

Reversible Temperature Dependence in Surface-Enhanced Raman Scattering of 1-Propanethiol Adsorbed on a Silver Island Film

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Intensity of the surface-enhanced Raman scattering (SERS) of 1-propanethiol adsorbed on a silver film prepared chemically has been measured over the 15–300 K surface temperature range. A reversible change in the SERS intensity with the temperature has been observed, with the intensity at 15 K being larger than that at 300 K by a factor of ~ 3 . Various factors that can affect the SERS intensity such as the laser-induced change in surface morphology, adsorption and desorption, and destruction of adatoms could be eliminated as a possible cause for the observed temperature dependence. Enhancement of the Raman intensity has been calculated over the experimental temperature range based on the electromagnetic (EM) model for SERS proposed by Gersten and Nitzan. It has been found that the observed temperature dependence can be explained qualitatively with the EM model calculation.

1. Introduction

Observation of surface-enhanced Raman scattering (SERS)^{1–4} made more than 20 years ago has stimulated various research activities in the areas of spectroscopy, surface science, etc. The phenomenon has been found to be rather general, being observable on rough surfaces of various metals prepared by many different ways for a wide variety of adsorbate molecules.² Intensive efforts have been made over the years, mainly focused on the optical properties of the substrates and the substrate–adsorbate interaction, to identify the origin of the enhancement.^{3,4} Even though the exact nature of the phenomenon is not firmly established yet, there is a general consensus that the electromagnetic (EM) effect arising from surface plasmon resonance plays a major role in most of the cases.^{5–9}

Silver island films are excellent surfaces for the investigation of the EM effect. Both experimental and theoretical evidences suggest that the plasmon resonance on an individual island plays an important role in causing SERS.^{10,11} For example, SERS from a periodic array of uniform silver ellipsoids was in excellent agreement with the theoretical prediction for an isolated ellipsoid.¹² However, on island films prepared by general means or on other less orderly surfaces, EM interaction among silver particles and the size and shape distributions of these particles would be also important in determining the nature and role of the plasmon resonance.

Temperature dependence of SERS intensity has been studied by some investigators mainly as an attempt to identify the specific features on the surface contributing to SERS.^{13–15} For example, Pockrand and Otto¹³ observed SERS of pyridine adsorbed on silver films prepared by evaporation at 120 K and reported that the SERS intensity decreased irreversibly and rather abruptly as the film was heated above 230 K. Such a decay of the SERS activity was attributed to the annealing of atomic scale

roughness, which led them to conclude the importance of the adatom model for SERS. The adatom model was also advocated by some investigators studying SERS on electrode surfaces immersed in electrolyte solutions at room temperature.^{14,15} The adatoms were thought to be stabilized by coadsorbed anions under this condition. Then, the irreversible loss of the SERS activity in various processes such as the increase in the solution temperature was taken as the evidence supporting the adatom model. The above consideration suggests that the adatom model would not be important for SERS on silver films prepared (or stored) under room conditions in the absence of appropriate anions.

In this paper, we report our recent observation of a reversible temperature dependence in SERS of 1-propanethiol adsorbed on a silver film prepared chemically. It will be shown that this temperature dependence can be explained qualitatively within the framework of the EM model by considering the temperature dependence of the surface optical property.

2. Experimental Section

The chemical procedure to prepare the silver film is as follows.¹⁶ Thirty milliliters of 2% AgNO₃ solution was mixed with 1–1.5 mL of 5% NaOH to produce dark brown AgOH precipitate. Ammonium hydroxide solution was added dropwise until the precipitate dissolved and the solution became transparent. Then, 9 mL of 10% D-glucose solution was added as a reducing agent in the presence of a sapphire window. The latter was chosen as the cryogenic substrate for its large thermal conductivity at low temperature. The substrate was precleaned with nitric acid to remove remaining silver film and was sonicated successively in several solvents before chemical deposition. A silver film prepared as above was dipped in 10 mM KCl solution for 3–4 min and rinsed with water. This treatment improved the surface quality of the film such as the mechanical stability and reproducibility of SERS activity. Then, the film was dipped in 1 mM 1-propanethiol solution in methanol for several minutes. The remaining solution on the film was removed by sufficient rinsing in water. 1-Propanethiol

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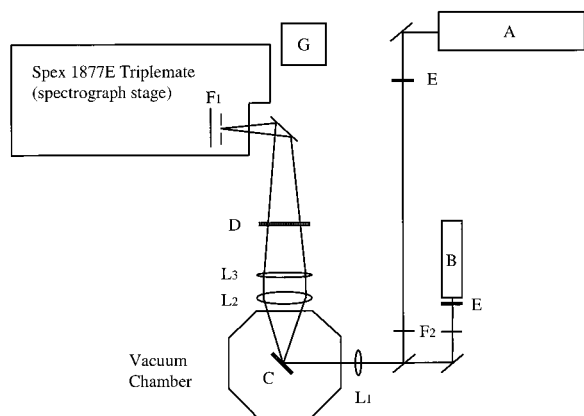


Figure 1. Schematic diagram for the low-temperature Raman instrumentation: A, argon ion laser; B, He/Ne laser; C, sample holder; D, holographic notch filter; E, laser line filter; F₁ and F₂, shutters; G, CCD detector; L₁, L₂, and L₃, optical assembly.

was purchased from TCI and was used without further purification. All the chemicals otherwise specified were reagent grade, and triply distilled water was used throughout.

A schematic of Raman instrumentation is shown in Figure 1. The sample was mounted on a holder attached to a helium cryostat (Janis Research CCS-600) inside a vacuum chamber with inner diameter of 6 in. The chamber was evacuated by a turbomolecular pump to the base pressure lower than 5×10^{-7} Torr. A liquid nitrogen cold trap was installed inside the chamber to remove volatile materials when needed. Sample temperature could be controlled within ± 0.1 K in the range of 10–300 K. The sample was irradiated with the 514.5 nm line of an argon ion laser (Spectra Physics model 164-06) or with the 632.8 nm line of a He/Ne laser (Research Electro-Optics model LHRP 2001). Typical laser power at the sample position was 50 mW for Ar⁺ laser and 10 mW for He/Ne laser. Raman scattering was collected at 90° and was analyzed using a spectrometer equipped with a CCD detector (the spectrograph stage of a SPEX 1877E spectrometer). Collimation and collection lens assembly consisting of lenses with 127 and 700 mm focal lengths was used. To improve the light throughput and thus to minimize the data acquisition time, the filter stage of the SPEX 1877E spectrometer was replaced with a holographic filter (Kaiser Optical System). With this modification, a factor of ca. 10 improvement in the signal-to-noise ratio was achieved. This modification along with use of shutters that synchronize excitation laser irradiation and Raman measurement was critical in performing the present experiments. This is because a severe laser-induced irreversible damage of the sample can occur after an extended period of laser irradiation (to be discussed). Slit width of the spectrometer was set at the spectral resolution of 7 cm^{-1} . A Spex DM3000R data system was used for data acquisition and processing. Slit width correction for a Raman bandwidth was made using the following relation.¹⁷

$$\delta = \delta' [1 - (S/\delta')^2] \quad (1)$$

Here δ and δ' are the corrected and measured full widths at half-maxima (fwhm). S is the spectral slit width.

3. Results and Discussion

A. General SER Spectral Feature. The SER spectra of 1-propanethiol adsorbed on the silver island film obtained with 514.5 nm excitation at various surface temperatures are shown in Figure 2. Overall patterns of these spectra are very similar

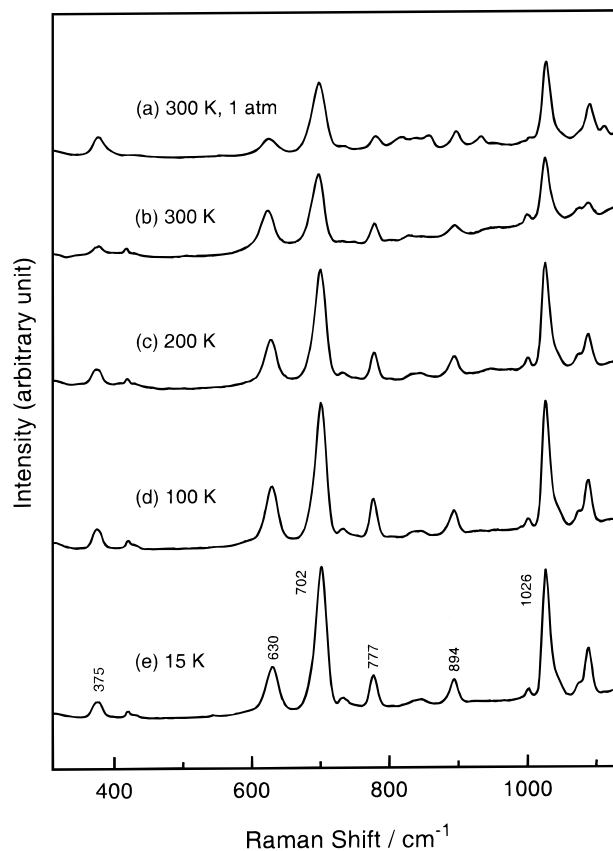


Figure 2. SER spectrum of 1-propanethiol on silver film (a) at 300 K, 1 atm (air) and those obtained in a vacuum at (b) 300 K, (c) 200 K, (d) 100 K, and (e) 15 K.

TABLE 1: Assignments^a and Spectral Data^b for Some Vibrational Modes of 1-Propanethiolate in a Basic Aqueous Solution (OR) and on the Silver Surface (SERS)

ORS	SERS		assignment
	15 K	300 K	
372 (9)	375 (14)	377 (14)	CCC deformation (T)
650 (11)	630 (19)	623 (24)	CS stretching (G)
727 (14)	702 (17)	697 (20)	CS stretching (T)
788 (11)	777 (10)	778 (10)	CH ₂ rocking (G)
893 (16)	894 (12)	894 (13)	CH ₂ rocking (T)
1032 (10)	1026 (11)	1025 (11)	CC stretching (T)

^a Taken from refs 18 and 19. T and G denote trans and gauche conformations with respect to the C(1)–C(2) axis. ^b Positions and bandwidths (fwhm) in cm^{-1} . Bandwidths are given in parentheses.

to each other except for some minor variations (to be explained). Also, they are similar to the SER spectra obtained in the silver sol solution reported by Joo et al.¹⁸ To reiterate the spectral interpretation in the above work, 1-propanethiol adsorbs dissociatively by losing its thiol proton, namely, as 1-propanethiolate, and the adsorption occurs via its sulfur atom. Two different conformations, namely, gauche (G) and trans (T) with respect to the C(1)–C(2) axis, are possible on the surface with variable intensity ratio determined by environmental factors such as the surface coverage. Vibrational assignments for the major Raman bands investigated here have been taken from the above and are listed in Table 1. In the SER spectrum (Figure 2a) obtained at 300 K without evacuation, several small peaks that do not find their counterparts in other SER spectra appear. These peaks disappeared after several hours of evacuation, as can be seen in Figure 2b, indicating that these are not due to chemisorbed 1-propanethiolate. Weakly bound molecules or

overlayers may be responsible for these. Another noticeable spectral difference between parts a and b of Figure 2 is in the G/T intensity ratio of the CS stretching modes at 625 (G) and 697 (T) cm^{-1} . Removal of the contaminants mentioned above seems to increase the fraction of the G conformer on the surface. Also can be seen in Figure 2 is that the G/T ratio decreases as the temperature is lowered. This is because the T form is a little bit more stable than the G form on the surface.¹⁹ The G/T ratio was also found to depend on the dipping condition. For example, dipping the film in 1×10^{-6} M solution of 1-propanethiol resulted in the G/T ratio of 4.5, which is larger by an order of magnitude than that in Figure 2b. This is in agreement with our previous observation of the concentration dependence in the sol solution.¹⁸

Table 1 lists the positions and widths of major vibrational bands in the SER spectra obtained at 15 and 300 K together with those in the ordinary Raman (OR) spectrum of 1-propanethiolate ion in basic aqueous solution. Comparing the values in the OR and SER spectra, one finds that the CS stretching modes undergo the most remarkable change upon surface adsorption. In the previous investigations on SERS of mercaptans, this was taken as evidence for the participation of the sulfur atom in the adsorption process, namely, chemisorption via formation of metal–sulfur bond(s).^{18,20} Also noticeable in the table is that the positions and widths of these bands show noticeable temperature dependence. For example, the CS stretching mode of the gauche conformer shifted gradually from 623 to 630 cm^{-1} and its width changed from 24 to 19 cm^{-1} as the surface temperature was lowered from 300 to 15 K. A similar trend was observed for the CS stretching mode of the trans conformer. Temperature dependences of other bands were much less or were hardly detectable. We also investigated SERS of 1-propanethiolate with 632.8 nm excitation. The positions and widths of the major bands were the same as in the 514.5 nm excitation within the experimental error, as expected.

Vibrational relaxation of molecular adsorbates on metal surfaces has been much investigated over the years,^{21–28} even though most of the experimental and theoretical studies have been focused on diatomic species such as CO on the well-defined crystal surfaces. Temperature dependence of the position and width of a vibrational band is thought to be an especially useful probe in this study. For example, vibrational energy relaxation via excitation of electron–hole pairs, which is important for high-frequency vibrations, results in temperature independence of vibrational bands.^{21–23} Temperature-dependent change in width but not in position is taken as the evidence for the vibrational energy relaxation via multiphonon emission.^{23,24} On the other hand, vibrational dephasing by way of anharmonic coupling to a low-frequency mode which undergoes resonant energy exchange with substrate modes is suspected when both the position and width show noticeable temperature dependence.^{25,26} Other relaxation processes are also possible for polyatomic adsorbates such as intramolecular dephasing and energy relaxation.^{29–31} In the case of 1-propanethiolate adsorbed on the silver island film investigated here, it is possible that the inhomogeneous broadening arising from the surface inhomogeneity especially at the adsorption site also contributes to the overall band broadening. Hence, some understanding on the inhomogeneous broadening would be required before detailed studies on vibrational relaxation are carried out by analyzing SERS band shapes. It seems to be clear, however, that the major relaxation mechanism for the CS stretching mode is different from those for other bands as indicated by their different temperature dependences.

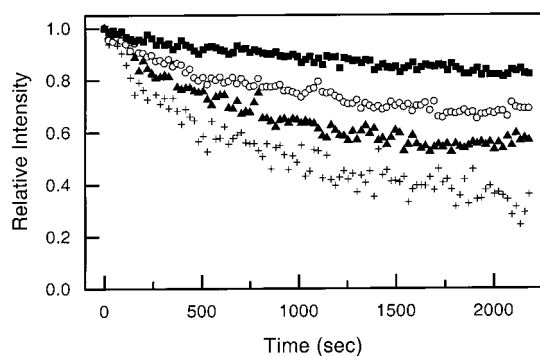


Figure 3. Laser-induced decay of the SERS intensity of the CS stretching vibration at 300 K (+), 100 K (▲), 70 K (○), and 40 K (■). 50 mW of a 514.5 nm laser was irradiated continuously.

One final concern in the present study is the irreversible decay of a SERS signal due to the damage caused by laser illumination over an extended period of time. This laser damage reported for SERS studies on metal film and electrode surfaces is thought to occur due to surface heating and photochemical effect of laser.^{32,33} We have investigated the laser-induced decay of the SERS intensity in this work, the main purpose of the study being to reduce the amount of decay as much as possible. The decay rate was found to depend on various factors such as laser power, wavelength, surface temperature, etc. Higher power, shorter wavelength, and the presence of air or oxygen resulted in faster decay. Laser-induced decays with 50 mW (at sample position) of 514.5 nm excitation at several surface temperatures in a vacuum are shown in Figure 3. It is seen that the decay is slower at lower temperature, indicating that the decrease in SERS activity has something to do with the surface diffusion of the silver atoms. The decay was quite slow at low temperature, say at 40 K, more than 80% of SERS signal remaining after 30 min of continuous laser irradiation. At room temperature, however, the decay rate was uncomfortably fast. Hence, we installed a mechanical shutter between the laser and sample such that laser was irradiated on the sample only during the spectral acquisition period, which was usually 1 s. The total laser irradiation time for the measurement of temperature dependence of SERS intensity to be described below did not exceed a few tens of seconds.

B. Temperature Dependence of SERS Intensity. The SER spectra of 1-propanethiolate on the silver island film were obtained at various surface temperatures between 15 and 300 K. The area of a band was evaluated as its intensity. To compensate for the minor temperature-dependent variation in conformational equilibrium, the intensities of the CS stretching vibrations of the G (630 cm^{-1}) and T (702 cm^{-1}) forms were summed. For other modes, only the T form bands were considered because correction for the conformational equilibrium was found not to be important. The solid curve in Figure 4a shows the temperature-dependent variation of the CS stretching vibration obtained at 514.5 nm excitation. This trace represents one batch of experiments in which the surface temperature was lowered from 300 to 15 K and then increased back to 300 K. Concomitant increase and decrease of the band intensity are noticeable. More important is the fact that the SERS intensity was restored to the original value after a cooling–heating cycle, which was confirmed by many duplicate experiments. Minor intensity fluctuation was not reproducible. Similar reversible temperature dependence was also observed at 632.8 nm excitation as shown in the same figure. To check the mode specificity of the temperature dependence, similar studies have been done for other vibrations also. Figure 4b compares the temperature

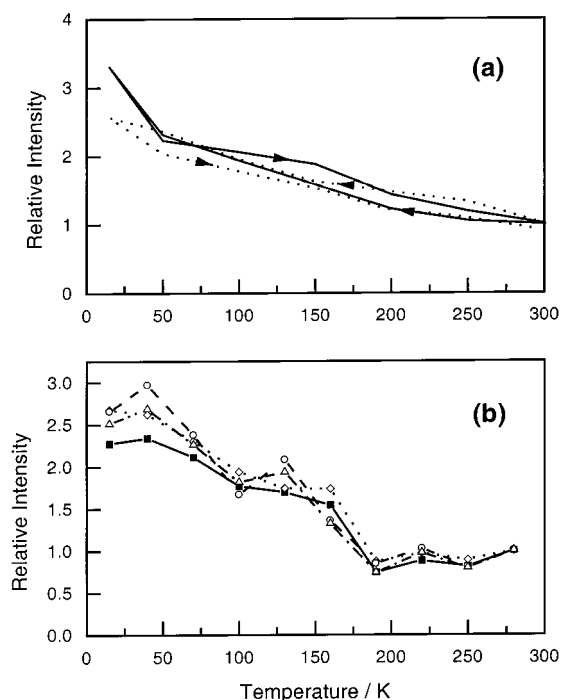


Figure 4. (a) Temperature-dependent change in SERS intensity of the CS stretching mode (G + T) of 1-propanethiol adsorbed on the silver surface in a cooling-heating cycle of 300 K → 15 K → 300 K. Excitation laser wavelengths are 514.5 (—) and 632.8 (···) nm. Normalized to the intensity at 300 K. (b) Intensity changes for the CCC deformation (375 cm⁻¹, ·◇·), CH₂ rocking (894 cm⁻¹, -○-), CC stretching (1026 cm⁻¹, ·-△·), and CS stretching (630 cm⁻¹ + 702 cm⁻¹, -■-) vibrations when the surface was cooled from 300 to 15 K. 514.5 nm excitation.

dependences of the CCC deformation (T, 375 cm⁻¹), CS stretching (G + T), CH₂ rocking (T, 894 cm⁻¹), and CC stretching (T, 1026 cm⁻¹) in a given batch of experiments. It is seen that all the bands display virtually the same temperature dependence. Reversibility of the temperature dependence was also observed for all the bands, even though not shown in Figure 4b.

One can think of various factors that may lead to variation in Raman scattering intensity as the temperature changes. The first and most obvious is the temperature-dependent change in the surface coverage such as the thermal desorption of the adsorbate at elevated temperature. The way the experiment was performed (300 K–15 K–300 K) in the high-vacuum system and reversibility of the intensity variation readily remove such a possibility. Second, one may suspect that surface condensation and evaporation of contaminants such as air and water may contribute in some way to the observed intensity variation. However, the fact that the temperature dependence looks monotonic, not abrupt, argues against such a possibility. Third, one may try to find a proper explanation from the intrinsic characteristics of Raman scattering. For example, population of the ground vibrational level increases as the temperature decreases, which results in the increase of Raman intensity. This is a minor effect, however, especially for the high-frequency modes observed and can be ignored. Other than the above, mode intensity of ordinary Raman scattering is known to be fairly constant as long as the interaction between the mode and the surrounding is weak. In fact, we measured the Raman scattering intensity of the CS stretching mode of silver 1-propanethiolate salt also and found it to be essentially invariant with temperature. The observed temperature dependence is not likely to be related to the relaxation mechanism either because

modes affected by different mechanisms display similar temperature dependence as observed. Finally, an explanation may be searched for in the surface enhancement mechanism. One does not have to invoke the adatom model for SERS here because the method for preparation of silver film adopted in this work precludes the existence of adatoms on the surface. Also, reversibility of the temperature dependence is a strong evidence against SERS mediated by adatoms in this case. A charge-transfer model^{34,35} is not likely to provide an adequate explanation either because various models presented so far do not involve terms that would be affected by temperature. This leaves the EM model for SERS as the potential source of explanation for the observed reversible temperature dependence.

Recently, Leung and co-workers³⁶ carried out temperature-dependent calculation of the EM enhancement in SERS using Gersten and Nitzan's model⁵ and showed that the SERS effect can be sustained at elevated temperatures (~900 K). In the classical treatment by Gersten and Nitzan, the EM enhancement for a molecule with polarizability α located at a distance H from a hemispheroid (semimajor axis a , semiminor axis b) with dielectric constant ϵ is given by

$$R = \frac{1}{|1 - \Gamma|^4} \left| 1 + \frac{(1 - \epsilon)\xi_0 Q'_1(\xi_1)}{\epsilon Q_1(\xi_0) - \xi_0 Q'_1(\xi_0)} \right|^4 \quad (2)$$

with

$$\Gamma = \frac{\alpha}{4(f\xi_1)^3} + \frac{2\alpha[\epsilon - 1]}{f^3} \sum_n \frac{(2n + 1)P_n(\xi_0) P'_n(\xi_0) [Q'_n(\xi_1)]^2}{\epsilon P'_n(\xi_0) Q_n(\xi_0) - P_n(\xi_0) Q'_n(\xi_0)} \quad (3)$$

Here, f , ξ_0 , and ξ_1 are defined as follows.

$$f = (a^2 - b^2)^{1/2} \quad (4)$$

$$\xi_0 = a/f \quad (5)$$

$$\xi_1 = (a + H)/f \quad (6)$$

P_n and Q_n are Legendre functions of the first and second kinds, respectively, and P'_n and Q'_n represent their derivatives. Equation 2 shows that the EM enhancement can be extremely large when the following condition is satisfied for the real part of ϵ .

$$\epsilon Q_1(\xi_0) - \xi_0 Q'_1(\xi_0) = 0 \quad (7)$$

This is the condition for a surface plasmon resonance of the spheroid. Another requirement for a large enhancement is that the imaginary part of ϵ be small at the resonance frequency satisfying eq 7.

Calculation of the surface temperature effect on the EM enhancement requires knowledge of the temperature dependences of the molecular polarizability (α) and the dielectric constant (ϵ) of the metal, the experimental data of which are not available over a wide temperature range. Leung and co-workers³⁶ assumed that α be temperature-invariant. To calculate ϵ at various temperatures, the expression in the modified Drude model presented by Ujihara was utilized.³⁷

$$\epsilon = (n + ik)^2 = 1 - \omega_p^2 / (\omega(\omega + i\omega_c)) \quad (8)$$

Here, n and k are the index of refraction and the extinction

coefficient, respectively. ω is the angular frequency of the electromagnetic wave, and ω_p and ω_c represent the plasmon frequency and collision frequency of the metallic electrons, respectively. Rearranging eq 8, the following simultaneous equations were obtained.

$$n^2 - k^2 = 1 - \frac{\omega_p^2}{\omega^2 + \omega_c^2} \quad (9)$$

$$2nk = \frac{\omega_p^2 \omega_c}{\omega(\omega^2 + \omega_c^2)} \quad (10)$$

Small change in ω_p with temperature was ignored, and the temperature dependence of ω_c was taken from Ujihara's work.³⁷

$$\omega_c = KT^5 \int_0^{\theta_D/T} \frac{z^4 dz}{e^z - 1} \quad (11)$$

Here θ_D is the Debye temperature and K is a constant. Then, ω_p and K were determined by solving eqs 9–11 with the room-temperature data for n and k at a given ω . With this K , ω_c at higher temperature was calculated using eq 11, which, in turn, was used together with ω_p to evaluate ϵ . Ujihara³⁷ showed that ω_c in eq 11 is an increasing function of T , i.e., the probability of electron–phonon scattering increases because the phonon population increases with T . This results in the increase in the imaginary part of the dielectric constant (eq 10) with T , leading to decrease in the EM enhancement. More specifically, k is nearly invariant with temperature in the visible to infrared range, while n is an increasing function of T . The method of Leung and co-workers is not adequate, however, to explain the factor of 3–4 increase in the EM enhancement near absolute zero temperature compared to that at room temperature observed in this work. As T approaches zero, ω_c in eq 11 and the imaginary part of ϵ in eq 10 approach zero, which results in infinite EM enhancement when light is in resonance with the surface plasmon frequency. Such a singular behavior at absolute zero occurs because relaxation mechanisms other than the electron–phonon scattering were ignored in the above approach. Hence, a modification is needed to evaluate ϵ at low temperature.

The absorptivity (A) of a metal can be expressed with n and k as follows.³⁸

$$A = \frac{4n}{(n+1)^2 + k^2} \quad (12)$$

The intraband-transition absorptivity of metals in the near-infrared is related to the electron–phonon relaxation time (τ) by the Mott–Zener formula.

$$A = \frac{2}{\omega_p \tau} \quad (13)$$

The expression for the effective relaxation time derived by McKay and Rayne is as follows.³⁹

$$\frac{1}{\tau} = \frac{1}{\tau_0} \left[\frac{2}{5} + 4 \left(\frac{T}{\theta_D} \right)^5 \int_0^{\theta_D/T} \frac{z^4 dz}{e^z - 1} \right] \quad (14)$$

The $2/5$ term is due to spontaneous emission of a phonon by a photon-excited electron, while the temperature-dependent term corresponds to phonon absorption and stimulated emission processes. There are other contributions to the temperature-invariant part of $1/\tau$ and A .⁴⁰ Among these, the interband-

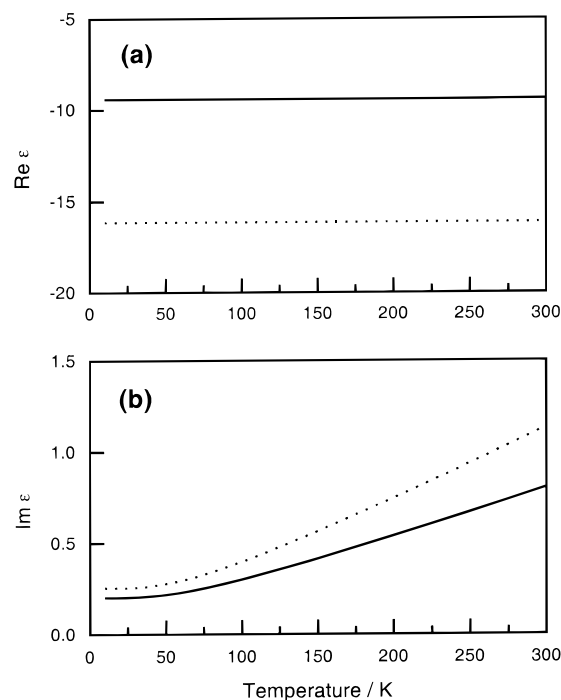


Figure 5. Temperature dependences of the (a) real and (b) imaginary parts of the dielectric function of silver metal calculated with the method described in the text. Light wavelengths are 514.5 (—) and 632.8 (⋯) nm.

transition contribution may be the most troublesome because visible wavelengths have been used to obtain SER spectra in this work, which would require the use of experimental data. Considering eqs 13 and 14 and the discussion made above, it is proposed here to use the following expression for the absorptivity.

$$A = A_0 + KT^5 \int_0^{\theta_D/T} \frac{z^4 dz}{e^z - 1} \quad (15)$$

From the measurement of the absorptivity of silver at 4.2 K reported by Biondi,⁴¹ A_0 can be taken as 0.012 and 0.007 at 514.5 and 632.8 nm, respectively. The constant K in eq 15 can be determined by comparing with the absorptivity (eq 12) calculated with the experimental n and k ($n = 0.130$, $k = 3.05$ at 514.5 nm⁴² and $n = 0.14$, $k = 4.02$ at 632.8 nm⁴³) at room temperature. With A_0 and K fixed, eq 15 can be used to evaluate A at any temperature. As was mentioned earlier, k of silver evaluated with eqs 9–11 in the visible region was rather insensitive to the temperature. In particular, temperature dependence of k was very weak at room temperature and below. Use of eq 15 in the present approach is equivalent to adding a small zero-point term to ω_c in eq 11. Sample calculations with eqs 9–11 after adding a small zero-point term to eq 11 resulted in a k that was not sensitive to T in the visible range. Hence, k was assumed to be temperature-independent, and n was evaluated as a function of temperature using eq 12. The real and imaginary parts of ϵ at 514.5 and 632.8 nm calculated as a function of temperature are shown in Figure 5. It is seen in the figure that the real part of ϵ is negative and nearly constant in the temperature range of 10–300 K, while the imaginary part decreases as the temperature goes down. Namely, larger EM enhancement is expected at lower temperature. It is to be mentioned that addition of the zero-point term made here is in general agreement with the modified model reported by Chiang et al. very recently.⁴⁴ In the latter work, a constant term was

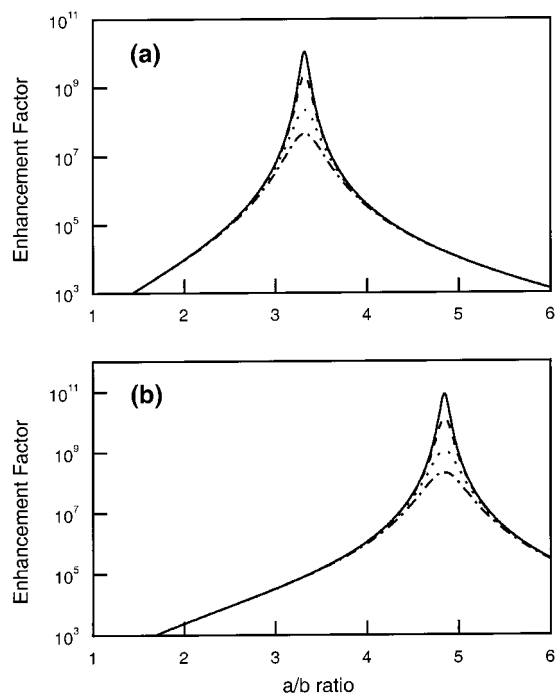


Figure 6. Calculated electromagnetic enhancement for SERS at (a) 514.5 and (b) 632.8 nm excitation as a function of the a/b ratio at the surface temperature of 10 K (—), 100 K (---), 200 K (···), and 300 K (—·—).

added to the electron–phonon frequency according to the Holstein model.⁴⁵ In addition, contribution from the electron–electron scattering to ω_c was also considered. At room temperature and below in the visible range, this term⁴⁶ makes a virtually constant contribution to ω_c because $(k_B T)^2 \ll (\hbar\omega/2\pi)^2$. Hence, the model by Chiang et al. would show a similar functional dependence on T as the present one. Then, the main difference between the two approaches lies in the fact that the experimental values for A_0 , n , and k have been utilized here while theoretical models in addition to the experimental data were used by Chiang and co-workers to evaluate the temperature dependence of ω_c .

Several parameters, namely, a , b , H , and α , are needed to calculate the EM enhancement factor (R). The molecular polarizability of 9.73 \AA^3 for 1-propanethiol was taken from ref 47. An order of magnitude change in α did not seriously affect the calculated enhancement ($\sim 1\%$), however. Even though R decreases monotonically but rapidly with H , the calculated temperature dependence is hardly affected by the latter. Hence, H of 1 nm was used in accordance with Leung and co-workers.³⁶ Concerning the geometrical parameters (a and b) of the spheroid, not the magnitudes of each parameter but the ratio (a/b) has been found to affect the calculated enhancement. This is because the surface plasmon resonance frequency is determined by this ratio. In the present calculation, a was set to 50 nm, by referring to the atomic force microscopic study of chemically prepared silver film reported by Pan and Phillips.⁴⁸ Our own measurement of the island radius for the silver films prepared in this work with scanning electron microscopy displayed a broad distribution in the range of 30–80 nm. Figure 6 shows the changes in the EM enhancements with 514.5 and 632.8 nm excitations as functions of the a/b ratio at several surface temperatures. The maximum enhancement occurs at the a/b ratios of 3.32 and 4.85 with 514.5 and 632.8 nm excitations, respectively, which correspond to the surface plasmon resonance condition. Also, the temperature-dependent change in the EM

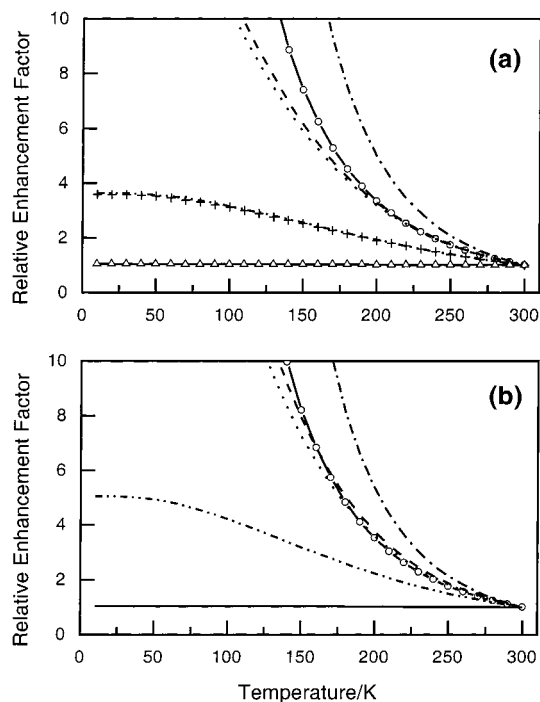


Figure 7. (a) Relative electromagnetic enhancement for SERS at 514.5 nm calculated as a function of temperature with the a/b ratio of 2.10 (—), 3.12 (---), 3.22 (- - -), 3.32 (—·—), 3.42 (···), 3.52 (+++), and 4.65 (Δ). The temperature dependence averaged over a uniform distribution of the a/b ratio (1–6) is shown as circles (—○—). Enhancement is normalized to the value at 300 K. (b) Similar data at 632.8 nm with the a/b ratio of 3.5 (—), 4.65 (---), 4.75 (- - -), 4.85 (—·—), and 4.95 (···). The temperature dependence averaged over a uniform distribution of the a/b ratio (1–6) is shown as circles (—○—).

enhancement is more rapid at these a/b ratios than at other values. To demonstrate this point more clearly, Figure 7 plots the EM enhancement as a function of temperature at several a/b ratios. It is seen that the increase in the calculated EM enhancement as the temperature is lowered from 300 to 15 K is larger than the experimental observation as the a/b ratio approaches the value for the resonance condition. At the a/b ratio of 3.32 satisfying exact resonance with 514.5 nm light, the EM enhancement at 15 K is ~ 300 times larger than that at 300 K. For a better match with the experimental data, one may then suppose that the a/b ratio of the prepared silver island film is a little bit different from 3.32, maybe close to 3.12 or 3.52 as indicated in Figure 7a. However, these a/b ratios result in temperature-invariant EM enhancement (Figure 7b) at 632.8 nm in complete disagreement with the experimental data. The calculated temperature dependences of the EM enhancement at 632.8 nm (Figure 7b) display similar patterns, and the same argument applies. Then, the only way to reconcile the calculated results with the experimental ones is to suppose that the silver film prepared chemically would consist of islands with a wide distribution of the a/b ratio, which is very likely. We have attempted the temperature-dependent calculations assuming a uniform distribution of the a/b ratio over the range of 1–6. The results at 514.5 and 632.8 nm excitations are included in parts a and b of Figure 7, respectively. The calculated temperature effect on SERS from islands with a uniform shape distribution is not as drastic as from islands with the a/b ratio satisfying the surface plasmon resonance condition. However, the temperature effect on the former is still larger than that in the experimental data by more than an order of magnitude. One plausible explanation for such a discrepancy is to suppose that the

distribution of the a/b ratio is severely asymmetrical, favoring small values. Since the temperature dependence of the EM enhancement gets weaker rapidly as the a/b ratio moves away from the optimum, such a distribution can result in a reduced temperature dependence as observed in the present work. Preparation of silver island films with well-defined microscopic structure and measurement of SERS activity over a wide temperature range would be useful in this regard. Another explanation for the above discrepancy may be found in the possible inaccuracy of the optical data used in the calculation. For example, a factor of 2–3 increase in the temperature-independent term of the absorptivity (A_0 in eq 15) leads to more than an order of magnitude decrease in the EM enhancement at low temperature. Accurate measurement of the optical properties of the prepared silver island films over a wide temperature range would be useful. One finally may suppose that the mismatch reflects the deficiencies of the original EM theory. For example, Leung and Tse⁴⁹ reported that consideration of a nonlocal effect⁵⁰ on the spherical silver islands results in orders of magnitude decrease of the SERS enhancement at frequencies close to the surface plasmon frequency. It would be interesting to see if the same effect can explain the moderate temperature dependence observed in this work. Regardless of the above difficulties, however, it seems that the EM model provides a qualitative explanation for the experimental observation that the SERS intensity increases as the surface temperature is lowered.

In summary, we observed reversible increase of the SERS intensity of 1-propanethiolate adsorbed on the silver island film, as the surface temperature was lowered. Various factors that can affect SERS intensity such as laser damage and change in surface coverage could be eliminated as the possible causes for the temperature dependence. The adatom model for SERS, which has often been invoked to explain the temperature dependence of SERS intensity, has been found inadequate also. Temperature dependence of SERS intensity has been calculated after a low-temperature modification of the model based on the electromagnetic enhancement of SERS, which was originally developed by Leung et al. to account for the high-temperature SERS activity. The results are in qualitative agreement with the experimental data. A better test of the present model, which will also be a test for the validity and limitation of the EM model for SERS, necessitates the use of the dielectric constant of silver measured over a wide temperature range. Another requirement is the temperature-dependent SERS measurement on silver island films prepared with well-defined a/b ratio. On such a film, the present results indicate that the SERS intensity at cryogenic temperature can be larger by some orders of magnitude than at room temperature when the laser frequency is tuned to the plasmon frequency. Then, a truly gigantic surface enhancement (10^{10} – 10^{12}) of Raman scattering may be achieved, which can find many practical applications.

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