

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

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Professional Employment

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Awards

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2017 The Spectroscopical Society of Japan Award for Young Scientists
2019 RSC PCCP Prize
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Chemical reactions of polyatomic molecular systems proceed on complex potential energy surfaces (PESs) with a vast degree of freedom of nuclear coordinates. For understanding molecular mechanisms underlying the chemical reactions, it is essential to map out the PESs and visualize how the molecules migrate and change its structure thereon. To this end, it is necessary to track the change of the electronic/vibrational structure of the molecule from the reactant all the way down to the product, with temporal resolution as high as possible.

We develop and apply advanced ultrafast laser spectroscopy based on state-of-the-art optical technology to study chemical reaction dynamics of the condensed-phase molecular systems. In particular, we exploit unique methodologies using sub-10-fs pulses (*e.g.*, ultrafast time-domain Raman spectroscopy and multidimensional electronic/vibrational spectroscopy), and track the molecular dynamics from the electronic and structural viewpoints, throughout the chemical reaction with an exquisite temporal resolution. Our particular interest

rests on elucidating sophisticated molecular mechanisms that underlie the reactions of functional molecular systems such as photoreceptor proteins, molecular assemblies, and metal complexes. On the basis of new insights that can be gained from our unique spectroscopic tools, we aim to establish a new avenue for the study of chemical reaction dynamics.

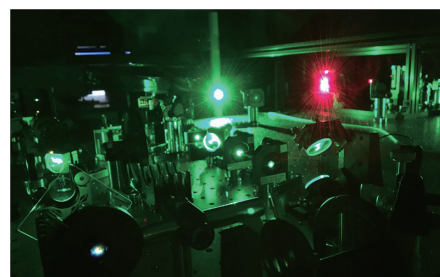


Figure 1. Setup for advanced ultrafast spectroscopy based on sub-10-fs pulses.

Selected Publications

- H. Kuramochi, 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).
- 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, K. Yonezawa, H. Kamikubo, M. Kataoka and T. Tahara, "Probing the Early Stages of Photo-
- reception in Photoactive Yellow Protein with Ultrafast Time-Domain Raman Spectroscopy," *Nat. Chem.* **9**, 660–666 (2017).
- 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, 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).

1. Realtime Observation of the Structural Changes upon Photoinduced Tight Bond Formation

Realtime observation of chemical bond formation and subsequent nuclear rearrangements is one of the ultimate goals of chemical science. Nevertheless, such attempts have been long hampered by a technical difficulty to trigger bond formation at well-defined, desired timing. The dicyanoaurate complex trimer ($[\text{Au}(\text{CN})_2^-]_3$) is the best suitable system in order to achieve this aim because the tight covalent Au–Au bonds are formed upon photoexcitation. Despite the apparent simplicity of the system, however, recent time-resolved studies failed to construct a consistent picture of its structural dynamics.

We used femtosecond time-resolved impulsive stimulated Raman spectroscopy to track ultrafast structural dynamics of the $[\text{Au}(\text{CN})_2^-]$ trimer upon the photoinduced Au–Au bond formation. This ultrafast “time-resolved time-domain” Raman technique allows us to monitor the change of the vibrational structure on the femtosecond timescale by inducing and observing coherent molecular vibrations at arbitrary timings with ultrashort pulses. The obtained femtosecond time-resolved Raman data reveal that the Au–Au stretching vibration at $\sim 90 \text{ cm}^{-1}$ exhibits a gradual frequency upshift in a few picoseconds, demonstrating a continuous bent-to-linear structural change on the triplet-state potential energy surface upon the Au–Au bond formation. This comprehensive ultrafast spectroscopic study settles the controversy on this prototypical molecular assembly.¹⁾

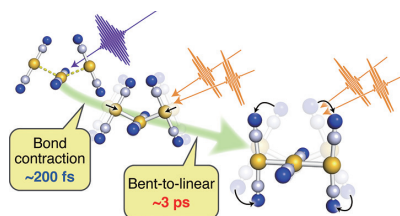


Figure 2. Schematic illustration of the structural changes in $[\text{Au}(\text{CN})_2^-]_3$ upon photoinduced tight Au–Au bond formation.

2. Femtosecond Polarization Switching of the [CrCo] Dinuclear Complex Crystal

Polarization switching has been considered a promising key operating principle of next-generation sensors and memory devices. Ferroelectric compounds have been extensively studied as promising candidates because they exhibit polarization switching upon application of the external electric field or heating. However, the speed (and thus efficiency) of the polarization switching in these materials is often limited by the change in the molecular structure, which occurs on the picoseconds or longer time scale. Also, the polarization state of the

ferroelectric compounds is, in many cases, dependent on their domain structure, making it difficult to realize large polarization at the macroscopic scale.

The crystal of the [CrCo] dinuclear complex has been shown to exhibit polarization switching upon the photoinduced phase transition.²⁾ Because the molecular orientation is well defined inside the crystal and the phase transition is accompanied by the charge transfer that does not require the change in the molecular structure, it has potential to realize the fast polarization switching at the macroscopic scale.

We studied photoinduced polarization switching dynamics in the crystal of the [CrCo] dinuclear complex by ultrafast pump–probe spectroscopy in the visible and mid-infrared regions. Our data clearly show that the photoinduced polarization switching is an ultrafast process with a time constant of 280 fs, demonstrating itself as the fastest polarization switching material realized using the metastable state. Moreover, the pump–probe data in the visible region reveal pronounced appearance of coherent nuclear wavepacket motion with a frequency as low as 22 cm^{-1} , which we attribute to a lattice vibrational mode. The pronounced non-Condon effect for its resonance Raman enhancement implies that this mode couples the relevant electronic states, thereby facilitating the ultrafast polarization switching.³⁾

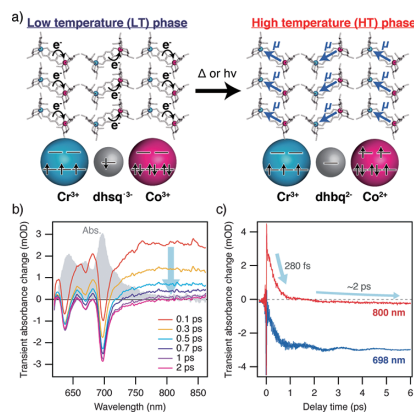


Figure 3. Schematic illustration of the change in the spin state associated with the phase transition. b) Time-resolved absorption spectra obtained after photoexcitation with the 9-fs pulse centered at 520 nm. c) Temporal profiles of the transient absorption signals.

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- 2) S. Kanegawa, Y. Shiota, S. Kang, K. Takahashi, H. Okajima, A. Sakamoto, T. Iwata, H. Kandori, K. Yoshizawa and O. Sato, *J. Am. Chem. Soc.* **138**, 14170–14173 (2016).
- 3) H. Kuramochi, G. Aoyama, H. Okajima, A. Sakamoto, S. Kanegawa, O. Sato, S. Takeuchi and T. Tahara, *Angew. Chem., Int. Ed.* **59**, 15865–15869 (2020).

Awards

KURAMOCHI, Hikaru; The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Award (2020).

KURAMOCHI, Hikaru; Morino Foundation for Molecular Science (2020).