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

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2020 The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology
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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 few-cycle ultrashort 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.

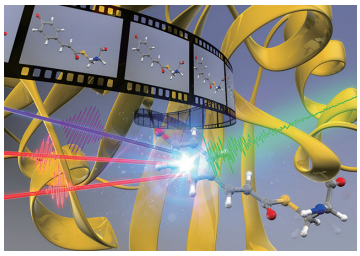

Figure 1. Schematic of the ultrafast nonlinear spectroscopy of complex molecules with few-cycle ultrashort pulses.

Selected Publications

- Y. Yoneda, T. Konishi, K. Suga, S. Saito and H. Kuramochi, "Excited-State Aromatization Drives Nonequilibrium Planarization Dynamics," *J. Am. Chem. Soc.* **147**, 12051 (2025).
- H. Kuramochi, T. Tsutsumi, K. Saita, Z. Wei, M. Osawa, P. Kumar, L. Liu, S. Takeuchi, T. Taketsugu and T. Tahara, "Ultrafast Raman Observation of the Perpendicular Intermediate Phantom State of Stilbene Photoisomerization," *Nat. Chem.* **16**, 22 (2024).
- Y. Yoneda and H. Kuramochi, "Room-Temperature Solution Fluorescence Excitation Correlation Spectroscopy," *J. Phys. Chem. Lett.* **15**, 8533 (2024).
- Y. Yoneda, and H. Kuramochi, "Rapid-Scan Resonant Two-Dimensional Impulsive Stimulated Raman Spectroscopy of Excited States," *J. Phys. Chem. A* **127**, 5276–5286 (2023).
- 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, 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).

1. Excited-State Aromatization Drives Non-Equilibrium Planarization Dynamics[1)]

Excited-state aromaticity is one of the most widely applied concepts in chemistry, often used as a rational guideline for predicting conformational changes in cyclic π-conjugated systems induced by photoexcitation. Yet, the details of the relationship between the corresponding photoinduced electronic and structural dynamics have remained unclear. In this work, we applied femtosecond transient absorption and time-resolved time-domain Raman spectroscopies to track a non-equilibrium planarization dynamics of cyclooctatetraene (COT) derivative associated with the excited-state aromaticity. In the femtosecond time-resolved Raman data, the bent-to-planar structural change was clearly captured as a continuous peak shift of the marker band, which was unambiguously identified with ^{13}C-labeling. Our findings show that the planarization occurs after a significant change in the electronic structure, suggesting that the system first becomes aromatic, followed by a conformational change. This work provides a unique framework for understanding the excited-state aromaticity from a dynamical aspect.

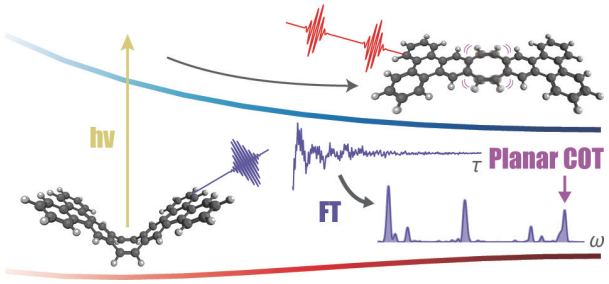

Figure 2. Schematic of time-domain Raman observation of the structural dynamics upon the onset of excited-state aromaticity.

2. Dynamic Excited-State Localization Induced by Jahn-Teller Distortion Observed by Coherent Vibrational Spectroscopy[2)]

Molecular symmetry is a central design element in functional materials, yet its dynamic modulation in the excited state and its consequences for optoelectronic properties remain largely unexplored, particularly in main-group p-block element complexes. We address this knowledge gap by investigating unique Al(III) dinuclear triple-helical complexes that combine high symmetry with twisted π-conjugated systems and achieve exceptional optical properties of unusually large Stokes shifts and high photoluminescence quantum yields. Using transient absorption spectroscopy with a 10 fs pump pulse, we detected coherent vibrational oscillations overlapped with transient absorption/stimulated emission signals. Analysis of the dephasing times of oscillatory signals revealed photoexcitation-triggered Jahn-Teller distortions in these high-symmetry p-block complexes, evidenced by a specifically short dephasing time constant of 410 fs associated with intraligand twisting vibrations. Our findings demonstrate that excited-state symmetry breaking, strongly coupled with intraligand twisting vibrations, is crucial in determining the remarkable photofunctional properties of large Stokes shifts and high photoluminescence quantum yields. This work elucidates the fundamental mechanisms underlying the performance of these Al(III) complexes and provides a conceptual framework for designing next-generation photofunctional materials by harnessing dynamic symmetry changes.

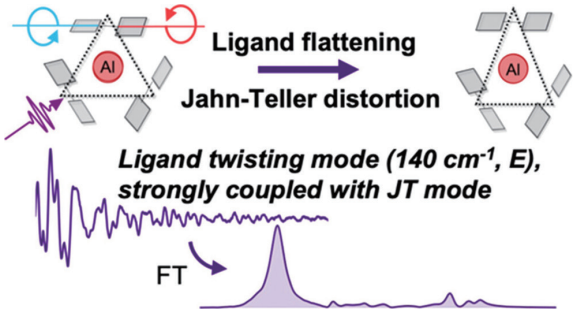

Figure 3. Schematic of the photoexcitation-triggered Jahn-Teller distortion in Al(III) dinuclear triple-helical complex.

3. Development of Two-Dimensional Fluorescence Excitation Correlation Spectroscopy

Polyatomic molecules in condensed phases undergo constant fluctuations in molecular structure and solvent environment. Fluorescence correlation spectroscopy (FCS) is advantageous in elucidating the fast fluctuation dynamics of freely diffusing molecules in solution, where a variety of chemical and biological processes occur. However, observing the fluctuation of diverse physical properties, such as electronic/vibrational spectra and ultrafast dynamics, still remains challenging. In this study, we developed fluorescence excitation cross-correlation spectroscopy for room-temperature solutions, which enables the study of spontaneous fluctuations in the excitation spectrum with microsecond time resolution. By employing Fourier transform spectroscopy with broadband femtosecond pulses and time-correlated single-photon counting, the method enables us to obtain an excitation wavelength-resolved fluorescence cross-correlation map in the microsecond to millisecond range, demonstrating the potential of this method to elucidate the transition between sub-ensembles in statistically equilibrium systems.

References

1) Y. Yoneda, T. Konishi, K. Suga, S. Saito and H. Kuramochi, *J. Am. Chem. Soc.* **147**, 12051 (2025).
2) T. Ehara, Y. Yoneda, T. Yoshida, T. Ogawa, Y. Konishi, T. Ono, A. Muranaka, H. Kuramochi, K. Miyata and K. Onda, *J. Am. Chem. Soc.* **147**, 26446 (2025).