

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

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Awards

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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
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Keywords

Ultrafast Spectroscopy, Nonlinear Spectroscopy, Chemical Reaction Dynamics

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.

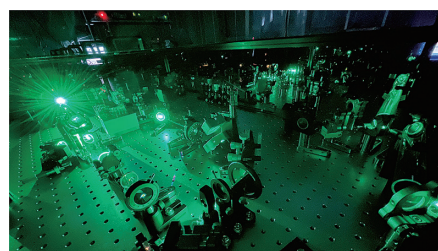


Figure 1. Setup for advanced ultrafast spectroscopy based on sub-10-fs pulses.

Selected Publications

- 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, 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).

1. Rapid-Scan Resonant Two-Dimensional Impulsive Stimulated Raman Spectroscopy of Excited States

Photochemical reactions occur in the electronically excited state, which is effectively represented by a multi-dimensional potential energy surface (PES) with a vast degree of freedom of nuclear coordinates. The elucidation of the intricate shape of the PES constitutes an important topic in the field of photochemistry and has long been studied both experimentally and theoretically. Recently, fully time-domain resonant two-dimensional Raman spectroscopy has emerged as a potentially powerful tool to provide unique information about the coupling between vibrational manifolds in the excited state.^{1,2)} However, the wide application of this technique has been significantly hampered by the technical difficulties associated with experimental implementation and remains challenging. We demonstrated fully time-domain resonant two-dimensional impulsive stimulated Raman spectroscopy (2D-ISRS) of excited states using sub-10-fs pulses based on the rapid scan of the time delay, which facilitates the efficient collection of time-domain signals with high sensitivity. As a proof-of-principle experiment, we performed 2D-ISRS of TIPS-pentacene in solution. Through 2D Fourier transformation of the high-quality time–time oscillatory signal, we obtained a 2D frequency–frequency correlation map of excited-state TIPS-pentacene in the broad frequency window of 0–2000 cm^{-1} . The data clearly resolve a number of cross peaks that signify the correlations among excited-stated vibrational manifolds. The high capability of the rapid-scan-based 2D-ISRS spectrometer presented in this study enables the systematic investigation of various

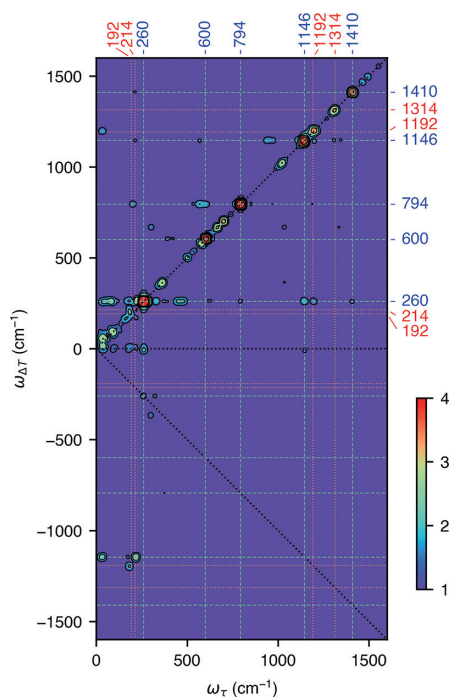


Figure 2. Two-dimensional frequency–frequency correlation map of excited-state TIPS-pentacene in chloroform.

photochemical reaction systems, thereby further promoting the understanding and applications of this new multi-dimensional spectroscopy.³⁾

2. Fourier Transform Excitation-Emission Spectroscopy with Phase-Locked Pulse Pairs

Polyatomic molecules in condensed phases undergo constant fluctuations in molecular structure and solvent environment. These fluctuations can lead to variations in the physical properties, reactivities, and functionalities. However, conventional ensemble measurements only provide statistically averaged information, making it challenging to observe the properties of individual molecules and transitions between sub-ensembles. In order to overcome this limitation, we aim to develop new single-molecule spectroscopic techniques capable of observing the fluctuations of electronic and vibrational transitions and reaction dynamics. Recently, we developed Fourier transform excitation-emission spectroscopy in a room-temperature solution. We send a phase-locked pulse pair of broadband pulses to a home-built confocal microscope and detect the fluorescence with time-correlated single photon counting. Fourier transform of the fluorescence interferogram obtained by scanning the interpulse delay provides a fluorescence excitation spectrum, which shows an identical spectral shape to the bulk absorption spectrum. We aim to achieve single-molecule sensitivity in this experiment and interrogate how the excitation energy of chromophores fluctuates with large amplitude spontaneous fluctuation of photoresponsive proteins.

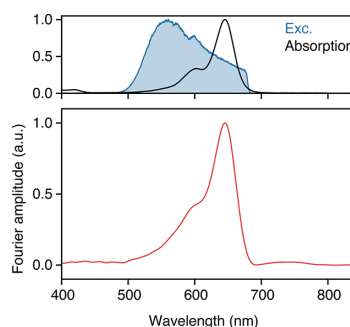


Figure 3. Fluorescence excitation spectrum of ATTO647N aqueous solution measured with broadband pulses. The excitation spectrum and bulk absorption spectrum are shown at the top.

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- 2) G. Fumero, C. Schnedermann, G. Batignani, T. Wende, M. Liebel, G. Bassolino, C. Ferrante, S. Mukamel, P. Kukura and T. Scopigno, *Phys. Rev. X* **10**, 011051 (2020).
- 3) Y. Yoneda, H. Kuramochi, S. Takeuchi and T. Tahara, *J. Phys. Chem. A* **127**, 5276–5286 (2023).