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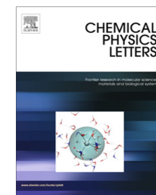

Research paper

Broadband stimulated Raman spectroscopy in the deep ultraviolet region

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ABSTRACT

We report broadband stimulated Raman measurements in the deep ultraviolet (DUV) region, which enables selective probing of the aromatic amino acid residues inside proteins through the resonance enhancement. We combine the narrowband DUV Raman pump pulse (<10 cm^{-1}) at wavelengths as short as 240 nm and the broadband DUV probe pulse (>1000 cm^{-1}) to realize stimulated Raman measurements covering a >1500 cm^{-1} spectral window. The stimulated Raman measurements for neat solvents, tryptophan, tyrosine, and glucose oxidase are performed using 240- and 290-nm Raman pump, highlighting the high potential of the DUV stimulated Raman probe for femtosecond time-resolved study of proteins.

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The function, activity and response of living organisms are closely related to the structural change of relevant proteins which takes place over a wide range of time scales. Therefore, it is of significant importance to track the structural change of proteins for elucidating the molecular mechanism behind the activation of biological functions. In photoreceptor proteins, the structural change of the protein is triggered by photoabsorption that induces a localized change in the embedded chromophore. This subtle, initial change brings about a chain of chemical reactions spanning a broad time range, which ultimately leads to the activation of a biological function [1–3]. Because the functional activation is synchronously triggered with light stimuli, photoreceptor proteins have been intensively studied with various time-resolved spectroscopic [4,5] and diffraction techniques [6–9] as the best system to investigate the structure–function relationship in proteins.

Time-resolved spectroscopy has provided detailed insights into the primary response of various photoreceptor proteins with excellent temporal and structural information. In particular, femtosecond Raman spectroscopies have mapped out the primary structural events that occur on the femtosecond time scale for various photo-responsive proteins, such as rhodopsin [10], green fluorescent protein [11,12], phytochrome [13], and photoactive yellow protein [14,15]. These studies successfully captured the primary structural dynamics of the chromophore in the proteins, which is actually the key initial process that triggers the activation of the biological function. On the other hand, information about the primary response of the surrounding amino acid residues has been rather limited. Because such a secondary response serves as the intermediary to the subsequent chain of chemical/biological reactions, it is very important to elucidate how the initial change in the chromophore propagates to the surrounding amino acid residues. It is one of the most important challenges to be tackled in protein science today, which will provide deep insights into the structural/functional cooperativity in proteins.

Time-resolved ultraviolet (UV) resonance Raman spectroscopy has played an indispensable role in elucidating the structural dynamics in proteins on the picosecond and later time scales [16–18]. In this technique, after initiating the photoreaction by exciting the chromophore, the change in the vibrational spectrum of the surrounding aromatic amino acid residues is selectively monitored by UV resonance Raman probing at around 220 nm, by taking advantage of the resonance enhancement [19]. However, this spontaneous Raman approach is inherently not suitable for studying femtosecond structural dynamics because the time resolution is practically limited up to several picoseconds in exchange for obtaining frequency resolution as high as ~10 cm^{-1}. To overcome this limit, the timing of the Raman probing has to be determined with femtosecond accuracy with respect to the actinic excitation, which is not possible in the picosecond spontaneous Raman approach that utilizes only picosecond probe pulses. Actually, this has been realized with stimulated Raman techniques

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in the frequency and time domains, i.e. femtosecond stimulated Raman spectroscopy (FSRS) [20–22] and time-resolved impulsive stimulated Raman spectroscopy (TR-ISRS) [23–25], respectively, which utilize femtosecond optical pulses. In FSRS, for example, the stimulated Raman process is induced by narrow-band picosecond Raman pump and broadband femtosecond probe pulses, which can define the timing to initiate the Raman transition with femtosecond temporal accuracy. Therefore, combined with the femtosecond actinic pump pulse, it enables tracking the change in the Raman spectrum on the femtosecond time scale. The advantage of FSRS is that it is relatively easy to perform experiments in various wavelength regions from UV (330–390 nm) [26–28] to near-IR (1190 nm) [29,30], although the inevitable background subtraction and inherent complex band shapes sometimes prevent straightforward interpretation. Further extending the spectral window of the FSRS measurements to the deeper UV region would allow us to track femtosecond dynamics of amino acid residues inside photoreceptor proteins.

In this letter, we demonstrate broadband stimulated Raman spectroscopy in the deep UV region (DUV-SRS), which can be a technical basis of FSRS experiments for studying ultrafast structural dynamics of the aromatic amino acid residues in proteins. We realize stimulated Raman probing in the DUV region by introducing the Raman pump and probe pulses at wavelengths as short as 240 nm, thereby enabling selective probing of the aromatic amino acid residues in proteins, such as tryptophan and tyrosine. The steady-state stimulated Raman measurements are demonstrated for neat solvents, tryptophan, tyrosine, as well as glucose oxidase, indicating the high potential and feasibility of DUV-FSRS experiments for time-resolved studies of the aromatic amino acid residues inside photoreceptor proteins.

A schematic diagram of the DUV-SRS setup is shown in Fig. 1. We used a Ti:Sapphire regenerative amplifier system (Legend Elite Duo, Coherent, 800 nm, 80 fs, 8 mJ, 1 kHz) as the light source. About 3.5 mJ of the total amplifier output was used for the DUV-SRS experiments, which was further split into two portions to generate the Raman pump pulse and broadband probe pulse. The major portion (3 mJ) was first converted to a narrow-bandwidth picosecond pulse at 400 nm (<10 cm^{-1}) with 1-mJ energy using a second-harmonic bandwidth compressor (SHBC, Light Conversion) [26,28,31–34]. This narrow-bandwidth 400-nm pulse was subsequently used to pump a narrow-bandwidth optical parametric amplifier (NB-OPA, Light Conversion), which was seeded by a white-light continuum. The NB-OPA delivered visible picosecond pulses (480–2400 nm, >150 μJ), and this output was further

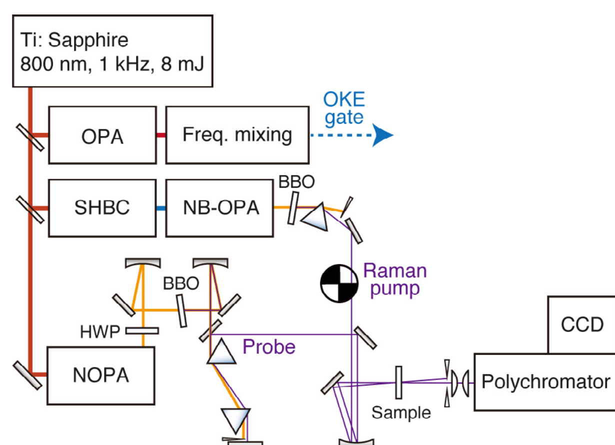

Fig. 1. Schematic diagram of the DUV-SRS setup. OPA: optical parametric amplifier; SHBC: second-harmonic bandwidth compressor; NB-OPA: narrow-band optical parametric amplifier; NOPA: noncollinear optical parametric amplifier; HWP: half wave plate; CCD: Charge coupled device.

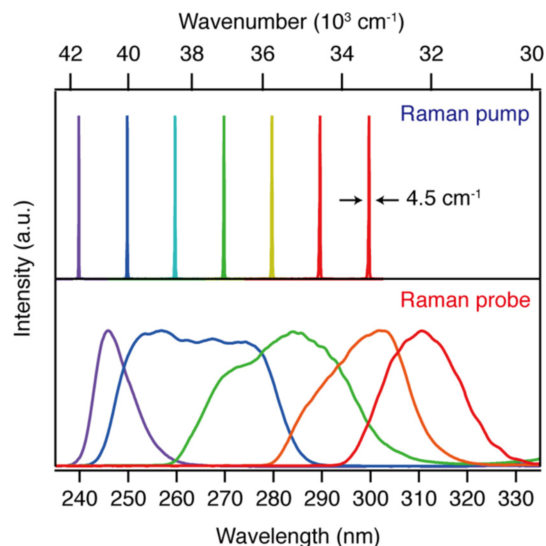

Fig. 2. Typical spectra of the DUV Raman pump and probe pulses.

frequency-doubled in an 8-mm-thick β-barium borate (BBO, type I, θ = 29.2°) crystal to generate narrow-bandwidth DUV Raman pump pulses (<10 cm^{-1}, ~20 μJ). The typical spectra of the Raman pump pulses are shown in Fig. 2. The remaining 0.5-mJ portion of the amplifier output was used for generating the broadband DUV pulse that was used as the Raman probe. Initially, we attempted to obtain a broadband DUV probe pulse by white-light continuum generation pumped by the second harmonic of the amplifier output as reported previously [27,28]. Although this approach enabled stimulated Raman measurements in the UV region (>330 nm), we found that the intensity of the DUV spectral component (<300 nm) of the white-light continuum was not high enough to perform stimulated Raman measurements with a reasonable accumulation time, keeping the signal-to-noise ratio high. Therefore, in the present work, we employed a more intense, broadband DUV pulse generated with a noncollinear optical parametric amplifier (NOPA [35–37]) as the Raman probe. The 0.5-mJ portion of the amplifier output drove a home-built single-stage NOPA. In this NOPA, a white-light seed pulse was generated in a 3-mm thick sapphire plate and was amplified in a 1.5-mm-thick BBO (type I, θ = 31°) crystal, delivering tunable pulses in the visible range (480–750 nm, <10 μJ). After the rotation of the polarization, the NOPA output was frequency doubled in a 20-μm-thick BBO crystal (type I, θ = 36.7°), generating a broadband UV pulse (240–375 nm) which was used as the Raman probe. For frequency doubling, the NOPA output was tightly focused to the BBO crystal (f = 76.2 mm) to broaden the spectrum of the second harmonic generated [38] while the focal position was carefully adjusted and placed slightly in front of the crystal to avoid the damage of the crystal. The typical DUV probe spectra are shown in Fig. 2. The full-width at the half maximum of the probe pulse exceeds 1000 cm^{-1}, which is broad enough to simultaneously record all the stimulated Raman bands from ~100 to 2000 cm^{-1}. The generated broadband DUV pulse was spectrally separated from the visible pulse, and the chirp was compensated by a pair of fused silica prisms with the apex-to-apex distance of ~25 cm. Chirp characteristic of the probe pulse was evaluated *in situ* by measuring the optical Kerr-effect (OKE) signal of water [39], as shown in Fig. 3. The gate pulse for the OKE measurement was generated by a femtosecond OPA (TOPAS-C, Light Conversion) which was pumped by the remaining 4-mJ output of the amplifier. This gate pulse is tunable in a wide frequency range (240–2600 nm) with <80-fs pulse duration, and it can be also used as the actinic pump

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