

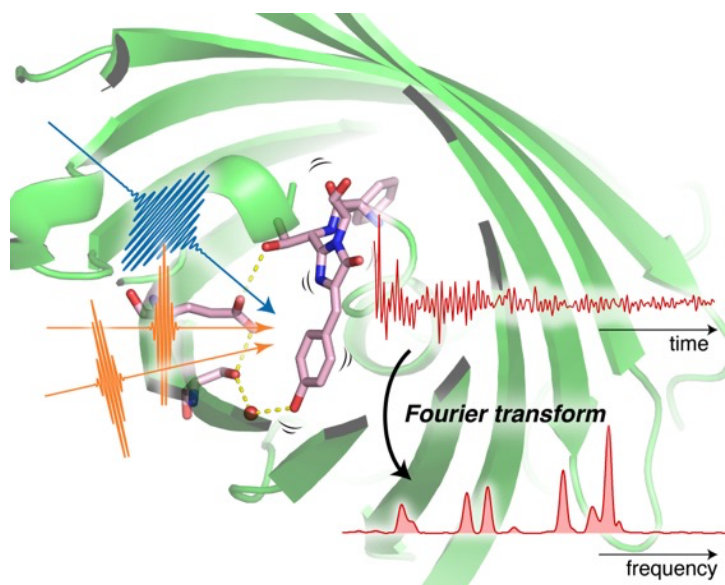
Mapping Structural Dynamics in Photochemistry with Ultrafast Nonlinear Spectroscopy

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Photochemical reactions of polyatomic molecules proceed on complex potential energy surfaces (PESs) having a vast degree of freedom of nuclear coordinates. For identifying and manipulating the reaction coordinates and molecular mechanisms that underlie the reaction, it is desirable to map out the PESs and clarify how the molecule evolves thereon from the electronic and vibrational viewpoints, which has been a long-standing central subject in both experimental and theoretical chemistries. Aiming at visualizing the electronic/structural dynamics governing the fate of photochemical reactions, we develop and apply ultrafast time-resolved time-domain Raman spectroscopy based on sub-10-fs pulses and realize tracking the change of the vibrational structure throughout photochemical reactions with unprecedented temporal resolution. In time-domain Raman spectroscopy, an ultrashort Raman pump pulse induces coherent nuclear wavepacket motion of the molecule, and it is subsequently recorded directly in the time domain using another ultrashort pulse (probe). The obtained time-domain Raman signal fully characterizes the Raman vibrational structure with amplitude, frequency, and phase information and yields a “frequency-domain” Raman spectrum through Fourier transform. While the Raman spectra obtained through time-domain Raman spectroscopy provide information equivalent to those obtained by ordinary “frequency-domain” Raman spectroscopy, the uniqueness of time-domain Raman spectroscopy is that it is performed only with the femtosecond pulses, and thus the timing to initiate Raman transition can be determined with femtosecond temporal accuracy. Therefore, by introducing the femtosecond actinic pump pulse before the induction of the Raman process, it is possible to track the structural change of reaction intermediates occurring on the femtosecond time scale. The high potential of this time-resolved time-domain Raman technique, which we call time-resolved impulsive stimulated Raman spectroscopy (TR-ISRS), was successfully demonstrated in the early studies.^{1,2,3} However, its application was severely limited to the studies of low-frequency vibrational dynamics of small molecules because of technical difficulties. To overcome this limit and study ultrafast structural dynamics of complex molecular systems, we developed a TR-ISRS spectrometer featuring highly stable 6-fs pulses, which enables us to track the change of the vibrational structure over a wide frequency range from the terahertz to 3000 cm⁻¹ region, with femtosecond time resolution and the sensitivity down to ~1 μOD.⁴ With these capabilities, we succeeded in visualizing the structural changes during fundamental chemical processes such as bond dissociation/formation,^{5,6} primary events in the photoreactions of

photoresponsive proteins,^{7,8,9} and the plasmon-driven adsorbate dynamics.¹⁰ Moreover, we extended TR-ISRS to multi-dimensional Raman spectroscopy by employing the actinic pump pulse whose temporal duration is also short enough to induce coherent nuclear wavepacket motion. This technique, two-dimensional impulsive stimulated Raman spectroscopy (2D-ISRS), circumvents cascading of the lower-order nonlinear processes, which has been a technical bottleneck to implement two-dimensional Raman spectroscopy in the past, and it can exclusively visualize the couplings between different vibrational modes in reactive excited states.¹¹ In the talk, we provide an overview of these studies and discuss how advanced ultrafast coherent nonlinear vibrational spectroscopy can be used to address fundamental questions in photochemistry/photobiology.



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