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P.T. Leung
Portland State University

M. H. Hider

Erik J. Sánchez

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Surface-enhanced Raman scattering at elevated temperatures

P. T. Leung,* M. H. Hider,[†] and E. J. Sanchez

*Department of Physics/Environmental Science and Resources Program, Portland State University,
P.O. Box 751, Portland, Oregon 97207-0751*

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The effect on surface-enhanced Raman scattering due to the increase in temperature of the metallic substrate is studied via a simple model for physisorbed molecules. Surface roughness is represented by a spherical or spheroidal island, and the temperature effects on the surface plasmon are accounted for via a slightly modified Ujihara model. It is found that the enhancement ratio in general decreases as substrate temperature increases. For noble metals like silver, this temperature effect is particularly pronounced at scattering frequencies close to that of the surface-plasmon resonance; and for frequencies well below the surface plasmon frequency, the enhancement ratio is relatively insensitive to the change of substrate temperature. A tentative explanation is provided for our modeling results, and the implications from these results are discussed.

Recent observations showing that surface-enhanced Raman scattering (SERS) can survive at highly elevated temperatures have opened up the possibility of applying the surface-enhanced effects to photochemistry at surfaces under realistic catalytic conditions.¹ For chemisorbed oxygen atoms at silver surfaces, it has been reported that SERS can be observed with an enhancement factor of 10^3 up to temperatures of 900 K. It has then been argued that both electromagnetic (EM) and chemical (modification of molecular dipole moment due to charge transfer) effects have played a role in contributing to the observed SERS signal at such a high temperature.¹ Hence it would be of interest to provide some theoretical evidence showing that the above mechanisms are indeed sustained up to such high temperatures.

In this Brief Report, we present a phenomenological study of the EM effect at elevated temperatures via a simple model for SERS. As is well known, the EM effect here refers to the huge local EM field caused by coupling of the surface-plasmon excitation with radiation in the presence of surface roughness. Here we shall model the SERS problem as the scattering of an incident plane wave from a molecular dipole interacting with a surface structure which is represented by a spheroidal particle. In order to simplify the mathematics involved, we shall demonstrate our formulation of the theory for the case of a spherical island, and shall present numerical results for both a spherical and a prolate spheroidal substrate. We refer the readers to Ref. 2 for more details on the analytical expressions for the general case in terms of the spheroidal harmonics. The temperature effect on the above EM mechanism will be accounted for by using a slightly modified temperature-dependent Drude model, which was published previously in the literature to describe the optical response of the substrate metal.³

According to the semiclassical approach of Gersten and Nitzan,² for the simple case with a spherical island (radius a) as the substrate, the Raman cross section (at frequency ω and molecule-substrate distance d) from a dipole-sphere system can be expressed in terms of the induced polarizability ($\Delta\alpha$) for the molecule due to the change of nuclear coordinate (Q) as

$$\sigma_{RS} = \frac{8\pi}{3} \left(\frac{\omega}{c}\right)^4 (\Delta Q)^2 \left(\frac{\partial\alpha}{\partial Q}\right)^2 \left| \frac{1}{1 - \alpha G_{\perp}} \left(1 + \frac{2\alpha_1^s}{(a+d)^3}\right) \right|^4, \quad (1)$$

where α is the molecular polarizability, and α_n^s the n th-pole polarizability of the sphere given by

$$\alpha_n^s = \{n(\varepsilon - 1)/[n(\varepsilon + 1) + 1]\} a^{2n+1}. \quad (2)$$

The function G_{\perp} for a radial oriented molecular dipole is given by

$$G_{\perp} = \sum_n \alpha_n^s (n+1)^2 / (a+d)^{2(n+2)}. \quad (3)$$

We have assumed a radial molecular orientation, since it is known that a maximum SERS signal can be obtained in this configuration.² We further assume the molecule to be located in vacuum, and $\varepsilon \equiv (n+ik)^2$ to be the dielectric function of the substrate sphere. The enhancement ratio R is defined to be the ratio of σ_{RS} in Eq. (1) to the same quantity in the absence of the substrate sphere. Thus we obtain^{2,4}

$$R = |[1/(1 - \alpha G_{\perp})][1 + 2\alpha_1^s/(a+d)^3]|^4. \quad (4)$$

For the case with a spheroidal substrate, R can be obtained in terms of the Legendre functions of the first and second kind with arguments depending on both the eccentricity of the spheroid and the molecule-substrate distance [see Eqs. (2.27) and (4.10) of Ref. 2]. We have further assumed the temperature dependence of the induced molecular polarizability to be negligible. Thus, to describe the temperature effect of the substrate on R , we need a model for the temperature dependence of the dielectric function of the substrate metal. To this end, we slightly modify an approach due originally to Ujihara,³ in which ε is described by the Drude model as

$$\varepsilon(T) = [n(T) + ik(T)]^2 = 1 - \omega_p^2 / \omega[\omega + i\omega_c(T)], \quad (5)$$

where ω_p is the plasmon frequency given in terms of the electron density (N) and effective mass (m^*) as

$$\omega_p = (4\pi N e^2 / m^*)^{1/2}, \quad (6)$$

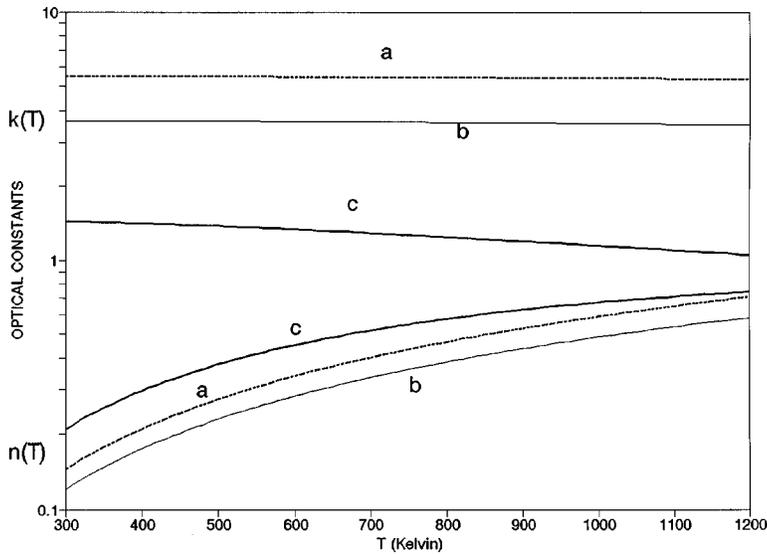


FIG. 1. The optical constants for silver as a function of temperature computed by using the modified Ujihara model. Curves *a*, *b*, and *c* are results obtained for scattering frequencies at 1.5, 2.1, and 3.5 eV, respectively.

and $\omega_c(T)$ is the temperature-dependent collision frequency of the metallic electrons. Note that although both N and m^* vary with temperature in principle, we have here assumed the small change in ω_p with temperature to be negligible.³ Thus by solving Eq. (5) we obtain two simultaneous equations for the temperature-dependent optical constants as $n \equiv n(T)$ and $k \equiv k(T)$ as follows:

$$n^2 - k^2 = 1 - \omega_p^2 / [\omega^2 + \omega_c(T)^2] \quad (7)$$

and

$$2nk = \{ \omega_p^2 / [\omega^2 + \omega_c(T)^2] \} \omega_c(T) / \omega. \quad (8)$$

We follow Ujihara to apply the temperature-dependent Debye mode for $\omega_c(T)$ as follows:

$$\omega_c = KT^5 \int_0^{\theta_D/T} z^4 dz / (e^z - 1), \quad (9)$$

where θ_D is the Debye temperature of the metal, and K is a constant which can be determined using Eq. (9) with room-

temperature values for the temperature and the collision frequency: T_0 and ω_{c0} , respectively. To proceed further, we shall vary slightly from the original Ujihara approach. Instead of using N and m^* to determine ω_p via (6), and then using (7) or (8) to find ω_{c0} , here we shall solve (7) and (8) *simultaneously* for ω_p and ω_{c0} using both $n_0 \equiv n(T_0)$ and $k_0 \equiv k(T_0)$ available in the literature.⁵ ω_c can then be obtained from Eq. (9), and hence $n(T)$ and $k(T)$ be solved from Eqs. (7) and (8). We believe this slightly modified-scheme will be more consistent with the optical data established in the literature.⁶

Figure 1 shows the results for $n(T)$ and $k(T)$ for silver at three different frequencies according to the above model up to the melting point of silver. It is seen that while the real index increases with temperature in a comparable fashion for all three frequencies, the extinction coefficient k decreases more appreciably only for high frequencies [in this case, for $\omega = 3.5$ eV, which is close to that of the surface-plasmon resonance (SPR) for a silver sphere]. With this at hand, the SERS signal as a function of temperature can then be studied

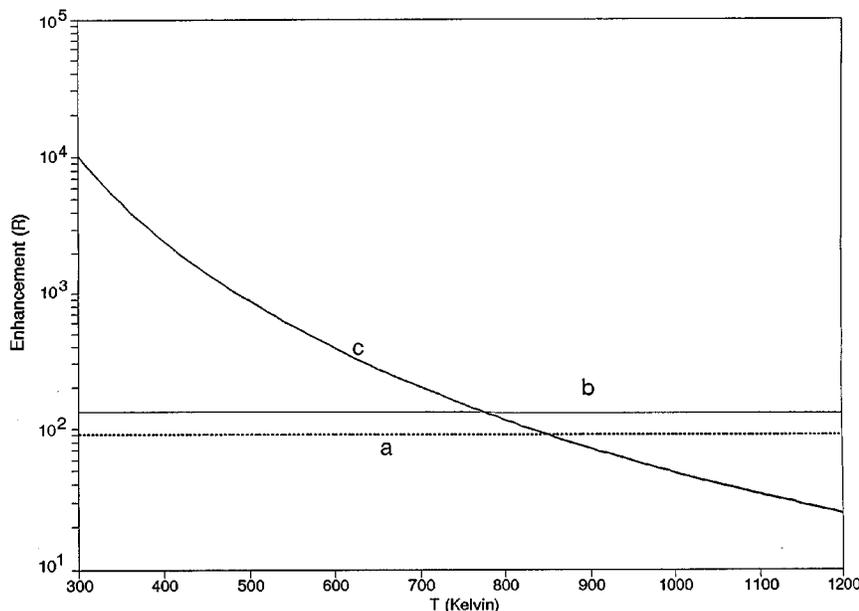


FIG. 2. SERS enhancement factor (R) as a function of temperature for a silver spherical island of radius 50 nm and a molecule-surface distance of 1 nm. Results for curves *a*, *b*, and *c* are for different scattering frequencies as labeled in Fig. 1.

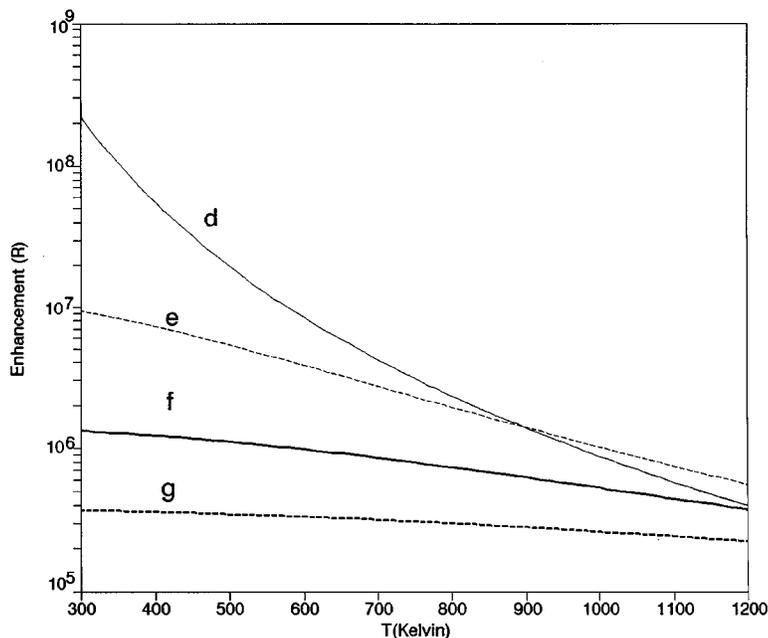


FIG. 3. Similar plots as in Fig. 2, but for a spheroidal substrate (with $a/b=5$, see text). The major axis a is set at 50 nm with the same distance $d=1$ nm. Curves d , e , f , and g show results at different excitation frequencies of 1.9, 1.8, 1.7, and 1.6 eV, respectively.

via Eqs. (2)–(5). Figure 2 shows the enhancement ratio R as a function of temperature at the three frequencies used in Fig. 1 for a spherical island substrate with the radius fixed at 50 nm and the molecule-surface distance d at 1 nm, respectively. It is interesting to point out that R generally goes down with temperature, with the rate of decrease being significant only for the frequency close to that of the SPR of silver. Furthermore, we observe that while R is orders of magnitude greater at room temperature when the frequency is close to that of the SPR, as is well known, it is possible that the rapid rate of decrease of R at this frequency may lead to an insignificant enhancement at elevated temperatures. In comparison, the SERS enhancement stays relatively constant, with the rise of temperature at frequencies lower than that of the SPR of silver, and can become relatively more appreciable at high temperatures. As a matter of fact, SERS signals observed at silver surfaces up to 900 K in Ref.

1 were obtained using an argon laser ($\omega \approx 2$ eV) as the excitation source.⁷ Figure 3 shows similar results for R , with the substrate being modeled as a prolate spheroid with the length of the major axis (a) five times that of the minor axis (b). It is known that in this case the SPR frequency is redshifted to about 2 eV.² Similar qualitative behavior can be seen as compared to the sphere case, except that the absolute values for R are much greater with a spheroidal substrate, as is well known. In Fig. 4, we show R as a function of temperature at a fixed frequency of 1.9 eV for spheroids of different a/b ratios. It is found that while the spheroid with the SPR closest to the fixed frequency has the largest rate of decrease in R with temperature ($a/b=5$ in this case), this rate of decrease depends mainly on the ratio of a/b and not much on the actual dimension of the lengths of the axis.

In order to explain partially the phenomenon observed in Figs. 2 and 3, we plot in Fig. 5 the real and imaginary parts

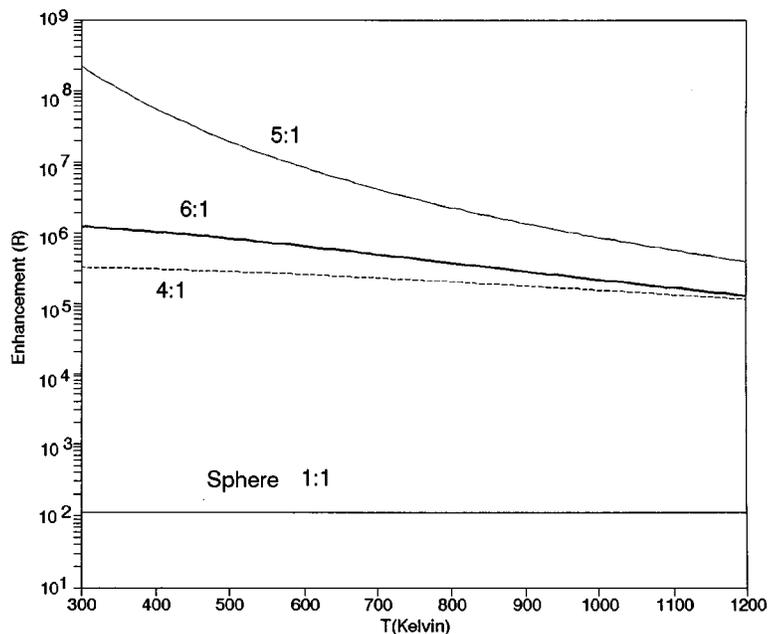


FIG. 4. Results for spheroidal substrates with different a/b ratio as indicated on the curves. The excitation frequency is fixed at 1.9 eV and d at 1 nm as in Figs. 2 and 3.

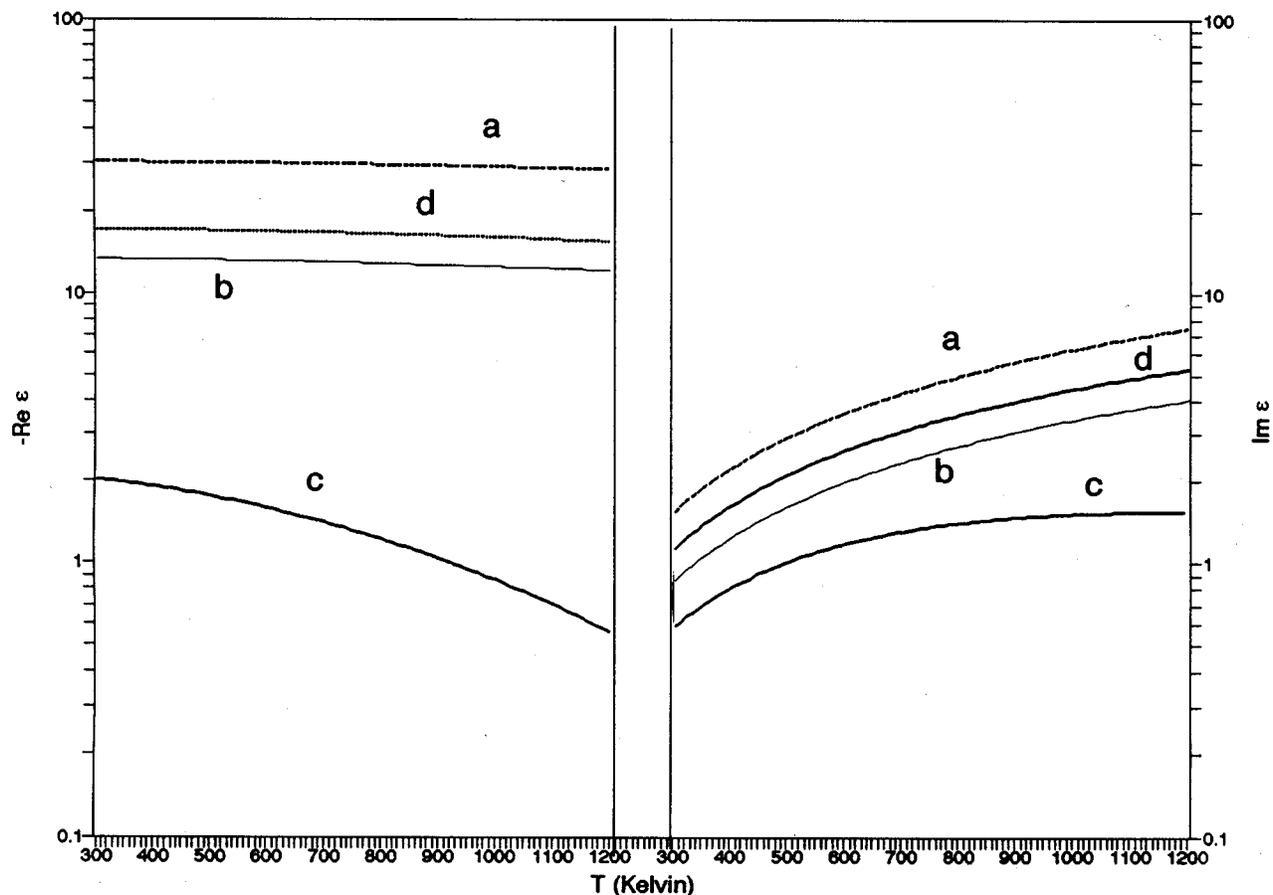


FIG. 5. The real and imaginary parts of the dielectric function for Ag as a function of temperature at different frequencies as labeled in Figs. 1 and 3.

of the dielectric function as obtained from Eq. (5), from which we see that the real part becomes in general less negative and the imaginary part increases as temperature increases. It is well known that for the plasmon field to be excited efficiently, the real part of ϵ has to be negative and the imaginary part has to be small.⁸ Thus the surface-plasmon enhancement effect from the substrate becomes less pronounced as the temperature goes up. It can also be noted that the temperature dependence of this drop in R is most sensitive for frequencies close to and above those of resonance for the particular substrate structure. As an example, we see that the large variation of ϵ with temperature at 3.5 eV (close to the SPR for a Ag sphere) contributes to the significant drop in R with temperatures at that frequency. The fact that the real part at 3.5 eV rises to merely below

zero at high temperatures (-0.56 at 1200 K), together with the increase of the imaginary part, lead to a significant diminution of the surface-plasmon enhancement. In fact, when we separate the enhancement factor in Eq. (4) into the image-field factor $(1 - \alpha G_{\perp})^{-1}$ (Ref. 2) and the plasmon-field factor, we find that only the latter factor drops appreciably with temperature at 3.5 eV. Thus we conclude that the EM enhancement effect can indeed survive in SERS at elevated temperatures, and, to optimize the enhancement at such temperatures, it can be more efficient if the scattering frequency is set off and below that of the SPR of the metal substrate.

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* Author to whom correspondence should be addressed.

† Also affiliated with Komatsu Silicon USA, 1333 Lawrence Expressway, Bldg. 400, Suite 440, Santa Clara, California 95051.

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