

Study of surface enhanced Raman signals from adsorbates on gold nanoparticle aggregates in solution through time-domain impulsive stimulated Raman spectroscopy

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[Abstract] Surface-enhanced Raman scattering is widely utilized as a sensitive tool to observe Raman signals from adsorbates on metallic substrates with considerable signal amplification through the plasmonic resonance. Although this drastic signal enhancement has been mainly exploited in the conventional spontaneous Raman so far, it is expected to provide a possibility to investigate the photoreaction dynamics of adsorbates at the single molecular level when implemented in the nonlinear Raman spectroscopy. In this study, we developed surface-enhanced impulsive stimulated Raman spectroscopy using sub-10-fs pulses, and successfully applied it to observe non-resonance Raman spectra of adsorbates on gold nanoparticle aggregates in solution. The observed time-domain vibrational trace was converted to the corresponding Raman spectrum through Fourier transformation, demonstrating that the Raman intensity is enhanced by a factor as large as 10^4 . With the surface-enhanced signals observed under various conditions, we discuss the signal enhancement in the time-domain Raman spectroscopy.

[Introduction] A weak Raman scattering signal from adsorbates on metallic substrates can be increased by multiple orders of magnitude through the plasmonic resonance, which is known as surface enhanced Raman scattering (SERS)^{1,2}. It was proposed that aggregated metallic nanoparticles create a so-called “hot spot” where the incoming and outgoing light fields relevant to the Raman scattering are amplified, realizing a high enhancement of the Raman intensity. This drastic enhancement offers a possibility to study not only the static structural properties but also the photophysical/photochemical dynamics of adsorbates at the single molecular level. For ultrafast structural studies of isolated adsorbates, in particular, it is highly advantageous to exploit nonlinear Raman schemes using ultrashort pulses, rather than the conventional spontaneous Raman process. Recently, a ground-state Raman spectrum of trans-1,2-bis(4-pyridyl)ethylene (BPE) adsorbed on gold nanoparticles was measured by stimulated Raman spectroscopy using femtosecond pulses.³ However, the observed Raman bands were spectrally distorted, which they attributed to the Fano-like resonance⁴, making the analysis of the Raman spectrum very difficult. This spectral distortion can be circumvented by observing the Raman-induced vibrational free induction decay directly in the time domain, i.e., impulsive stimulated Raman spectroscopy (ISRS). In this presentation, we report our recent development of surface enhanced ISRS

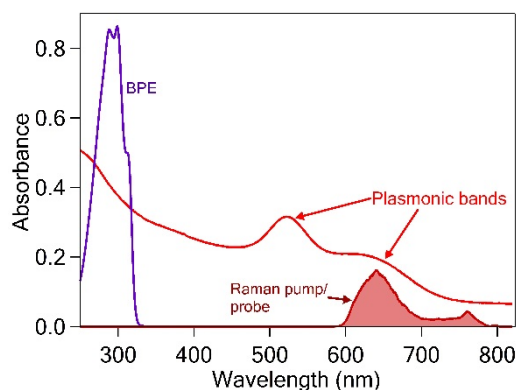


Figure 1: Steady-state absorption spectra of BPE solution (purple) and BPE functionalized GNAs (red) with Raman pump/probe spectrum (brick red).

spectroscopy using sub-10-fs pulses and its application to a colloidal solution containing BPE-functionalized gold nanoparticles aggregates (GNAs) stabilized with a silica coating (figure 1).

[Methods] The ISRS measurements were carried out using ~ 8 fs visible pulses (600 – 800 nm) that is resonant with the plasmonic absorption band of GNAs. The ultrashort pulses were divided into the Raman pump and probe pulses, and they were focused together into a flow cell. The nuclear wavepacket motion in BPE was induced by the Raman pump pulse through the non-resonance impulsive Raman process, and it was monitored by the probe pulse as oscillatory features in the time-resolved signals. The obtained time-domain vibrational signals were converted to Raman spectra through Fourier transformation.

[Results and Discussion] Figure 2a (red) shows a time-domain vibrational trace obtained by the ISRS measurement of BPE-functionalized GNAs in an aqueous solution. The observed oscillatory component is converted to the corresponding Raman spectrum through Fourier transformation (Fig. 2b, red), which agrees nicely with a reported Raman spectrum of BPE. The observation of the Raman bands from such a dilute solution with a BPE concentration as low as 10 μM indicates that BPE Raman signal is greatly enhanced through the SERS mechanism realized by the GNAs. Thus, the present measurement clearly demonstrates that the SERS signal is successfully observed by the time-domain Raman spectroscopy. To examine how much the Raman signal is enhanced, we also measured ISRS signals of an ethanol solution of BPE (20000 μM) under the identical optical condition (Fig. 2a,b, purple). In the obtained Fourier transform spectrum, several Raman bands due to solvent ethanol are weakly seen, and the Raman bands assignable to BPE can be recognized only after considerable magnification. By comparing the Fourier amplitudes of each Raman band obtained from BPE adsorbed on GNAs and dissolved in solution, the enhancement factor was estimated to be in the range of $10^3 - 10^4$ for the prominent BPE bands at 1018, 1198, 1604, and 1647 cm^{-1} . Our further study showed that the signal intensity due to BPE adsorbed on GNAs is saturated at a sufficiently low (< 10 nJ/pulse) Raman pump pulse energy, implying that the Raman scattering is efficiently induced even with much weaker incoming light field through the plasmonic resonance. In the presentation, we show the surface-enhanced ISRS signals observed under various conditions, and discuss the signal enhancement in the time-domain Raman spectroscopy.

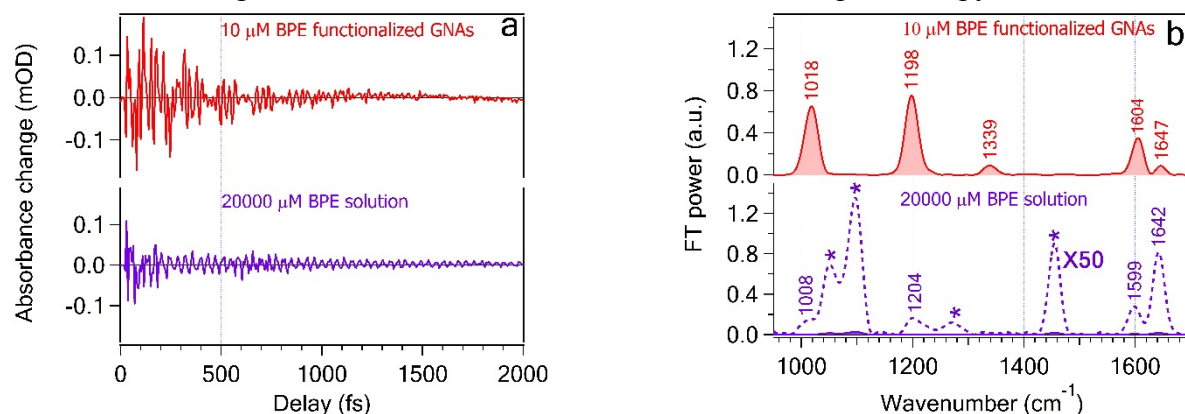


Figure 2: The ISRS signals observed for BPE adsorbed on GNAs (red) and BPE dissolved in ethanol (purple), which were measured using the Raman pump (22.2 nJ, < 8 fs) and probe (3.5 nJ, < 8 fs) pulses. (a) Time-resolved vibrational traces. (b) Fourier transform power spectra of the oscillatory components shown in (a). A magnified trace ($\times 50$) of the ethanol data is also shown with a dotted curve. The * marks represent the solvent bands.

[References]

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