Research Center of Integrative Molecular Systems
Division of Trans-Hierarchical Molecular Systems

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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. Setup for advanced ultrafast spectroscopy based on sub-10-fs pulses.
1. Towards Sub-10-fs Time-Resolved Spectroscopy of Single Molecules at Room Temperature

In complex biological molecular systems, the slow (µs–ms), large-amplitude structural fluctuation significantly modulates the molecular environment inside/outside the molecule, affecting the reactivity at the relevant local sites. Elucidating how such a fluctuation modulates and regulates particular “fast” local chemical reaction dynamics is vital to interrogating the sophisticated molecular mechanisms behind the functions. Nevertheless, the relevant information cannot be accessed by conventional time-resolved spectroscopy because it only provides statistically averaged information about the ensemble. Unraveling how the slow spontaneous fluctuation regulates the chemical reaction inevitably requires observation of the dynamics at the single-molecule level. To this end, we have been developing ultrafast spectroscopy that can track the reaction dynamics of single molecules at room temperature with a temporal resolution as high as <10 fs. Recently, we constructed a confocal microscope as a platform to perform single-molecule ultrafast spectroscopy, and successfully verified that we could detect single molecules. Using a newly developed high-repetition-rate ultrashort laser, ultrafast spectroscopy with single-molecule sensitivity is now underway.

2. Generation of Wavelength-Tunable Sub-10-fs Pulses at a Multi-MHz Repetition Rate

Time-resolved spectroscopy at the single-molecule level inevitably requires extremely high sensitivity, so the light source having high stability and repetition rate is essential. Typically, an optical parametric oscillator (OPO) or a supercontinuum laser is employed as a light source, which offers stable, tunable outputs with a >MHz repetition rate. However, measurements using OPO have a limitation in the temporal resolution (~200 fs) and lack spectral information of detected transients due to the narrow bandwidth. Supercontinuum laser offers broad bandwidth, but its pulse duration is limited to a few ps due to nontrivial phase structure. To realize ultrafast spectroscopy of various complex molecules with single-molecule sensitivity, we need a light source having wavelength tunability, high repetition rate, ultrashort pulse duration, and high stability. We developed a light source for generating sub-10-fs pulses at a multi-MHz repetition rate. Using a ytterbium fiber chirped-pulse-amplification system, we generated pulses tunable from 500–950 nm with broad bandwidths. The outputs were dispersion-compensated, and the typical pulse duration of the compressed output was <10 fs, as shown in Figure 2. Shot-to-shot and long-term (>hours) fluctuations were evaluated to be <0.3% rms. This high stability holds promise for the application to single-molecule spectroscopy. We will use this high repetition-rate ultrashort light source for ultrafast spectroscopy of single molecules under the microscope and aim to investigate primary events in photoactive proteins with single-molecule sensitivity.

3. Development of Ultrabroadband Two-Dimensional Electronic Spectrometer

Two-dimensional electronic spectroscopy (2D-ES) is a powerful tool for studying the dynamics and structure of molecules having multiple chromophores with high temporal and frequency resolution. 2D-ES disentangles and visualizes how the optical transitions of each chromophore are coupled and how the excitation energy transfers among them. The technique has been successfully utilized to elucidate the primary energy transfer dynamics in photosynthetic systems and various other biological and materials systems. When the technique is applied to the transients, it is even possible to visualize the migration of wavepackets and/or dynamic heterogeneity. While its success, the spectral range of most of the previous 2D-ES measurements has been limited to <100 nm, hampering us from gaining full insights into the intricate electronic dynamics of condensed-phase complex molecular systems. Aiming to broaden the spectral coverage of 2D-ES and enable investigating electronic and nuclear dynamics comprehensively, we constructed an ultrabroadband 2D-ES setup covering >200 nm for the excitation axis and >400 nm for the detection axis. As shown in Figure 3, the typical data measured for a molecular thin film fully resolve auto- and cross-correlations of the electronic transitions of the ground and excited states over the broad spectral region.

Reference


Awards

YONEDA, Yusuke; Best Presentation Award at The 15th Annual Meeting of Japan Society for Molecular Science (2021).

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