Remarks on the Substrate−Temperature Dependence of Surface-Enhanced Raman Scattering

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It is pointed out that the variation of the plasmon frequency of metal with temperatures, though generally extending to a very limited amount, could however have significant effects on the recently observed dependence of surface-enhanced Raman scattering (SERS) on substrate temperatures.

Since the first observation of the possibility of sustaining surface-enhanced Raman scattering (SERS) at elevated temperatures (up to those needed under realistic catalytic conditions),[1] there have been several theoretical and experimental studies[2−4] aimed at a more comprehensive understanding of this phenomenon. In particular, the recent systematic study carried out by Pang, Hwang, and Kim[4] has provided the first evidence for the qualitative validity of a model based on the temperature variation of the substrate optical properties.[2,3] The main observation of this experiment[4] on the SERS of 1-propanethiol on a silver island film involves a reversible change of the SERS signal with the change of substrate temperatures over the range 15−300 K. While the original theoretical models[2,3] were aimed at SERS at elevated temperatures (T > 300 K), it was nevertheless applied in an interesting way by the researchers in ref 4 via an extrapolation of the original models into the low-temperature regimes. It is the purpose of the present communication to point out a relatively subtle effect that was completely overlooked by all the previous works[2−4] in the understanding of the dependence of SERS on the substrate temperatures. This effect has to do with the very small variation of the plasmon frequency of the substrate metal as a function of temperature. As we show below, once this effect is accounted for, the observation reported in the recent experiment[4] turns out to depend critically on the morphology of the silver islands. In particular, according to the present model, the ellipsoidal nature of the islands has to play a crucial role in leading to the phenomenon observed at the scattering frequencies used in the experiment.[4]

To be partially self-contained, let us first recapitulate some key equations of the previous models.[2,3] In these works, the enhancement ratio for SERS was calculated by following Gersten and Nitzan.[5] For a spheroidal island surface with dimensions a and b ($<a$), this ratio can be obtained in the following form:

$$R = \left|\frac{1+X}{1-Y}\right|_4 \qquad (1)$$

where

$$X = \frac{(1-\epsilon)\xi_0 Q_1'(\xi_1)}{\epsilon Q_1(\xi_0) - \xi_0 Q_1'(\xi_0)}$$

and

$$Y = \frac{\alpha}{f^3}(\epsilon - 1)\sum_n \frac{(2n+1)P_n(\xi_0)\, P_n'(\xi_0)\, [Q_n'(\xi_1)]^2}{\epsilon P_n'(\xi_0)\, Q_n(\xi_0) - P_n(\xi_0)\, Q_n'(\xi_0)}$$

with P_n and Q_n being the Legendre functions, ϵ the dielectric function of the substrate, and other variables defined as $f = (a^2 - b^2)^{1/2}$, $\xi_0 = a/f$, $\xi_1 = (a + d)/f$. In the simple case of a sphere, the results reduce to

$$R = \left|\frac{1}{1-\alpha G_\perp}\left(1 + \frac{2\alpha_1^s}{(a+d)^3}\right)\right|^4 \qquad (2)$$

where the nth pole polarizability and the "image-field factor" are given, respectively, by

$$\alpha_n^s = \frac{n(\epsilon - 1)}{n(\epsilon + 1) + 1} a^{2n+1}$$

and

$$G_\perp = \sum_n \alpha_n^s \frac{(n+1)^2}{(a+d)^{2(n+2)}}$$

Note that α in the above equations is the molecular polarizability (taken as 10 Å^3) and d is the molecule−substrate distance. The main dependence of R on the substrate temperature enters through ϵ when the optical properties of the substrate metal are being characterized by a temperature-dependent Drude model, as follows:

$$\epsilon(T) = 1 - \frac{\omega_p^{\,2}(T)}{\omega[\omega + i\omega_c(T)]} \qquad (3)$$

where the bulk plasmon frequency is given by

$$\omega_p = \sqrt{\frac{4\pi N e^2}{m^*}} \qquad (4)$$

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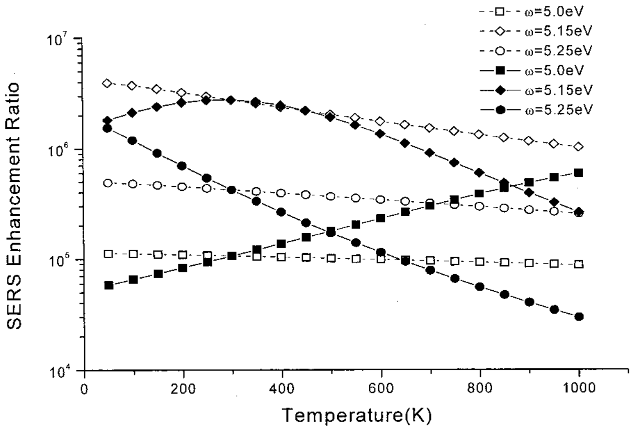

Figure 1. SERS enhancement ratio as a function of substrate temperature for a spherical silver island substrate at three excitation frequencies: (a) $\omega = 5.15$ eV (resonant), (b) $\omega = 5.0$ eV, and (c) $\omega = 5.25$ eV (both off resonant) according to the local electromagnetic theory.[3] The molecule−substrate distance and sphere radius are fixed at 10 and 50 Å, respectively. The curves with filled symbols show results incorporating the variation of ω_p with temperature, while the unfilled ones show those ignore such a variation.

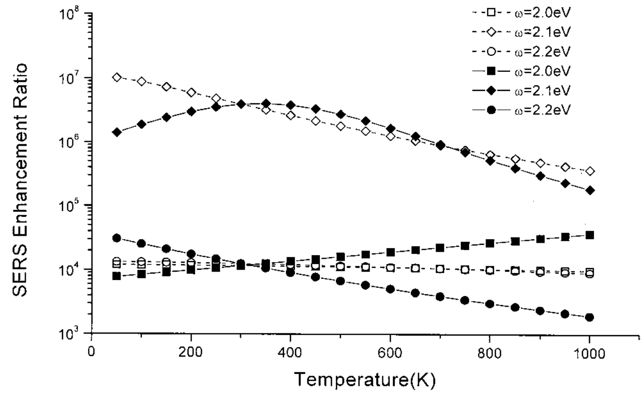

Figure 2. Similar to Figure 1, but for a spheroidal substrate with $a = 50$ Å and $b = 10$ Å. Note that the resonance frequency is red-shifted to about 2.1 eV.

with N the number density and m^* the effective mass of the electrons. In the previous models, the main focus was on the temperature dependence of the collision (damping) frequency $\omega_c(T)$ via both electron−phonon and electron−electron interactions; in addition, the nonlocal nature of the dielectric response was also considered.[6] However, in all these previous studies,[2−4] the very small temperature variation in ω_p has been unanimously ignored, being aware that such variation can at most extend up to a few percent for a temperature range up to the melting point of the metal. Indeed, the same approximation can be traced back to the first theoretical study of the temperature variation of metallic reflectivity of light in the 1970s.[7] It was actually based on this work[7] that our first SERS model[2] was built. We want to point out here that while such an approximation may be valid for certain optical phenomena such as ordinary reflection and absorption,[7] it becomes critically unjustified for phenomena involving the surface plasmon resonance (SPR) of the metal surface such as SERS. In fact, such a significance was also noted before in the literature in the study of the thermoreflectance from a SPR device.[8]

To illustrate this effect, let us assume a simple picture with the dependence of ω_p on temperature coming exclusively from $N = N_0[1 + \gamma(T - T_0)]^{-1}$, provided that we assume a certain fixed number of free electrons ($\sim$1) associated with each metal atom. Here γ is the volume expansivity of the metal, which is taken to be 5.7×10^{-5} K^{-1} for silver.[9] Hence we assume $\omega_p(T) = \omega_0[1 + \gamma(T - T_0)]^{-1/2}$. Using this simple estimate, we find that ω_p for silver decreases by about 2% as T goes from 300 to 1000 K. The variation of m^* with T is complicated in general; moreover, it will likely further decrease ω_p at elevated temperatures. Assuming m^* is constant, we have recalculated certain R for the "local-response model", with $\omega_c(T)$ as given in ref 3 where ω_p had then been assumed constant with temperature change. The present results incorporating the very small change of ω_p are shown in Figures 1 and 2, for a spherical and spheroidal island surface, respectively. We have also included the change in size of the islands with temperature to be consistent. As can be clearly seen from both figures, the very small temperature variation in ω_p can lead to dramatic changes in the calculated R. In particular, we see that R for a scattering frequency close to that for surface plasmon resonance (ω_{sp}) becomes much smaller at high temperatures due to this slight dependence of ω_p on T, whereas that for a frequency below ω_{sp} increases significantly and even overtakes the "resonant values" at higher temperatures for the sphere case. In fact, the observed behavior is very reasonable and can be understood physically as follows. Since SERS depends significantly on the surface plasmon resonance of the metal and since $\omega_{sp} \propto \omega_p$ ($\omega_{sp} = \omega_p/\sqrt{3}$ for a sphere), the slight decrease in ω_p at high T will bring the "resonant case" (at room temperature) off-resonance, and just the opposite will occur for the "off-resonant case" when the frequency is below ω_{sp}. In the case when T is cooled from room temperature (300 K), ω_p increases and brings both cases more off-resonant. Similar reasoning can account for the case when $\omega > \omega_{sp}$, in which the increase in temperature will bring ω_{sp} farther from ω. Hence it seems desirable to perform SERS at a frequency off and below resonance at elevated temperatures.[2,3]

As far as the recent experiment is concerned,[4] the phenomenon was studied at low temperatures (15−300 K). From Figure 1 for the "off-resonant" case, we see that the increase in R as T decreases from 300 K can occur only for frequencies above that of ω_{sp} due to the variation of $\omega_p(T)$, which are much higher than those used in the experiment (515 and 632 nm) for spherical islands. However, the islands prepared in the experiment[4] were actually ellipsoidal, and it is well-established that ω_{sp} is much lower for ellipsoidal particles and can go down all the way to the near-IR region for particles with large aspect ratios.[5] As illustrated in Figure 2, ω_{sp} decreases to about 2.1 eV for a spheroidal island of aspect ratio equal to 5. We believe that this is the main reason for the researchers in ref 4 to have observed an increasing trend in R as T decreases from 300 to 15 K. The experiment, of course, observed the result from an ensemble average of ellipsoidal islands. As long as the islands sampled have resonant frequencies mostly below that of the source, an increasing trend will be observed. Hence, future "single-island" experiments will be desirable to further clarify and verify more quantitatively the present modeling results.

In conclusion, we want to emphasize that the change from a "monotonic variation behavior" to a "three-scenario behavior" as illustrated in Figures 1 and 2, due to the variation of $\omega_p(T)$, is a very general phenomenon. We have also confirmed this by incorporating the nonlocal dielectric response of the substrate for the sphere case using our previous model.[3]

Thus, we conclude that the variation of ω_p with temperature, though only slightly in general, must not be ignored in understanding surface phenomena that depend on the excitation of surface plasmon of the substrate such as SERS.

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