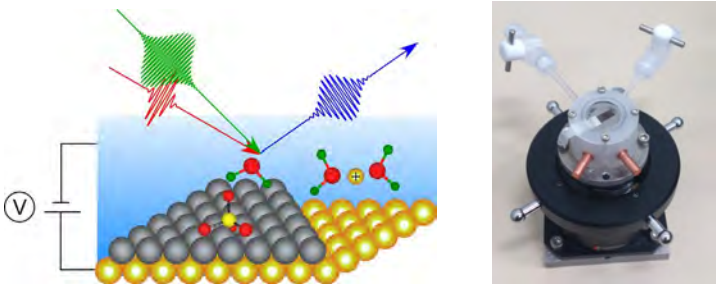

Fig. 2 HD-VSFG measurements at an electrode interface.

In the single-molecule spectroscopy project, we are aiming at clarifying the structural inhomogeneity and structural dynamics of biopolymers using new single-molecule spectroscopic methods developed at RIKEN, in particular two-dimensional fluorescence lifetime correlation spectroscopy (2D-FLCS). In FY2019, we developed a new multifocus optical system for fluorescence correlation spectroscopy. This system utilizes a beamsplitter array to spatially separate excitation beams. Fluorescence from each spot is individually detected with a single-photon avalanche photodiode (SPAD) through a fiber bundle. The combined use of beamsplitters and multiple SPADs allowed us to obtain a higher detection uniformity among focal spots than the existing multifocus FCS systems. We also developed dynamic-quenching two-dimensional fluorescence lifetime correlation spectroscopy (DQ 2D FLCS). In this new method, one can elucidate the microsecond conformational dynamics of biopolymers with only single dye labeling, instead of double labeling required for ordinary FRET-based 2D FLCS. In DQ 2D FLCS, the difference in solvent accessibility of the labeled dye makes its fluorescence lifetime different, which is used for distinguishing different conformers. By applying DQ 2D FLCS to a singly labeled DNA hairpin, we successfully detected microsecond interconversion dynamics between the open and closed forms. In the coming years, we will continue the development of new sensitive single-molecule spectroscopic methods and apply them to important fundamental problems of biomolecular dynamics such as heterogeneity, hierarchy, and cooperativity.

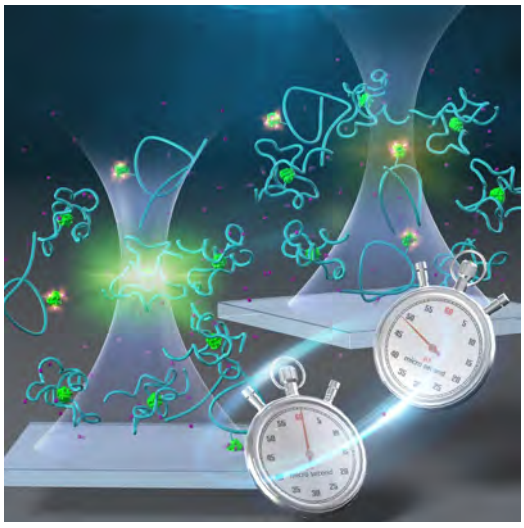

Fig.3 Measurement of conformational dynamics of biopolymers using dynamic-quenching two-dimensional fluorescence lifetime correlation spectroscopy

(3) Members as of March, 2020

(Chief Scientist)
Tahei Tahara
(Senior Research Scientist)
Kunihiko Ishii, Satoshi Nihonyanagi
(Research Scientist)
Hikaru Kuramochi
(Special Postdoctoral Researcher)
Korenobu Matsuzaki
(Visiting Researcher)
Tsukasa Takanashi, Wooseok Heo
(Contract Researcher)
Feng Wei
(Postdoctral Researcher)
Bidyut Sarkar, Woongmo Sung, Li Liu
Ahmed Mohammed, Pardeep Kumar
(Junior Research Associate)
Atsushi Sayama
(Student Trainee)
Chun-Fu Chang
(Assistant)
Tomoko Kato

(4) Representative research achievements

1. "Tracking photoinduced Au-Au bond formation through transient terahertz vibrations observed by femtosecond time-domain Raman spectroscopy", H. Kuramochi, S. Takeuchi, M. Iwamura, K. Nozaki, T. Tahara, **J. Am. Chem. Soc.** 141, 19296-19303 (2019).
2. "Protein dynamics preceding photoisomerization of the retinal chromophore in bacteriorhodopsin revealed by deep-UV femtosecond stimulated Raman spectroscopy", S. Tahara, H. Kuramochi, S. Takeuchi, T. Tahara, **J. Phys. Chem. Lett.** 10, 5422-5427 (2019).
3. "In situ observation of the potential-dependent structure of an electrolyte/electrode interface by heterodyne-detected vibrational sum frequency generation", A. Sayama, S. Nihonyanagi, Y. Ohshima, T. Tahara, **Phys. Chem. Chem. Phys.** 22, 2580-2589 (2020).
4. "Hidden isolated OH at the charged hydrophobic interface revealed by two-dimensional heterodyne-detected VSFG spectroscopy", M. Ahmed, K. Inoue, S. Nihonyanagi T. Tahara, **Angew. Chem. Int. Ed.** 59, 9498-9505 (2020).
5. "Microsecond conformational dynamics of biopolymers revealed by dynamic-quenching two-dimensional fluorescence lifetime correlation spectroscopy with single dye-labeling", B. Sarkar, K. Ishii, T. Tahara, **J. Phys. Chem. Lett.** 10, 5536-5541 (2019).

Supplementary

Laboratory Homepage
https://www.riken.jp/en/research/labs/chief/mol_spectro/index.html
https://spectroscopy.riken.jp/?lang=en