

**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 complex molecular 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 ultrafast spectroscopy; (2) Study of soft interfaces using novel interface-selective nonlinear spectroscopy; (3) Study of structural dynamics of biomolecules by developing new single-molecule spectroscopy.

**(2) Current research activities (FY2022) and plan**

**(A) Ultrafast spectroscopy**

We studied ultrafast photochemical processes involving gold complexes and gold nanoparticles using femtosecond time-resolved spectroscopy. First, we studied gold complex oligomers which form chemical bonds between gold atoms in the excited state. We performed transient absorption measurements and obtained electronic spectra of the generated excited states. By analyzing their concentration dependence and coherent nuclear wavepacket motion observed as the modulation of the transient absorption spectra, we revealed that various gold complex oligomers with different sizes (dimer, trimer, tetramer, and pentamer) are generated with photoexcitation, which is in sharp contrast to what was previously claimed by another group. Second, we realized surface-enhanced impulsive stimulated Raman spectroscopy (TR-SE-ISRS) for the first time and successfully observed the ultrafast dynamics of molecules (BPE) adsorbed on gold nanoparticle assemblies (GNAs). Upon photoexcitation of the localized surface plasmons of GNAs, we observed the simultaneous depletion of the plasmon resonance signal of GNAs and the SE-ISRS signal of the adsorbates. Subsequently, both signals recovered to the original level but the recovery of the adsorbate signal was substantially delayed, indicating that the observed change of the adsorbate arises not only from the reduced surface enhancement effect but also from the change of the adsorption condition of the adsorbate. We concluded that the photoexcited adsorbate is relocated first, and then relaxes to a precursor state which has relatively weak interaction with GNAs before full relaxation to the original state.

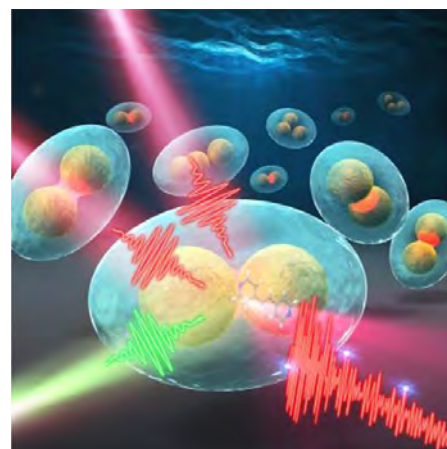


Fig. 1. Realization of surface-enhanced impulsive Raman spectroscopy of adsorbates on gold nanoparticle assemblies. Ref. 5, open access CC-BY-NC-CD.

**Future plan.** We will continue the study of ultrafast dynamics of complex molecular systems. Furthermore, we develop new ultrafast spectroscopy that can yield information on the potential energy surfaces of reacting excited-state molecules.

**(B) Interface-selective nonlinear spectroscopy**

We study the structure and dynamics of molecules at interfaces using heterodyne-detected vibrational sum-frequency generation (HD-VSFG), time-resolved (TR-) HD-VSFG, and two-dimensional (2D-) HD-VSFG spectroscopies developed in RIKEN. In FY2022, we investigated the model battery interfaces of a platinum electrode and acetonitrile solutions containing dilute or superconcentrated lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) using in situ HD-VSFG, with applying negative potentials close to the metal lithium potential. The results showed that the structures of the electrode interfaces are

remarkably different with these two solutions and indicated that acetonitrile decomposes in the dilute solution, whereas the TFSI<sup>-</sup> anion decomposes in the superconcentrated solution. This study clarified the stabilization mechanism of superconcentrated electrolyte solutions, which is crucial to develop more tolerant electrolyte solutions for high-voltage rechargeable batteries. As for the study of the interfacial dynamics, we have measured 2D HD-VSFG spectra of water at the air/water interface using the interferometric excitation scheme. Thanks to the high-time resolution of this scheme, we succeeded in observing the spectral change in the early stage of spectral diffusion of the interfacial water.

**Future plan,** Using TR-HD-VSFG and 2D HD-VSFG spectroscopies, we will further elucidate the ultrafast vibrational dynamics of water at the air/water interface. As for the study of buried material interfaces, we will further study the properties of oxides/water, polymer/water, and electrode/electrolyte interfaces to clarify fundamental molecular processes at material interfaces.

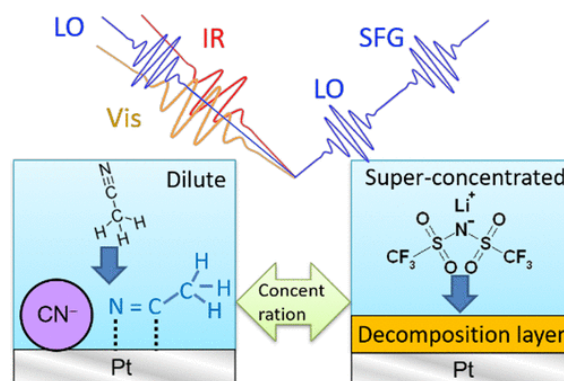


Fig. 2. Sketch of the Pt/acetonitrile electrolyte solution interfaces. Acetonitrile is decomposed in the negative potential in the dilute solution (left), whereas TFSI<sup>-</sup> anion is decomposed in the concentrated solution (right), Reprinted with permission from J. Phys. Chem. C. 127, 10524-10531 (2023).

### (C) Single-molecule spectroscopy

In the single-molecule spectroscopy project, we conducted research aiming at elucidating conformational heterogeneity and dynamics of biomolecules using a novel single-molecule fluorescence method, two-dimensional fluorescence lifetime correlation spectroscopy (2D FLCS), which was originally developed in RIKEN. In FY2022, we carried out two researches. First, we studied the microsecond dynamics of a fluorescent protein, LSSmOrange. The fluorescence properties of fluorescent proteins are dependent on the structure of their chromophores and the dynamic network of amino acid residues around the chromophores. We investigated the spontaneous dynamics of LSSmOrange protein using 2D FLCS. Our results revealed a few-microsecond dynamics between two fluorescent states, which we concluded has an origin fundamentally different from that reported previously for eGFP. Second, we developed a new analytical method of photon data based on concentration perturbation. We previously developed the independent fluorescence component analysis (IFCA) for resolving the structural inhomogeneity of biomolecules based on photon data obtained with a time-correlated single photon counting experiment performed under the single-molecule condition. In this year, we demonstrated a new implementation of IFCA, which utilizes a global analysis of multiple 2D correlation maps obtained from solutions containing analytes with different concentration ratios.

**Future plan,** In the coming years, we will promote research by applying 2D FLCS to elucidate fundamental properties of biomolecular dynamics such as heterogeneity, hierarchy, and cooperativity, as well as to detect non-equilibrium dynamics of enzymatic reactions. In addition, we will develop new methods of single-molecule fluorescence spectroscopy based on 2D FLCS by incorporating approaches of multivariate data analysis. Through these activities, we aim at establishing 2D FLCS as a versatile single-molecule method

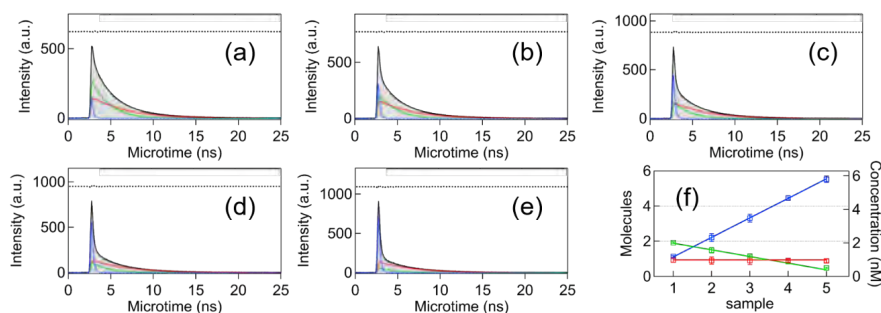


Fig.3 Independent fluorescence component analysis on five dye-mixture solutions.

### (3) Members

#### (Chief Scientist)

Tahei TAHARA

#### (Senior Research Scientist)

Kunihiko ISHII, Satoshi NIHONYANAGI

#### (Research Scientist)

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Sandeep YADAV

#### (Senior Visiting Scientist)

Shoichi YAMAGUCHI, Masahisa OSAWA,  
Satoshi TAKEUCHI

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Munetaka IWAMURA, Hikaru KURAMOCHI  
Anton MYALITSIN, Prashant SINGH

#### (Assistant)

Tomoko Kato

### (4) Representative research achievements

1. “Why the photochemical reaction of phenol becomes ultrafast at the air-water interface: The effect of surface hydration”, T. Ishiyama, T. Tahara, and A. Morita, **J. Am. Chem. Soc.** 144, 6321-6325 (2022).
2. “Ultrafast vibrational dynamics of the free OD at the air/water interface: Negligible isotopic dilution effect but large isotope substitution effect”, M. Ahmed, S. Nihonyanagi, and T. Tahara, **J. Chem. Phys.** 156, 22, 224701/1-9 (2022).
3. “A general design strategy to precisely control the emission of fluorophores via a twisted intramolecular charge transfer (TICT) process”, K. Hanaoka, S. Iwaki, K. Yagi, T. Myochin, T. Ikeno, H. Onno, E. Sasaki, T. Komatsu, T. Ueno, M. Uchigashima, T. Mikuni, K. Tainaka, S. Tahara, S. Takeuchi, T. Tahara, M. Uchiyama, T. Nagano, and Y. Urano, **J. Am. Chem. Soc.** 144, 19778-19790 (2022).
4. “Spectroscopic mapping of the gold complex oligomers (dimer, trimer, tetramer, and pentamer) by excited-state coherent nuclear wavepacket motion in aqueous solution,” M. Iwamura, R. Urayama, K. Nozaki, L. Liu, H. Kuramochi, S. Takeuchi, and T. Tahara, **Phys. Chem. Chem. Phys.** 25, 966-974 (2023).
5. “Photoexcited plasmon-driven ultrafast dynamics of the adsorbate probed by femtosecond time-resolved surface-enhanced time-domain Raman spectroscopy”, P. Kumar, H. Kuramochi, S. Takeuchi, and T. Tahara, **J. Phys. Chem. Lett.** 14, 2845-2853 (2023).

### Supplementary



Photo of three research groups in Molecular Spectroscopy Laboratory (MSL)

### Laboratory Homepage

[https://www.riken.jp/en/research/labs/chief/mol\\_spectro/index.html](https://www.riken.jp/en/research/labs/chief/mol_spectro/index.html)

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