Elucidation of Function, Structure, and Dynamics of Condensed-Phase Molecular Systems by Advanced Ultrafast Laser Spectroscopy

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Education

2007	B.S. Tokyo Institute of Technology
2013	Ph.D. Tokyo Institute of Technology

Professional Employment

2013	Special Postdoctoral Researcher, RIKEN
2016	Research Scientist, RIKEN
2017	JST-PRESTO Researcher
2020	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Awards

2017	The 8th Research Incentive Award of RIKEN
2017	The Spectroscopical Society of Japan Award for Young Scientists
2019	RSC PCCP Prize
2020	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Award
2020	Morino Foundation for Molecular Science
2020	The 13th Young Scientist Awards of the Japan Society for Molecular Science
2021	The 13th Inoue Science Research Award

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We develop and apply advanced ultrafast laser spectroscopy based on state-of-the-art optical technology to study the chemical reaction dynamics of the condensed-phase molecules. In particular, we focus on exploiting unique methodologies based on sub-10-fs pulses (*e.g.*, time-domain impulsive vibrational spectroscopy and multidimensional spectroscopy) and tracking molecular dynamics from electronic and structural viewpoints throughout the chemical reaction with exquisite temporal resolution. We also develop a novel methodology and light source to probe ultrafast dynamics of single molecules in the condensed phase at room temperature, with the aim to understand chemical reaction dynamics at the single-molecule level. Our particular interest rests on elucidating sophisticated molecular mechanisms that underlie the reactions of functional molecular systems such as proteins, molecular assemblies, and metal complexes. On the basis of new insights that can be gained from our advanced spectroscopic approaches, we aim to establish a new avenue for the study of chemical reaction dynamics.

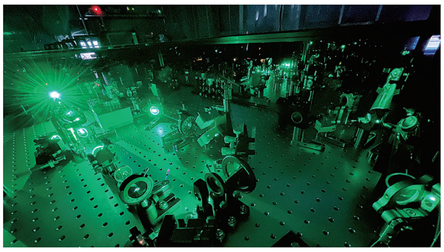

Figure 1. Setup for advanced ultrafast spectroscopy based on sub-10-fs pulses.

Selected Publications

- H. Kuramochi and T. Tahara, "Tracking Ultrafast Structural Dynamics by Time-Domain Raman Spectroscopy," *J. Am. Chem. Soc.* **143**, 9699–9717 (2021).
- H. Kuramochi, S. Takeuchi, M. Iwamura, K. Nozaki and T. Tahara, "Tracking Photoinduced Au–Au Bond Formation through Transient Terahertz Vibrations Observed by Femtosecond Time-Domain Raman Spectroscopy," *J. Am. Chem. Soc.* **141**, 19296–19303 (2019).
- H. Kuramochi, S. Takeuchi, H. Kamikubo, M. Kataoka and T. Tahara, "Fifth-Order Time-Domain Raman Spectroscopy of Photoactive Yellow Protein for Visualizing Vibrational Coupling in Its Excited State," *Sci. Adv.* **5**, eaau4490 (2019).
- H. Kuramochi, S. Takeuchi, K. Yonezawa, H. Kamikubo, M. Kataoka and T. Tahara, "Probing the Early Stages of Photoreception in Photoactive Yellow Protein with Ultrafast Time-Domain Raman Spectroscopy," *Nat. Chem.* **9**, 660–666 (2017).
- T. Fujisawa, H. Kuramochi, H. Hosoi, S. Takeuchi and T. Tahara, "Role of Coherent Low-Frequency Motion in Excited-State Proton Transfer of Green Fluorescent Protein Studied by Time-Resolved Impulsive Stimulated Raman Spectroscopy," *J. Am. Chem. Soc.* **138**, 3942–3945 (2016).
- H. Kuramochi, S. Takeuchi and T. Tahara, "Femtosecond Time-Resolved Impulsive Stimulated Raman Spectroscopy Using Sub-7-fs Pulses: Apparatus and Applications," *Rev. Sci. Instrum.* **87**, 043107 (2016).

1. Tracking Ultrafast Dynamics with Time-Domain Raman Spectroscopy

In traditional Raman spectroscopy, narrow-band light is irradiated on a sample, and its inelastic scattering, *i.e.*, Raman scattering, is detected. The energy difference between the Raman scattering and the incident light corresponds to the vibrational energy of the molecule, providing the Raman spectrum that contains rich information about the molecular-level properties of the materials. On the other hand, by using ultrashort optical pulses, it is possible to induce Raman-active coherent nuclear motion of the molecule and to observe the molecular vibration in real time. This time-domain Raman measurement can be combined with femtosecond photoexcitation triggering chemical changes, which enables tracking ultrafast structural dynamics in a form of "time-resolved" time-domain Raman spectroscopy, also known as time-resolved impulsive stimulated Raman spectroscopy (Figure 2). Through our extensive efforts, time-resolved impulsive stimulated Raman spectroscopy now realizes high sensitivity and a wide detection frequency window from THz to 3000 cm^{-1}, and has seen success in unveiling the molecular mechanisms underlying the efficient functions of complex molecular systems. We recently overviewed its application to the study on femtosecond structural dynamics of complex molecular systems such as photoresponsive proteins and molecular assemblies,1) and reported another application to the ultrafast structural dynamics of a fluorescent protein.2) In the latter, we studied excited-state proton transfer (ESPT) dynamics of LSSmOrange, which has been extensively used for multi-color bioimaging owing to its large Stokes shift. The chromophore of LSSm Orange takes a neutral form in the ground state, but the bright orange fluorescence is emitted from the anionic form that is generated through ESPT upon photoexcitation. This ESPT has been known to proceed in a biphasic manner, but its origin has been unknown. We investigated the chromophore structural dynamics during ESPT and unveiled that the chromophore exists in both *trans* and *cis* forms in the ground state, and they are simultaneously photoexcited and undergo ESPT in parallel with significantly different time scales.

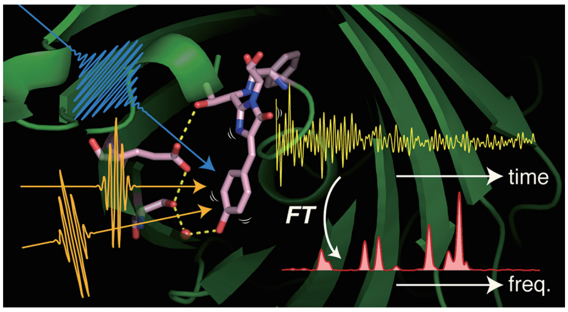

Figure 2. Schematic illustration of time-resolved time-domain Raman spectroscopy. Reprinted with permission from ref. 1. Copyright 2021 American Chemical Society.

2. Generation of Sub-10-fs Pulses with Ultrabroadband Spectral Coverage

Electronic/vibrational coherence has been used as a probe to gain detailed insights into the chemical reaction dynamics. Moreover, it has recently attracted tremendous interest as a control knob for directing and thus enhancing chemical reactions in the desired way. Observing and manipulating such coherences of the condensed phase polyatomic molecules inevitably require extremely short pulses with broad spectral coverage to monitor relevant electronic transitions thoroughly. Nevertheless, generating such ultrashort pulses has been primarily limited in the visible spectral region from the viewpoint of spectroscopic applications, where long-term high stability is required. We developed light sources to generate highly stable sub-10-fs pulses in a broad spectral coverage from UV to NIR. The light source is based on a Yb:KGW regenerative amplifier. Through various nonlinear optical processes such as optical parametric amplification, self-phase modulation, and subsequent sum-frequency mixing, we generate pulses tunable from 300–1400 nm with bandwidths that support the pulse duration well below 10 fs at Fourier transform limit, as shown in Figure 3. We compensate group delay dispersion of these pulses by a combination of chirped mirrors and a pulse shaper, and the intensity profiles of the compressed pulses retrieved from Frequency-Resolved Optical Gating (FROG) measurement show that the compressed pulses have a pulse duration as short as 4.5 fs. Applications of these pulses to ultrafast spectroscopy of functional molecules are now in progress.

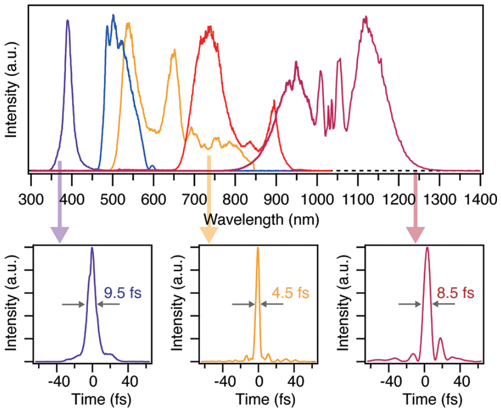

Figure 3. (Top) Typical spectra of the broadband pulses that support Fourier transform limit pulse duration of <10 fs. (Bottom) Intensity profiles of the compressed pulses retrieved from the FROG data.

References

1) H. Kuramochi and T. Tahara, *J. Am. Chem. Soc.* **143**, 9699–9717 (2021).
2) P. Kumar, E. Fron, H. Hosoi, H. Kuramochi, S. Takeuchi, H. Mizuno and T. Tahara, *J. Phys. Chem. Lett.* **12**, 7466–7473 (2021).

Awards

KURAMOCHI, Hikaru; The 13th Inoue Science Research Award (2021).
KURAMOCHI, Hikaru; The 13th Young Scientist Awards of the Japan Society for Molecular Science (2020).