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

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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.

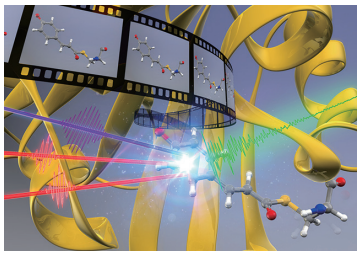

Figure 1. Schematic of the ultrafast nonlinear spectroscopy of complex molecules with few-cycle ultrashort pulses.

Selected Publications

- 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, 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).

1. Room-Temperature Solution Fluorescence Excitation Correlation Spectroscopy

Polyatomic molecules in condensed phases undergo constant fluctuations in molecular structure and their surrounding environment. These fluctuations lead to temporal and spatial variations in the physical properties and reactivities of the molecules, whose understanding is particularly crucial for elucidating functionalities of complex macromolecules such as proteins. Conventional ensemble measurements are insensitive to such fluctuations and resultant heterogeneity and provide only statistically averaged information, making it challenging to elucidate the properties of individual molecules and transitions between sub-ensembles. Single-molecule fluorescence spectroscopy enabled the study of the physical properties and dynamics of individual molecules. However, the long measurement time necessary for detecting intrinsically weak single-molecule fluorescence limits these studies to systems where spontaneous fluctuations are suppressed and slow, such as molecules fixed in polymer or crystalline matrices or at low temperatures, to ensure that the variations in properties of the individual molecules are not washed out during a measurement. Consequently, it remains a challenge to elucidate how properties and dynamics of individual molecules evolve in response to spontaneous fluctuation among sub-ensembles in complex and heterogeneous room-temperature solution systems, where a variety of chemical and biological processes take place. In this study, we developed fluorescence excitation correlation spectroscopy (FECS) for room-temperature solutions, which enables the study of spontaneous fluctuation of the excitation spectrum with microsecond time resolution. By employing Fourier transform spectroscopy with broadband femtosecond pulses and time-correlated single-photon counting, we achieved fluorescence excitation spectroscopy of a room-temperature solution at the single-molecule level. Based on this single-molecule measurement, we obtained an excitation wavelength-resolved fluorescence autocorrelation function in the microsecond to millisecond range, demonstrating the potential of this method to elucidate fast, spontaneous, time-dependent changes of excitation spectra in statistically equilibrium systems.[1] With further development, this method will allow the study of spectral exchange associated with transitions between sub-ensembles of solution-phase molecules with unprecedented time resolution.

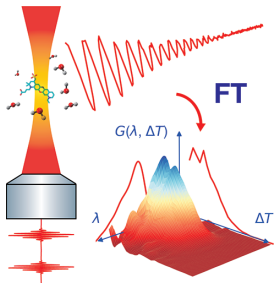

Figure 2. Schematic of fluorescence excitation correlation spectroscopy of a room temperature solution.

2. Development of Sub-10-fs Time-Resolved Absorption Spectroscopy in the Short-Wave-Infrared Region

Femtosecond time-resolved absorption spectroscopy is an ideal tool for studying the ultrafast dynamics of molecules in electronically excited states. By using ultrashort optical pulses whose pulse duration is shorter than the vibrational periods of the molecule, time-resolved absorption measurements also enable one to observe coherent nuclear wavepacket motion and provide fruitful information about the excited-state molecular structure. However, due to technical difficulties, time-resolved absorption measurements with such high temporal resolution have been so far limited in the visible spectral region, leaving the dynamics in the shortwave-infrared (SWIR) region unexplored. Recently, transient species that exhibit absorption in the SWIR region have attracted much attention, such as excited singlet and triplet states of singlet fission systems. In this study, we developed a time-resolved absorption spectrometer in the SWIR region with sub-10 fs temporal resolution. In the setup, the broadband sub-10 fs pulse generated by a noncollinear optical parametric amplifier (NOPA[2]) is used as the pump, and the SWIR continuum (800–1700 nm) generated by the idler output of a newly constructed collinear OPA is used as the probe. The time-resolved absorption data of TIPS-pentacene in chloroform measured with the developed setup are shown in Figure 3. The $S_n \leftarrow S_1$ excited-state absorption band of TIPS-pentacene is observed at 1350 nm, which shows a clear temporal modulation of the spectral position caused by coherent nuclear wavepacket motion in the S_1 state. Fourier transformation of the oscillatory signal reveals the vibrational bands of the Franck–Condon state up to 1410 cm^{-1}, as well as the nonresonant solvent Raman bands up to 3000 cm^{-1}. These results demonstrate that the spectrometer has the capability to monitor the ultrafast electronic/structural dynamics in the SWIR region with high temporal resolution (< 10 fs).

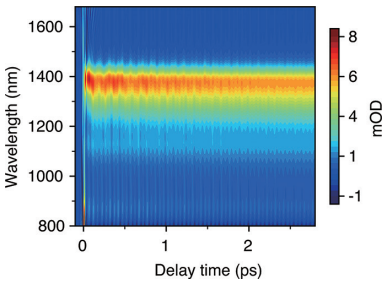

Figure 3. 2D map of the transient absorption signal recorded for TIPS-pentacene in chloroform solution upon photoexcitation with sub-10-fs visible pulse. The clear oscillatory feature represents coherent nuclear wavepacket motion launched in the S_1 state.

References

1) Y. Yoneda and H. Kuramochi, *J. Phys.Chem. Lett.* **15**, 8533 (2024).
2) Y. Yoneda and H. Kuramochi, *J. Phys. Chem. A* **127**, 5276 (2023).

Award

YONEDA, Yusuke; PCCP Prize 2024 (2024).