Intensity enhancement of vibrational sum frequency generation by gap-mode plasmon resonance

Masanari Okuno[a], Taichi Tokimoto[a], Miharu Eguchi[a], Hideaki Kano[b], Taka-aki Ishibashi[a],*

[a] Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan
[b] Department of Applied Physics, Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan[1]

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ABSTRACT

A metal sphere–plane structure consisting of gold nanoparticles, *p*-methylbenzenethiol and a gold substrate was measured by vibrational sum frequency generation spectroscopy with four excitation wavelengths, 630, 680, 720, and 780 nm. The enhancement factors of Raman signals were estimated to be 250 and 10^4 for the 532 and 647 nm excitation. Contrastingly, we found that the enhancements of VSFG signals were much smaller, a factor of 5 at maximum. We speculate that the small enhancement factor of VSFG signals is due to the coherent nature of the VSFG process or the extinction of the infrared laser by the gold nanoparticles.

1. Introduction

It is of great importance to reveal the molecular structure of adsorbates on metal surfaces in chemistry. Surface enhanced Raman scattering (SERS) spectroscopy is widely used to investigate molecular adsorbates because of its high sensitivity [1–3]. Recent development of SERS has enabled us to obtain Raman spectra from a single molecule [4]. However, the quantitative approach to adsorbates by SERS spectroscopy is limited by the poor reproducibility of signal enhancements. This is because precise control of surface roughness that mainly governs the enhancement of SERS through the excitation of surface plasmon polaritons is not an easy task. Shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) is one approach to overcome these disadvantages [5]. However, the preparation of core–shell nanoparticles in SHINERS is slightly difficult.

Recently, gap-mode plasmonic excitation Raman scattering spectroscopy [6–9], based on a sphere–plane structure, has been developed to overcome disadvantages of conventional SERS spectroscopy. In the case that the distance between a metal sphere and a metal surface approaches a few nanometers, a plasmonic cavity, in which the local electric field is strongly enhanced, is formed [10]. It was reported that the gap-mode excitation enables us to obtain Raman signals of adsorbed molecules on atomically flat metal surfaces, which are inactive in conventional SERS. Furthermore, it has a high reproducibility of signal enhancements thanks to its well-defined structure, while many experimental parameters are uncontrollable in conventional SERS experiments. Thus, gap-mode resonance Raman spectroscopy has attracted much attention as a new tool to investigate molecules on surfaces. Studies on gap-mode plasmon excitation are in their initial stages and application has been limited to spontaneous Raman and hyper-Raman spectroscopy so far [11]. Meanwhile, the conventional surface enhancement has been extensively explored in many spectroscopic techniques such as spontaneous Raman [1–3], coherent Raman [12], spontaneous hyper-Raman [13], infrared absorption [14,15], second harmonic generation (SHG) [16], and sum frequency generation (SFG) spectroscopy [17,18]. In this situation, it is valuable to investigate characteristics of the gap-mode resonance in other spectroscopy for further application.

Here, we evaluate the intensity enhancement of vibrational sum frequency generation (VSFG) by the gap-mode plasmon resonance. VSFG spectroscopy, which is based on a second order nonlinear process [19], is a highly surface-specific method as is SERS spectroscopy. VSFG spectroscopy is useful for obtaining information on molecular structure at interfaces. The second order nonlinear susceptibility $\chi^{(2)}$ of a macroscopic sample originates from the hyper-polarizabilities β of molecules contained in it, and each can be expressed as [20],

$$\beta_{lmn}^i \alpha \frac{\partial \mu_n}{\partial Q_i} \frac{\partial \alpha_{lm}}{\partial Q_i},$$

(1)

* Corresponding author.
   E-mail address: ishibashi.takaaki.gn@u.tsukuba.ac.jp (T.-a. Ishibashi).
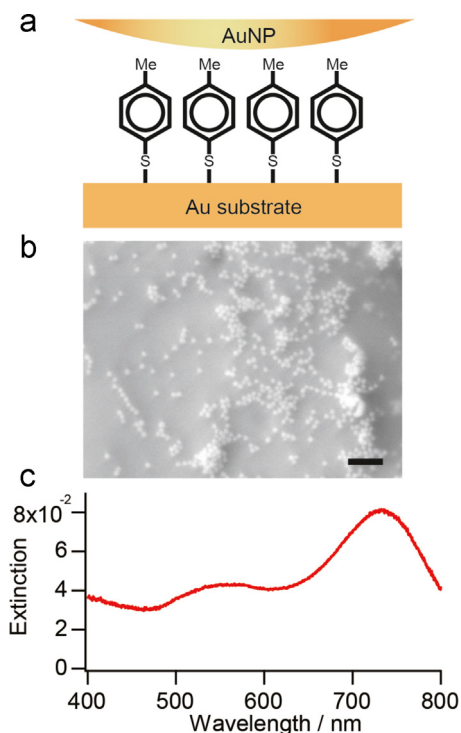
Figure 1. (a) Schematics of the sphere–plane structure consisting of Au-NPs, MBT and Au substrate. (b) SEM image of the sample with NPs. The scale bar is 100 nm. (c) Extinction spectrum obtained from the sphere–plane sample.

where Q_i is the i-th vibrational normal coordinate, and $\partial\mu_n/\partial Q_i$ and $\partial\alpha_{lm}/\partial Q_i$ are the infrared transition dipole and Raman polarizability tensor associated with it, respectively. Eq. (1) shows that VSFG is a sequential and coherent process consisting of the infrared absorption process and the anti-Stokes Raman transition. Therefore, one would expect that VSFG signals would be enhanced by the gap-mode excitation as well as spontaneous Raman signals. In this study, we measured a sphere–plane system consisting of metal surface and nanoparticles (NPs) as shown in Figure 1a. We compared the VSFG intensities of the self-assembly monolayer of *p*-methylbenzenethiol (MBT) with and without NPs and then examined the signal enhancement.

2. Experimental

2.1. Sample preparation

p-Methylbenzenethiol (MBT), purchased from Tokyo Chemical Industry, was used to form a self-assembled monolayer (SAM) on a gold substrate. The gold layer was vapor-deposited on a glass plate. The SAM was prepared by immersing the gold substrate in an ethanol solution of MBT with the concentration of 1 mM for 2 h and rinsed with ethanol. The gold nanoparticles (Au-NPs) with the diameter of ca. 15 nm were deposited on the SAM-covered gold substrate by dipping in the colloidal solution for overnight and rinsing with water. Au-NPs were prepared by reducing tetrachloroauric(III) acid (Sigma Aldrich) with citrate (Kanto Chemical) [8]. Figure 1b shows a typical scanning electron microscope (SEM) image of the sample with NPs.

2.2. Reflection absorption spectroscopy

Commercially available absorption spectrometer (UV-2600, Shimadzu) was used in reflection geometry with an integrating sphere (diameter: 60 mm). Barium sulfate was used as the reference.

2.3. Confocal Raman microspectroscopy

Our home-made Raman microspectrometer was used to measure the samples. A diode-pumped solid state (DPSS) laser (J200GS-11, Showa Optronics) and a Kr⁺ laser (BeamLok 2060-Kr, Spectra Physics) were used as the sources for obtaining 532 and 647 nm excitation Raman spectra, respectively. The incident laser was introduced into a microscope objective (60×/NA 0.9, Nikon) and then a back scattered Raman signal was collected with the same objective. The Raman signal was guided into a polychromator (Omni-Λ, Zolix) and finally detected by a CCD camera (PIXIS 100B, Roper Scientific). The laser power was 4 mW in 532 nm excitation and 0.5 mW in 647 nm excitation, respectively.

2.4. VSFG spectroscopy

Our VSFG spectrometer with wavelength tenability of the visible pulse is described in Ref. [21]. A Ti:sapphire regenerative amplifier (Legend Elite, Coherent) was used to generate laser pulses centered at 800 nm with pulse duration of 100 fs. The amplifier produced ~3.5 mJ of energy/pulse with repetition rate of 1 kHz. The output was divided into two. The first output was used to pump a commercial optical parametric amplifier (TOPAS-C. Coherent) to obtain a broadband infrared beam, whose central wavelength was ~3450 nm (~2900 cm⁻¹) with FWHM of 200 cm⁻¹. The other part was introduced into a narrow bandwidth second harmonic generator (SHBC, Coherent) to generate spectrally narrow 400 nm (pulse width: ~10 ps, bandwidth: ~8 cm⁻¹). The output of the second harmonic generator was used to pump an optical parametric amplifier (TOPAS 400, Coherent) to obtain the tunable visible beam (bandwidth: ~10 cm⁻¹). The infrared and visible beams were overlapped in time and space at the sample. The incident angles of the IR and visible laser beams were ~60 and ~70°, respectively. The generated VSFG signal was introduced into a polychromator (TRIAX550, Horiba Jovin Yvon) after a prism monochromator (CT25-UV, JASCO) and then was detected by a LN-cooled CCD camera (Roper Scientific). The SSP polarization combination (for S-, S-, and P-polarized VSFG, visible, and IR, respectively) was employed. A *z*-cut quartz plate was used as the reference. During the measurements, the samples were moved laterally by using stepping motor stages and the sample area of several square millimeters was averaged.

2.5. Infrared reflection–absorption spectroscopy

IRRAS measurements were performed using a dried-air purged DA8 spectrometer (Bomen) with a LN-cooled MCT detector and a monolayer/grazing angle specular reflectance accessory (Specac). The infrared beam was P-polarized by a polarizer (KRS-5, WP25H, Thorlabs, Inc.). The incident angle was 76° related to the surface normal. The interferograms were collected at 2 cm⁻¹ resolution with 500 times accumulation.

3. Results and discussion

3.1. Spontaneous Raman measurements

Figure 1c shows the reflected absorption spectrum of the sample. In the spectrum, a broad feature associated with the gap-mode resonance between the Au-NPs and the surface is seen, being consistent with previous studies [8,22]. By reference to this spectrum, the wavelengths of the visible pulse in the VSFG measurements were chosen to be 630, 680, 720, and 780 nm. The experiments with the visible pulses of 630 and 780 nm correspond to the Raman measurements with 532 and 647 nm excitation, respectively, because the observed VSFG signals were ~530 and ~635 nm in these VSFG measurements.