

Femtosecond Time-Domain Raman Spectroscopy

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Since its discovery 90 years ago, Raman spectroscopy has been developing continuously, and it is now one of the most important spectroscopies which is extensively utilized in various fields of science and technology. In ordinary Raman spectroscopy, the energetically-shifted inelastic light scattering (Raman scattering) is measured, and the energy shift from the excitation light provides information about the vibrational energy of the molecules. On the other hand, with an ultrashort optical pulse that has a duration shorter than the vibrational period, we are able to carry out time-domain Raman spectroscopy, in which we induce coherent nuclear motion of the molecule by the impulsive Raman process and observe Raman-active vibrations directly in the time domain. Because the data obtained in such time-domain measurements and those obtained in the frequency domain are transformable to each other with Fourier transformation, in principle, the vibrational information obtainable with time-domain Raman spectroscopy is equivalent to that obtained by ordinary frequency-domain Raman spectroscopy.

The uniqueness of time-domain Raman spectroscopy is that it is performed with use of only femtosecond pulses. Thus, by combining it with a femtosecond pump pulse that starts chemical reactions, we can trace the temporal change in the vibrational structure of transients with a femtosecond accuracy. Based on the idea, time-resolved impulsive stimulated Raman spectroscopy (TR-ISRS) was developed for investigating ultrafast dynamics by Raman spectroscopy, and its high potential was demonstrated by applying it to simple molecules in solution [1-3]. In TR-ISRS, we use three femtosecond pulses: The first pulse (P1) photoexcites molecules to start chemical reactions, the second pulse (P2) is irradiated after a certain delay time (ΔT) to induce coherent nuclear wavepacket motion in the transient species, and the third pulse (P3) measures the wavepacket motion through the oscillation of the transient absorption and/or stimulated emission signal. Fourier transform of the observed oscillation provides the time-resolved Raman spectrum at the time delay at ΔT . Because only femtosecond pulses are used in the TR-ISRS measurements, we can change the delay time with a femtosecond accuracy. Therefore, we can trace the temporal change of the sample through the evolution of femtosecond time-resolved Raman spectra. Recently, we constructed an apparatus employing sub-7-fs pulses, which allows us to obtain time-resolved Raman spectra of the transient in all the fundamental frequency region from terahertz to over 3000 cm^{-1} by the time-domain approach [4]. Using this setup,

we demonstrated that TR-ISRS is applicable to an excited-state molecule that has a lifetime as short as 200 fs [5].

In this presentation, I talk about the progress of femtosecond time-domain Raman spectroscopy, in particular, recent applications of TR-ISRS to the ultrafast dynamics of complex molecular systems such as photo-responsive proteins, i.e., green fluorescence protein (GFP) and photoactive yellow protein (PYP) [4,5]. I also discuss new possibilities of femtosecond time-domain Raman spectroscopy in the future.

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