Surface-Enhanced Electronic Raman Scattering at Various Metal Surfaces

Ryuto Kamimura, Toshiki Kondo, Kenta Motobayashi, and Katsuyoshi Ikeda

Surface-enhanced Raman scattering (SERS) has been extensively used to obtain vibrational information at metal/dielectric interfaces because of its extremely high chemical sensitivity and surface selectivity. Since the discovery of this effect in 1970s, however, the origin of the spectral background has remained questionable. Because the “background” signals dominate in the low-frequency region, it is necessary to deeply understand this phenomenon for analyzing SERS spectra properly in the wide spectral range. Herein, scattering spectra for various metal surfaces are measured with and without excitation of plasmonic resonances in the wide frequency ranges covering both Stokes and anti-Stokes branches, including very low-frequency region. The comparison of the spectra between smooth surfaces and plasmonic rough surfaces of Au, Ag, and Pt and the theoretical evaluation of local fields at the metal/air interfaces indicate that electronic Raman scattering accounts for the background continuum in SERS spectra. This is also confirmed by the comparison of the spectra with and without ultrathin Ag films on a same Au surface. An analytical method of SERS spectra is demonstrated in which both contributions of electronic Raman scattering and vibrational Raman scattering are considered.

1. Introduction

Surface-enhanced Raman scattering (SERS) is well recognized as a powerful tool for chemical identification at metal surfaces. In this spectroscopic method, inelastic light scattering by molecular vibrations, i.e., vibrational Raman scattering (VRS), gain intensity from plasmonic local fields excited at a metal/dielectric interface. Because both excitation and emission of the VRS process benefit from the local fields, SERS is extremely sensitive to molecules in the vicinity of a metal surface. Despite the broad interests in the SERS technique as a surface-selective vibrational spectroscopic tool, there is a dearth of information about the microscopic origin of the SERS effect. For example, vibrational peaks in SERS spectra are always superimposed on a background continuum, which is recognized as one of the major experimental anomalies in SERS spectroscopy. In most SERS studies, the background continuum has been just ignored or subtracted from raw spectra. Since the signal-to-noise ratio of SERS spectra suffers from the existence of the spectral background, many efforts have been made to depress the SERS background in intensity. However, vibrational peak intensities in SERS spectra tend to correlate with the background continuum intensity, implying that the depression of SERS background is rather competitive with the enhancement of the detection sensitivity.

There are two predominant mechanisms for generation of the SERS background: inelastic light scattering by conduction electrons in a metal substrate, i.e., electronic Raman scattering (ERS), and photoluminescence (PL). When SERS is measured at a metal/dielectric interface, it is obvious that ERS always occurs in the metal phase regardless of the degree of the contribution to the spectral background. Therefore, the question is which mechanism dominantly contributes to the SERS background generation. Recently, several studies showed that the origin of the SERS background on Au surface can be well explained by ERS rather than PL. For other metals, however, the origin of the background generation is still under discussion. Such controversy about the mechanism is partly due to a lack of information about ERS in metals; the cross section of ERS in noble metals is generally very small. The reason of this is related to the short penetration depth of visible light and the screening of light-induced charge fluctuation due to the long-range Coulomb interaction. Indeed, most of ERS studies have focused on strongly correlated electronic systems such as high-temperature superconductor. It is still unclear whether plasmonic enhancement of ERS makes a considerable contribution to the SERS background in a variety of metals. The other reason of the controversy about the mechanism is that selection rules for optical transitions may be modified through excitation of surface plasmon polaritons in SERS system; dipole-forbidden optical transitions such as intraband emission may be allowed by the large momentum of plasmon polaritons.

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/pssb.202100589.

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DOI: 10.1002/pssb.202100589
In this work, scattering spectra for pure metal surfaces of Au, Ag, and Pt are compared with and without plasmonic enhancement. Au and Ag are the most common noble metals in the fields of SERS spectroscopy and plasmonics.[11,13] In contrast, Pt is known to be SERS-inactive because the plasmon resonance is strongly damped by localized d-electrons near the Fermi level of Pt.[12,13] Instead, owing to its d-electrons, this transition metal has been extensively used as a heterogeneous catalyst for various reactions such as the cathode of fuel cells.[14] In addition to these pure metals, atomically thin Ag films on Au surface are also studied in terms of the SERS background generation. At smooth surfaces of these metals where plasmon resonances are absent, characteristic features of ERS are clearly observed in their scattering spectra. At rough metal surfaces with broad plasmonic resonance features, the intensities of the scattered signals are enhanced in accordance with trends in local field enhancement at respective metal/air interfaces, which is a strong support that ERS is the dominant origin of the SERS background.

2. Methods

2.1. Sample Preparation

Polycrystalline beads of Au, Ag, and Pt were prepared by flame melting of the end of metal wires with the purity of 99.999% for Au, 99.95% for Ag, and 99.99% for Pt. Their half-cut beads were mechanically polished and extensively annealed to obtain mirror finished smooth surfaces. These surfaces were carefully cleaned using piranha solution for Au and Pt and hydrogen peroxide/aqueous ammonia for Ag before spectroscopic use. SERS-active plasmonic surfaces of these metals were fabricated by electrochemical surface roughening procedures[12] using a function generator (WF1948, NF Corporation). The applied potential cycles are summarized in Table S1, Supporting Information. The obtained rough surfaces were extensively cleaned in boiling water. For Au, single crystalline beads were also prepared by slow cooling after flame melting of Au wires, which was followed by mechanical polishing and annealing of the half-cut beads so that (111) or (100) faces were obtained.[4] These defined surfaces were annealed in Ar-flow using an induction heater (EASYHEAT 0224, Ambrell, Ltd.) before use. Atomically thin Ag films were formed on both single-crystalline and polycrystalline surfaces of Au using the underpotential deposition (UPD) with the scan rate of 5 mV s⁻¹ in 0.1 M H₂SO₄ solution containing 1 mM AgNO₃.[15,16]

2.2. Scattering Measurements

Scattering spectra for metal surfaces with and without surface roughness were measured using two different types of home-built inverted Raman microscope systems equipped with an objective of 0.6 N.A. and a CCD polychromator (PIXIS 400 BR & IsoPlane, Princeton Instruments). The sensitivity of the CCD polychromator was calibrated using a NIST traceable intensity calibration light source (IntelliCal, Princeton Instruments). The excitation energy dependence of scattering spectra was measured using two different light sources: 1.96 eV (632.8 nm) from a He–Ne laser (HNL100L, THORLABS) and 1.58 eV (785 nm) from a laser diode (NovaPro FIBER WL Hires785-45 SM, RGB lasersysteme GmbH), and also using conventional Raman filters (RazorEdge longwave-pass edge filters, Semrock) to remove Rayleigh scattered light. For comparison of scattering responses in the anti-Stokes and Stokes branches, ultranarrow band notch filters (reflecting volume Bragg grating, OptiGrate Corp) was used to remove the Rayleigh scattering under excitation of 1.96 eV (NEO-30MS1, NEOARK).[8,17]

2.3. Analytical Procedure for ERS Spectra

The absolute wavenumber (ν > 0 in cm⁻¹) and the relative wavenumber (νₐ in cm⁻¹) were used in the following description by considering the connection to traditional wavenumber plotting. A power spectrum for ERS, IERS(νₐ), was connected with the imaginary part of the dynamic susceptibility, χₐERS(ν), by the following expressions[8,9]

\[
I_{ERS}(νₐ) = K \cdot (ν₀ + νₐ)^3 \cdot [n(ν₀)] \cdot χₐERS(ν) \tag{1}
\]

for anti-Stokes branch and

\[
I_{ERS}(νₐ) = K \cdot (ν₀ - νₐ)^3 \cdot [n(ν₀) + 1] \cdot χₐERS(ν) \tag{2}
\]

for Stokes branch of the spectrum. Here, ν₀ is the photon energy for the incident laser (ν₀ = 1/632.8 nm = 15802.8 cm⁻¹ [1.96 eV]) or 1/785 nm = 12738.9 cm⁻¹ [1.58 eV] in the present case). ν₀ is the energy exchanged between photon and electron, i.e., the energy difference between the initial and final states of scattered electrons in the conduction band of the metal. νₐ and νₐ₀ were the Raman shifts relative to ν₀ in the anti-Stokes and Stokes branches, i.e., νₐ₀ = ν₀ and νₐ = ν₀. The cubic terms of the scattered photon energies, (ν₀ + νₐ)³ and (ν₀ - νₐ)³, expressed the scattering efficiency factors for the anti-Stokes and Stokes processes, respectively; the cubic weighting was valid when the signals are measured using a photon counter. K is an instrumental function. χₐERS is determined by integrating the thermally occupied electronic states, which are described by the Fermi-Dirac function, over the distribution of excited wave vectors, resulting in a source for the broad continuum in the ERS spectra. [n(ν)] and [n(ν) + 1] correspond to thermal factors for the anti-Stokes and Stokes processes, respectively, and n(ν) is the Bose–Einstein distribution described as n(ν) = [exp(hν / kₐ T) - 1]⁻¹, where h, c, and kₐ are Planck’s constant, the velocity of light and the Boltzmann constant, respectively. The microscopic origin of the general Bose–Einstein weighting for ERS is related to the thermal occupation of photon states. From Equation (1) and (2), the well-known relation between Stokes and anti-Stokes branches (Anti-Stokes)/(Stokes) = [n(ν)]/[n(ν) + 1] = exp(−hcν / kₐ T)

is obtained by neglecting the small difference in the scattering efficiency factors.[18]

2.4. Estimation of Local Field Enhancement

The enhancement factor (EF) of SERS intensities due to the electromagnetic effect is known to be roughly proportional to the fourth power of local field enhancement[11]
EF $\propto |E_{\text{loc}}(\vec{r}_0 + \vec{v})/E_0(\vec{r}_0 + \vec{v})|^2 |E_{\text{loc}}(\vec{r}_0)/E_0(\vec{r}_0)|^2$
\[\approx |E_{\text{loc}}(\vec{r}_0)/E_0(\vec{r}_0)|^4, \quad (4)\]

where $E_{\text{loc}}$ and $E_0$ denote the amplitude of the local and free-
space electric fields, respectively. Here, we assumed both ERS
and VRS gain intensity from propagating surface plasmons
(SPs) at a metal/dielectric interface (kSP) or a metal/air interface
for respective metals; surface-enhanced ERS (electronic SERS)
and surface-enhanced VRS (vibrational SERS) are hereinafter referred to as ESERS
and VSERS, respectively. The complex wavevector of propagating
SP is written as $k_{\text{SP}} = k_0 \left( \epsilon_m \epsilon_d \epsilon_m + \epsilon_d \right)^{1/2}$ and $k_{\text{SP}}^\ast = k_0 \left( \epsilon_m \epsilon_d \epsilon_m + \epsilon_d \right)^{1/2}$
by assuming that the dielectric loss is small
enough. The wavevector of photon in free space, $k_0$
is the wavevector of photon in free space, $k_0$ is the dielectric constant for the dielectric layer, and $\epsilon_m$ and $\epsilon_d$ are real
and imaginary parts of the dielectric constant for a metal. To deal
with highly damping Pt, however, the contribution of the dielectric
loss must be treated rigorously using [20]
\[k_{\text{SP}} = k_0^ \ast + i k_{\text{SP}} = k_0 \left( \epsilon_m \epsilon_d (\epsilon_m + \epsilon_d) + \epsilon_m^2 \epsilon_d + k_{\text{SP}}^2 \right)^{1/2}, \quad (5)\]
The propagation length of SP is written as
\[L_{\text{SP}} = 1/2 k_{\text{SP}}^\ast \quad (6)\]

3. Results and Discussion
3.1. Scattering Spectra for Smooth Surfaces of Pure Metals

In the absence of plasmon resonances, scattered signals under moderate CW excitation are expected to be generated by the
ERS process when the excitation energy is smaller than the inter-
band transition energy of metal; the contribution of nonlinear
optical effect or near-field effect is excluded in this case. Figure 1a shows Stokes branches of scattering spectra for the smooth surfaces of pure Au, Ag, and Pt obtained using two different excitation energies (for the conventional energy plotting, $h\nu$ in eV is used instead of $\nu$ in cm$^{-1}$). The signal intensities are normalized by the scattering efficiency factor, $G_0 / \nu$, and the incident photon numbers, $I_0 / h\nu_0$, where $I_0$ denotes the incident

**Figure 1.** a) Scattering spectra for smooth surfaces of pure Au, Ag, and Pt, measured using two different excitation energies: 1.58 and 1.96 eV. The signal intensities were normalized by the scattering efficiency factor, $G_0 / \nu$, and the incident photon numbers, $I_0 / h\nu_0$. b) Reflectance spectra calculated for normal incidence to Au, Ag, and Pt surfaces using the dielectric constants of respective metals [20].
light intensity. Note that the appearance of fringes below 1.5 eV is due to the etaloning in the CCD detector, which was not taken into account in the instrument factor $K$. For the 1.58 eV excitation (785 nm), the signal intensities for Au and Ag were much smaller than that for Pt. This is because the Fermi surfaces in these noble metals are much more spherical compared with that in Pt$^{21}$; light-induced density fluctuations are effectively screened by the long-range Coulomb interaction in such electronic system, resulting in the reduction of the cross sections. (Although the scattering volume, governed by the penetration depth of metal, also affects the cross section, this contribution seems to be negligible as shown in Figure S1, Supporting Information.) For the 1.96 eV excitation (632.8 nm), on the other hand, the largest signal intensity is found in Au. This is apparently because the excitation energy is pre-resonant to the $sp$-$d$ interband transition of Au; as shown in Figure 1b, the reflectance of Au significantly decreases above the excitation energy. (In contrast, the low reflectivity of Pt in the entire visible range is due to nonresonant dielectric loss, meaning that there is no resonant enhancement of ERS for Pt.)

The correlation between the anti-Stokes and Stokes branches of scattering spectra were examined using the 1.96 eV excitation, because of the experimental difficulty in measuring the anti-Stokes branch with extremely weak signal intensities under 1.58 eV excitation. Figure 2a shows the raw scattering spectra for smooth surfaces of pure Au, Ag, and Pt measured using the ultranarrow band notch filters. The anti-Stokes intensities are rapidly decreased in all metals, which is a typical behavior in Raman scattering. As is known, the anti-Stokes and Stokes processes in Raman scattering are connected each other via the time-reversal symmetry.$^{18}$ Therefore, when the measured scattering signals are indeed originated from ERS, both the anti-Stokes and Stokes branches must provide same $\chi_{ERS}^2$ by reducing the Bose–Einstein weighting, according to Equation (1) and (2).$^{19}$ This is indeed confirmed in Figure 2b; the symmetry of the response between the Stokes and anti-Stokes branches is well verified in all metals when the local temperature of 300 K was assumed for calculating the Bose–Einstein weighting. It is evident that the scattering signals from smooth metal surfaces in the absence of plasmon resonances are originated from the ordinary ERS process.

3.2. Scattering Spectra for Rough Surfaces of Pure Metals

It is nontrivial whether the SERS background is dominantly originated from plasmon-enhanced ERS, although the scattering signals from smooth metal surfaces can be successfully ascribed to the ERS process. Indeed, there have been the extensive contentsions about the origin of SERS background by considering the other possibilities such as plasmon-induced PL.$^{5,10}$ To examine which mechanism is dominant, SERS spectra for rough surfaces of metals were measured using the ultranarrow band notch filters under the 1.96 eV excitation (632.8 nm). In general, one of the technical difficulties for comparing SERS properties between various metals is to control the photon-SP coupling efficiency. In this work, we have employed two different approaches. One is to compare SERS spectra on a same geometric metal surface with and without atomically ultrathin foreign metal films, which will be discussed later. The other is to use a rough metal surface consisting of various nanostructures with different sizes and shapes. This system gives rise to broad plasmon resonances in the wide spectral range, which can reduce the difference in the photon-SP coupling efficiency. Figure 3 shows the surface morphology of the electrochemically roughened metal surfaces used in the SERS measurements. Although the morphological properties are different among these surfaces, the inhomogeneous nanostructures made the plasmon resonances broaden. For the electrochemically stable Au and Pt, the roughness factors were estimated to be 6.4 for Au and 13.8 for Pt using surface oxide formation in sulfuric acid solution (Figure S2, Supporting Information). For Ag, the roughness factor was estimated to be 18.6 using the underpotential deposition of Pb (Figure S3, Supporting Information).$^{22}$ It is noted that the results obtained by the different methods are comparable because both methods directly measure the number of metal
atoms exposed to the surface using surface-specific reactions. The plasmonic resonance properties of these surfaces are presented in Figure S4, Supporting Information.

Figure 4a shows raw SERS spectra for these roughed surfaces of pure metals, which are presented in the log-scale due to the large difference in intensity. The small vibrational features indicated by the dotted circle is due to unavoidable carbonaceous contaminants in ambient conditions. The vibrational peak at 570 cm\(^{-1}\) in the SERS spectrum of Pt is due to residual surface oxides\(^{23}\) formed in the electrochemical roughening process (as shown in Figure S2b, Supporting Information, most of the surface is still metallic). For the spectral continuum, Ag gives the largest SERS background unlike in the case of ERS on smooth surface. It is noted that the spectral background intensities decay quasiexponentially in the anti-Stokes branch, which is typically seen when the signals are originated from Raman scattering processes\(^{24}\). This implies that the origin of SERS background in Ag and Pt is also ascribed to ERS signals rather than PL, just like in the case of Au.\(^{6-8}\) To examine this, the ratios of the SERS intensity to the ERS intensity (\(I_{\text{SERS}}/I_{\text{ERS}}\)) for respective metals with and without surface roughness were calculated from Figure 2a and 4a, as shown in Figure 4b. The values of \(I_{\text{SERS}}/I_{\text{ERS}}\), i.e., the apparent EFs, are roughly in the order of \(10^4\) for Ag, \(10^3\) for Au and \(10^1\) for Pt, except for the low-Raman shift (\(\tilde{\nu}_{\Delta}\)) region below 200 cm\(^{-1}\), where additional enhancement is seen. These apparent EFs include not only the plasmonic enhancement but also the increase of the surface area due to the surface roughening. Indeed, the EF value obtained for nonplasmonic Pt is close to the roughness factor of the Pt surface, indicating that the plasmonic enhancement is weak in this case. In contrast, the EF values for plasmonic Au and Ag are apparently larger than the roughness factors of these surfaces, suggesting the contribution of the plasmonic enhancement of ERS signals. Accordingly, the purely plasmonic contributions to EFs for ERS, i.e., the apparent EFs divided by the roughness factor, (\(I_{\text{SERS}}/I_{\text{ERS}}/\gamma\)), are estimated to be in the order of \(10^3\) for Ag, \(10^2\) for Au and \(10^1\) for Pt (more quantitative analysis of the plasmonic effect will be provided later). For the additional enhancement seen in the low Raman-shift region below 200 cm\(^{-1}\), the plausible mechanism is nonplasmonic modification of \(\chi''_{\text{ERS}}\) due to the surface roughness because this feature is observed even in the highly damping Pt. There are two different mechanisms for the surface roughness induced ERS: weakening of the screening of light-induced charge

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**Figure 3.** Surface morphologies of roughed surfaces of Au, Ag, and Pt, obtained using a FE-SEM (JSM-7001 F, JEOL).

**Figure 4.** a) Raw SERS spectra for rough surfaces of pure Au, Ag, and Pt measured using the ultra-narrow band notch filters under the 1.96 eV excitation (632.8 nm). b) The ratios of the SERS intensity to the ERS intensity for respective metals with and without surface roughness, which were calculated using the raw spectra shown in Figure 2a and 4a.
fluctuation and momentum transfer from the microscopic surface roughness.[2b] Both effects can relax the usual momentum conservation rule, resulting in the enhancement of cross section for ERS. Indeed, when SERS spectra are measured in situ during the surface roughening process of Au, the rapid increase of the signal intensity was observed in the low Raman-shift region prior to the evolution of SERS activity.[8]

The correlation between the experimentally obtained plasmonic enhancement \( \frac{I_{\text{SERS}}}{I_{\text{ERS}}} = r \) and the local field enhancement was evaluated quantitatively by calculating the field enhancement at the respective metal/air interfaces. According to Equation (6), the propagation lengths of SP at a planar metal/air interface for the photon wavelength of 632.8 nm in free space are calculated to be 64.6 μm for Ag, 9.8 μm for Au, and 2.6 μm for Pt. Using Equation (7), then, \( \text{EF}_{\text{SERS}} \approx \left| \frac{E_{\text{loc}}(\omega)}{E_0(\omega)} \right|^4 \) is calculated to be 335 for Ag, 33 for Au, and 0.2 for Pt. (Similarly, \( \text{EF}_{\text{V}} \) is estimated to be 10⁵ for Ag, 5000 for Au, and 180 for Pt using Equation (8).) These values can be a good indicator to evaluate trends in the relation between the dielectric loss of metal and the plasmonic effect even though the excited SPs are scattered by surface roughness in the practical SERS systems. Figure 5 shows the plots of the purely plasmonic EF \( \frac{I_{\text{SERS}}}{I_{\text{ERS}}} \) versus the theoretically calculated \( \text{EF}_{\text{SERS}} \). Here, the values for \( \frac{I_{\text{SERS}}}{I_{\text{ERS}}} \) were taken at 1.93 eV, where the non-plasmonic enhancement of \( \chi^{(2)} \) is absent. Clearly, the observed EFs are related to the theoretical values of EFs, strongly suggesting that the ERS accounts for the SERS background.

3.3. Scattering Spectra for Atomically Thin Ag Films on Au

The contention that the SERS background is originated from plasmon-enhanced ERS signals is further confirmed by measuring scattering spectra for atomically thin Ag films formed on both smooth and rough Au surfaces.[15] This ultrathin Ag film, fabricated using the UPD technique (see Figure S3, Supporting Information), is referred to as AgUPD. In this experiment, the metal dependence of the SERS background can be evaluated for the same surface morphology.

When AgUPD is formed on a smooth Au surface (AgUPD/Au), the ERS intensity should decrease because the cross section of ERS at 1.96 eV is much lower in Ag than in Au. This is indeed seen in Figure 6a. Such intensity decrease was similarly observed on Au(111), as shown in Figure S5, Supporting Information. According to the previous report on surface X-ray analysis, the
AgUPD/Au(111) maintains the atomic bilayer structures even under ambient conditions. Thus, the intensity decrease shown in Figure 6a is ascribed to the contribution of the atomically thin Ag films, even though the penetration depth of photons is much larger than the thickness of AgUPD (see Figure S1, Supporting Information). This indicates that ERS is highly surface-sensitive.

Next, when AgUPD was formed on a SERS-active rough Au surface, the induced change was rather opposite from the result on the smooth surface; the spectral background intensities on the rough Au were enhanced by formation of AgUPD, as shown in Figure 6b. This is reasonably explained by the fact that the dielectric loss of SP was decreased by the presence of the AgUPD. Figure 6c shows that the spectral profile of the $I_{\text{SERS}}/I_{\text{ERS}}$ for AgUPD/Au is rather similar to that for pure Au, suggesting that the background continuum is originated from the plasmonic enhancement of ERS signals generated from the Au underlayer. If the PL is the dominant origin of the SERS background in Ag surfaces, the spectral profile for the AgUPD/Au should be much more close to that of Ag. Only the plasmon-enhanced ERS mechanism can properly explain these behaviors observed on various metal surfaces with and without surface roughness.

3.4. Enhanced Signals of ERS and VRS in SERS Spectra

SERS is typically used to obtain chemical information at metal/dielectric interfaces such as electrode/electrolyte interfaces. According to the results demonstrated in the above sections, SERS spectra should consist of discrete peaks of VSERS generated in the dielectric phase of the interface and a background continuum of ESERS generated in the metal phase of the interface. Given that both ERS and VRS are inelastic light scattering processes by different Raman scatterers, the relation between $I_{\text{ERS}}$ and $\chi_{\text{ERS}}^m$ in Equation (1) and (2) are applicable for the relation between $I_{\text{VSERS}}$ and $\chi_{\text{VSERS}}^m$, while $\chi_{\text{ERS}}^m$ is determined by integrating the thermally occupied electronic states. $\chi_{\text{VSERS}}^m$ is given by the vibrational states of polyatomic molecules. On the other hand, the EFs are different between ESERS and VSERS as shown in Equation (7) and (8). EFVSERS is typically several orders of magnitude larger than EFERS due to the rapid decay of the electric field in the metal phase. Plasmonic enhancement of ERS, i.e., ESERS, is described as

$$I_{\text{ESERS}}(\tilde{\nu}_S) = K \cdot (\tilde{\nu}_0 + \tilde{\nu}) \cdot [n(\tilde{\nu})]$$

$$\cdot \left[ \frac{E_{\text{loc}}(\tilde{\nu}_0 + \tilde{\nu})}{E_0(\tilde{\nu}_0 + \tilde{\nu})} \right]^2 \cdot \left[ \frac{E_{\text{loc}}(\tilde{\nu}_0)}{E_0(\tilde{\nu}_0)} \right]^2 \cdot g_m \cdot \chi_{\text{ERS}}^n(\tilde{\nu})$$

for anti-Stokes branch and

$$I_{\text{ESERS}}(\tilde{\nu}_S) = K \cdot (\tilde{\nu}_0 - \tilde{\nu}) \cdot [n(\tilde{\nu}) + 1]$$

$$\cdot \left[ \frac{E_{\text{loc}}(\tilde{\nu}_0 - \tilde{\nu})}{E_0(\tilde{\nu}_0 - \tilde{\nu})} \right]^2 \cdot \left[ \frac{E_{\text{loc}}(\tilde{\nu}_0)}{E_0(\tilde{\nu}_0)} \right]^2 \cdot g_m \cdot \chi_{\text{ERS}}^n(\tilde{\nu})$$

for Stokes branch. Similarly, plasmonic enhancement of VRS, i.e., VSERS, is described as

$$I_{\text{VSERS}}(\tilde{\nu}_S) = K \cdot (\tilde{\nu}_0 + \tilde{\nu}) \cdot [n(\tilde{\nu})]$$

$$\cdot \left[ \frac{E_{\text{loc}}(\tilde{\nu}_0 + \tilde{\nu})}{E_0(\tilde{\nu}_0 + \tilde{\nu})} \right]^2 \cdot \left[ \frac{E_{\text{loc}}(\tilde{\nu}_0)}{E_0(\tilde{\nu}_0)} \right]^2 \cdot g^d \cdot \chi_{\text{VRS}}^m(\tilde{\nu})$$

for anti-Stokes branch and

$$I_{\text{VSERS}}(\tilde{\nu}_S) = K \cdot (\tilde{\nu}_0 - \tilde{\nu}) \cdot [n(\tilde{\nu}) + 1]$$

$$\cdot \left[ \frac{E_{\text{loc}}(\tilde{\nu}_0 - \tilde{\nu})}{E_0(\tilde{\nu}_0 - \tilde{\nu})} \right]^2 \cdot \left[ \frac{E_{\text{loc}}(\tilde{\nu}_0)}{E_0(\tilde{\nu}_0)} \right]^2 \cdot g^d \cdot \chi_{\text{VRS}}^m(\tilde{\nu})$$

for Stokes branch. Here, $g^m$ and $g^d$ denote the coupling efficiencies of Raman transitions to the plasmonic cavity in the metal and dielectric phase, respectively; $g^d$ explains the surface selection rules because the coupling efficiency is affected by the orientation and the position of molecular dipoles in the cavity. On the other hand, $g^m$ would be less sensitive to $\tilde{\nu}$ because free electrons are the source of the signals. For ESERS, therefore, the experimentally obtained $I_{\text{ESERS}}/I_{\text{ERS}}$, shown in Figure 4b, corresponds to the Purcell factor as follows

$$I_{\text{ESERS}}/I_{\text{ERS}} = \left[ \frac{I_{\text{ESERS}}(\tilde{\nu}_0 + \tilde{\nu})}{I_{\text{ERS}}(\tilde{\nu}_0 + \tilde{\nu})} \right]^2 \cdot \left[ \frac{I_{\text{ESERS}}(\tilde{\nu}_0)}{I_{\text{ERS}}(\tilde{\nu}_0)} \right]^2 \cdot g^m \propto \left[ \frac{I_{\text{ESERS}}(\tilde{\nu}_0 + \tilde{\nu})}{I_{\text{ERS}}(\tilde{\nu}_0 + \tilde{\nu})} \right]^2$$

(13)

Now, when the Raman frequency shift $\tilde{\nu}$ is small, one can expect the ratio of $I_{\text{VRS}}/I_{\text{ERS}}$ to $I_{\text{VRS}}$ is nearly constant: $I_{\text{VRS}}/I_{\text{ERS}} \approx C.$ Then, we obtain

$$I_{\text{SERS}}(\tilde{\nu}_S) = I_{\text{ESERS}}(\tilde{\nu}_S) + I_{\text{VSERS}}(\tilde{\nu}_S)$$

$$= K \cdot (\tilde{\nu}_0 + \tilde{\nu}) \cdot [n(\tilde{\nu})] \cdot I_{\text{ESERS}}/I_{\text{ERS}}$$

$$\cdot \chi_{\text{ERS}}^n(\tilde{\nu})$$

(14)

for anti-Stokes branch and

$$I_{\text{SERS}}(\tilde{\nu}_S) = I_{\text{ESERS}}(\tilde{\nu}_S) + I_{\text{VSERS}}(\tilde{\nu}_S)$$

$$= K \cdot (\tilde{\nu}_0 - \tilde{\nu}) \cdot [n(\tilde{\nu}) + 1] \cdot I_{\text{ESERS}}/I_{\text{ERS}}$$

$$\cdot \chi_{\text{ERS}}^n(\tilde{\nu})$$

(15)

for Stokes branch, where $\chi_{\text{SERS}}^n(\tilde{\nu}) \equiv \chi_{\text{VRS}}^m(\tilde{\nu}) + C \cdot g^d \cdot \chi_{\text{VRS}}^m(\tilde{\nu})$.

To examine the validity of Equation (14) and (15), we have measured SERS spectra for monolayers of 4-methylbenzenethiol (MBT) on SERS-active rough surfaces of Au and Ag. Figure 7a and 8a show raw SERS spectra of MBT measured on Au and Ag, respectively. In both surfaces, distinctive Raman bands of MBT are clearly observed together with the background continuum in the Stokes branches, and these signals rapidly drop in the anti-Stokes branches. Their reduced spectra, i.e., $\chi_{\text{SERS}}^n$ spectra of MBT on Au and Ag are presented in Figure 7b and 8b, respectively, indicating that the symmetry of the response between the Stokes and anti-Stokes branches is well verified in both the vibrational peaks and the electronic continuum. (The detailed procedure for obtaining $\chi_{\text{SERS}}^n$ is presented in our previous work.) As for the Au surface, the symmetry of the response becomes low in the high frequency
region; for example, the stretching mode of CS at 1079 cm$^{-1}$ has different intensities in the Stokes and anti-Stokes branches. This is because the assumption of $E_{\text{VSERS}}^E/EF_{\text{ESERS}} \approx C$ is not appropriate near the edge of the interband transition of Au. For the Ag surface, on the other hand, the symmetry of the response is verified in the entire frequency range. Therefore, under electronic non-resonant excitation condition, Equation (14) and (15) are widely applicable for analyzing SERS spectra. The conversion of raw SERS spectra into the $\chi_{\text{SERS}}^0$ spectra is particularly effective to extract low-frequency vibrational information; since the ESERS signals are extremely strong in the low frequency region, the low-frequency vibrations such as $\delta\text{Au-S-Ph}$ or $\nu\text{Ag-S}$ are not clearly observed in the raw SERS spectra, which are unveiled in the $\chi_{\text{SERS}}^0$ spectra.

4. Conclusion

The origin of the SERS background has been extensively studied on various metal nanostructures using both the moderate CW excitation and the intense pulsed laser excitation. In this work, we focused on analyzing the background generation under moderate CW excitation, which is a typical condition in conventional SERS spectroscopy. Among various models proposed for the origin of the background, only ERS must have the symmetry of the response between the Stokes and anti-Stokes branches, because the Stokes and anti-Stokes transitions are connected with the time-reversal symmetry. In this work, scattering spectra were measured on the atomically thin Ag film on Au covered with monolayers of MBT molecules, measured using the ultranarrow band notch filters under the 1.96 eV excitation (632.8 nm). b) Reduced spectrum for rough Ag covered with monolayers of MBT, obtained from (a) by assuming the local temperature of 300 K.

Figure 7. a) Raw SERS spectrum for rough Au covered with monolayers of MBT molecules, measured using the ultranarrow band notch filters under the 1.96 eV excitation (632.8 nm). b) Reduced spectrum for rough Au covered with monolayers of MBT, obtained from (a) by assuming the local temperature of 300 K.

Figure 8. a) Raw SERS spectrum for rough Ag covered with monolayers of MBT molecules, measured using the ultranarrow band notch filters under the 1.96 eV excitation (632.8 nm). b) Reduced spectrum for rough Ag covered with monolayers of MBT, obtained from (a) by assuming the local temperature of 300 K.
such a correlation between the Stokes and anti-Stokes branches in the wide frequency range covering $10 < \nu < 1500$ cm$^{-1}$, indicating that ERS accounts for the background generation in SERS spectra. The theoretical calculations of the local modes were also conducted for both sides of the interface to evaluate the plasmonic enhancement of ERS and VRS. For Ag and Au, the significant plasmonic enhancement effect was confirmed for both ERS and VRS. For highly damping Pt, the plasmonic effect for enhancing ERS was negligible while that for VRS was still available.

The fact that ERS is the dominant source of the SERS background means that the generation of the spectral background is an intrinsic phenomenon of SERS. Therefore, the depression of the background intensity is essentially difficult, except for the ultralow temperature spectroscopy. One possible method to suppress the background intensity without losing VSERS sensitivity would be to use the so-called long-range surface plasmon (LRSP) mode.\(^{[25]}\)

In this double-interface SP mode excited at both sides of a thin metal film, the mode field is expelled to the dielectric phase of the interfaces, resulting in the decrease of the plasmonic enhancement of ERS in the metal phase. From the viewpoint of vibrational spectroscopy, the extraction of Raman susceptibility from measured SERS spectra is also the practical way to perform vibrational analysis without suffering from the background continuum, as shown in Figure 7 and 8. Since the ERS behavior is well described as resulting from the thermal population of photon states and the joint density states of electron–hole excitation in a metal, the reduction of the Bose–Einstein weighting from measured SERS spectra considerably improve the analyzability of vibrational information especially in the low frequency region below 200 cm$^{-1}$.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This research was supported in part by Grant-in-Aid for Scientific Research (B) (no. 21H01882) from JSPS, Japan. The SEM measurement was supported by the Equipment Sharing Division, Organization for Co-Creation Research and Social Contributions, Nagoya Institute of Technology. Part of this work was carried out under the Interdisciplinary Research Project Program of the Nagoya Institute of Technology.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

Bose–Einstein weighting, inelastic light scattering by electrons, surface plasmon, underpotential deposition.

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