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# Intensity of Raman scattering from molecules adsorbed on a metallic grating

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A simple phenomenological model is presented for the calculation of intensity of Stokes scattered light due to vibrations of molecules adsorbed on a metallic grating or a rough metal surface. The surface roughness is assumed to be represented by a superposition of sinusoidal gratings of different periodicities, with each amplitude small compared to the wavelength of the incident light. Enhancements of the surface-plasmon field and the resulting induced surface charge density arising from resonant excitation of transverse surface plasmons are calculated explicitly. In our model, the net enhancement of the Raman cross section is shown to arise from two different types of contribution. The first contribution represents the usual mechanism involving the modulation of the molecular polarizability $\overleftrightarrow{\alpha}$ in the presence of the enhanced electromagnetic field at the molecular site, with the possibility of an additional enhancement due to the conversion of the near-zone Stokes field into the scattered radiation field by the metal surface. The second contribution comes from the modulation of the surface polarizability $\overleftrightarrow{\beta}$ arising from the finite spatial extent of the induced surface charge density at the surface. For vibrations of molecular monolayers perpendicular to the surface, it is shown that the additional polarizability contribution can become larger than the first contribution if the barrier potential for the conduction electron tunneling to the molecular site is less than about 1 eV.

## I. INTRODUCTION

During the last few years, several theoretical models have been proposed to explain the observation of surface-enhanced Raman (SER) scattering[1-3] from molecules adsorbed on metals like Ag. Although there exists a class of such models[4-9] which do not require any surface roughness for SER scattering, it is now generally believed that the surface roughness[2,10] plays a significant role in the large enhancement ($10^4$–$10^6$) of molecular Raman cross sections. For a flat surface,[11] the enhancement of the cross sections, compared to their bulk values, is usually much smaller.[8] It is thus important to examine carefully the role played by the surface roughness on a submacroscopic scale, and calculate the resulting intensity of SER scattering in terms of parameters which may be deduced from experiments.

In the class of theories[3,9,12] where the surface roughness indeed plays a crucial role, Moskovits[12] and Chen *et al.*[3] have suggested that because of submacroscopic bumps on the metal surface the enhancement is caused by the resonant excitation of transverse collective electronic modes of the bumps, with a resulting increase in the electric field at the molecular site. A similar classical enhancement of Raman cross section, due to an increase in the electric field resulting from the excitation of surface electromagnetic wave in an attenuated-total-reflection prism configuration, was considered earlier by Chen *et al.*[13] Very recently, we have proposed[14,15] that for metal-molecule systems with very low barrier potentials for tunneling of the conduction electrons to the molecular site, there is a significantly large additional contribution to Raman scattering due to the modulation of the induced surface charge density associated with the resonant excitation of the so-called transverse "surface plasmons." In this paper, we present calculations of both these contributions in terms of the roughness parameters of the surface and the complex dielectric function, $\epsilon(\omega)=\epsilon_1=(\omega)+i\epsilon_2(\omega)$, of the rough metal. Instead of dealing with measurements for surfaces with random roughness, the data on sinusoidal metallic gratings will be more suitable for a comparison[16] of our results directly with such observations.

When a light wave of frequency $\omega$ is incident on a metal surface, it induces an oscillating surface charge density of the form

$$n_s(\vec{r},\omega)=(-\tfrac{1}{4}\pi e)\vec{\nabla}\cdot\vec{E}(\vec{r},\omega),\quad \vec{\nabla}\cdot\vec{E}=-\vec{E}\cdot\vec{\nabla}\epsilon/\epsilon \tag{1.1}$$

where the dielectric function $\epsilon(\vec{r},\omega)$ for a flat metal-vacuum system varies rapidly in the direction normal to the surface (taken to be the $z$ direction). Outside the surface barrier, the variation of $n_s$ is essentially determined by the length $(\hbar^2/2m\Phi_B)^{1/2}$, where $\Phi_B$ is the surface-barrier potential for the electrons as measured from the Fermi energy $\epsilon_F=(\frac{1}{2})mv_f^2$, and inside the metal it is determined by the lengths $(\hbar^2/2m\epsilon_F)^{1/2}$ and $v_f/\omega$. In the presence of adsorbed molecules at the metal surface, the modified surface-barrier potential $\Phi$, and hence $n_s(\vec{r},\omega)$, are functions of the molecular vibrations $\delta\vec{R}(t)$. In our model,[14,15] the resulting modulated-surface dipole moment (MSDM) in the $z$ direction gives rise to the Raman-shifted scattered photons. This is in addition to the scattering due to the modulation of the molecular polarizability in the modified field at the molecular site. For a metal having $\epsilon_1(\omega) < -1$, with appropriate surface roughness or periodic grating grooves, i.e., when the incident light can efficiently excite the transverse surface plasmons (quasistationary superficial waves[17]), both these contributions can become quite large. However, for molecular monolayers with effective distances less than 3–4 Å from the metal surface and surface barrier heights less than 1 eV, we find that the quantum tunneling contribution from MSDM dominates over the contribution due to the classical field enhancement (CFE) at the molecular site.

In Sec. II of this paper, we review the classical method of calculating the electromagnetic field distribution induced by a light wave incident on a rough metal surface. The departure of the real rough surface from the flat plane surface, $z=0$, is assumed to be small compared to the wavelength of light, and the so-called "first-approximation" of Rayleigh[18] is used in such a calculation. The change in the dielectric function while crossing the surface is assumed to be represented by a step function in this classical method, and we present the complete expressions[19] for the field amplitudes both inside and outside the metal. It is shown how the surface-plasmon field is enhanced when the surface-plasmon relation is satisfied by the frequency $\omega$ and the (tangential) wave vector $K_g$ of the bound surface-plasmon wave.

The step-function model of the dielectric function considered in Sec. II leads to a $\delta$-function type of structure for the induced surface charge density via (1.1). In terms of the surface barrier potential and the Fermi energy, this structure is modified phenomenologically in Sec. III to account for the smooth variation of the dielectric function near the metal surface. The outside molecular potential is then approximated by a sum of dipole potentials[20] due to partial charges localized on individual atoms in the molecules, including their images in the metal. The inside potential is taken to be the screened potential from these partial charges. This allows us to calculate the modulated-surface charge density linear in the molecular vibrational amplitude $\delta\vec{R}(t)$, and hence to find the modulated-surface dipole moment $\vec{p}_s(t)$ and the derivative of the surface polarizability $\vec{\beta}$. The only nonvanishing component of $\vec{p}_s$ is in the $z$ direction (normal to the surface).

In Sec. IV, we calculate the intensities of Stokes scattering due to $\vec{p}_s(t)$ of Sec. III (MSDM contribution), as well as due to the direct modulation of the molecular polarizability $\tilde{\alpha}$ in the presence of the enhanced surface-plasmon field (CFE contribution). We explicitly show how the polarization properties of the scattered wave are different in these two cases. This may allow the separation of these contributions in those situations when they are of the same order in magnitude. In the visible frequency range, Ag is the best metal for exciting surface plasmons, and hence gives maximum enhancement. For Au, the maximum enhancement in the visible is about $10^2$ times less than Ag. For low surface barrier potentials, the enhancement due to the MSDM contribution dominates for the first few monolayers, and can be as large as $10^5$–$10^7$ for certain molecules adsorbed on Ag. The enhancement due to CFE contribution will dominate when molecular distances are large, but its magnitude is less than about $10^4$ in Ag, when $\xi_g K_g \simeq 0.2$. Here, $\xi_g$ is the amplitude of the grating, with periodicity $\vec{g}$. We discuss our results in Sec. V.

## II. INDUCED ELECTROMAGNETIC FIELDS IN THE PRESENCE OF SURFACE ROUGHNESS

The theory of Wood's anomalous diffraction gratings and the excitation of intense quasistationary superficial waves on metallic surfaces has been known for a long time.[17,18] If in the absence of grating grooves or roughness, the flat surface is denoted by the plane $z=0$, and the real surface due to the grating grooves or roughness is given by

$$z=\xi(x,y)=\sum_{\vec{g}}\xi_g e^{i\vec{g}\cdot\vec{r}_{\parallel}},\quad \vec{g}=(g_x,g_y),\quad \vec{r}_{\parallel}=(x,y) \tag{2.1}$$

one can determine field distributions everywhere by using the first approximation of Rayleigh, when each amplitude $\xi_g$ is small compared to the wavelength of the incident light. In such a linear theory, each two-dimensional spatial Fourier component of $\xi$ can be treated independently and the final results may be obtained by a simple superposition. The higher-order interference and mixing effects can then be studied, if necessary, by using the method of successive approximations.

Let us consider the case of a semi-infinite metal (Fig. 1), with a single surface defined by (2.1) and the $z$ axis pointing into the metal. The bulk dielectric function of the metal is assumed to be $\epsilon(\omega)=\epsilon_1(\omega)+i\epsilon_2(\omega)$, with $\epsilon_2 \ll \epsilon_1$. Let a light wave of frequency $\omega$ represented by an electric field

$$\begin{gathered}\vec{E}_{\text{inc}}(\vec{r},t)=E_1 e^{i\vec{k}_t\cdot\vec{r}_{\parallel}} e^{ik_z z} e^{-i\omega t},\\ k_z=\frac{\omega}{c}\cos\theta_i,\quad |\vec{k}_t|=k_t=\frac{\omega}{c}\sin\theta_i,\quad \vec{\nabla}\cdot\vec{E}_{\text{inc}}=0\end{gathered} \tag{2.2}$$

be incident on the metal surface. For the given frequency $\omega$, the problem is to solve Maxwell's

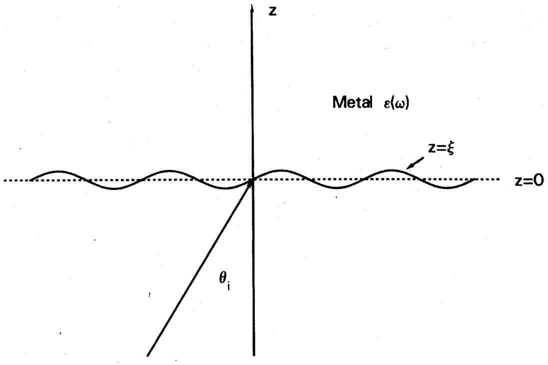

FIG. 1. Schematic diagram showing light incident on a metallic grating. The surface of the grating is defined by $z=\xi(x,y)$ as a small departure from the flat plane $z=0$.

equations

$$\vec{\nabla}\times\vec{\nabla}\times\vec{E}(\vec{r},\omega)-\frac{\omega^2}{c^2}\epsilon(\omega,\vec{r})\vec{E}(\vec{r},\omega)=0\,, \tag{2.3}$$

$$\vec{B}(\vec{r},\omega)=\frac{c}{i\omega}\vec{\nabla}\times\vec{E}(\vec{r},\omega)\,, \tag{2.4}$$

where, in terms of the step function (theta function), the dielectric function is represented by

$$\epsilon(\omega,\vec{r})=\epsilon(\omega)\Theta(z-\xi)+\Theta(\xi-z)\,. \tag{2.5}$$

The *local* tangential components of the electric and magnetic fields $\vec{E}$ and $\vec{B}$, respectively, have to be continuous across the actual surface $z=\xi(x,y)$. One of the boundary conditions on the tangential components of $\vec{B}$ may be replaced, if convenient, by the continuity of the normal component of $\vec{D}=\epsilon\vec{E}$ across the surface $z=\xi$. Note that (2.3) and (2.5) imply that

$$\vec{\nabla}\cdot\vec{E}=0,\quad z\neq\xi \tag{2.6}$$

both inside and outside the metal.

In the first approximation, where one calculates effects only to the first order in $\omega\xi/c$, the solution of the above problem has already been given by Marvin *et al.*[19] We will, therefore, only briefly discuss the method, and write the final answer in our notation.

Without any loss of generality, in the linear theory we can consider only one spatial Fourier component at a time, and write

$$\xi(x,y)=\xi_g e^{i\vec{g}\cdot\vec{r}_\parallel} \tag{2.7}$$

for the surface roughness under consideration. In the $x$-$y$ plane, let us denote the unit vectors parallel to $\vec{g}$ and perpendicular to $\vec{g}$ by

$$\hat{e}_{2g}=\hat{g},\quad \hat{e}_{1g}=\hat{g}\times\hat{z}\,, \tag{2.8}$$

respectively. Locally, in terms of the vectors $\hat{e}_{1g}$ and $\hat{e}_{2g}$, the tangential ($t$) and the normal ($n$) components of any vector on the surface $z=\xi(x,y)$ are given by

$$\vec{F}_t\cdot\hat{e}_{1g}=\vec{F}\cdot\hat{e}_{1g}\,,\quad \vec{F}_t\cdot\hat{e}_{2g}=\frac{\vec{F}\cdot\hat{e}_{2g}+ig\xi F_z}{[1+(ig\xi)^2]^{1/2}}\,, \tag{2.9}$$

$$F_n=\frac{F_z-ig\xi\vec{F}\cdot\hat{e}_{2g}}{[1+(ig\xi)^2]^{1/2}}\,. \tag{2.10}$$

Explicitly, for $g\xi\ll 1$, these imply that at $z=\xi$ the following four quantities

$$\begin{gathered}\vec{E}\cdot\hat{e}_{1g},\quad (\vec{\nabla}\times\vec{E})\cdot\hat{e}_{1g}\ \text{or}\ (E_z-ig\xi\vec{E}\cdot\hat{e}_{2g})\epsilon\,,\\ \vec{E}\cdot\hat{e}_{2g}+ig\xi E_z,\quad (\vec{\nabla}\times\vec{E})\cdot\hat{e}_{2g}+ig\xi(\vec{\nabla}\times\vec{E})_z\end{gathered} \tag{2.11}$$

must be continuous to satisfy the boundary conditions.

It is clear that in the solutions of Maxwell's Eqs. (2.3) and (2.4), in addition to the usual Fresnel reflected and transmitted waves, with tangential wave vectors equal to the incident tangential wave vector $\vec{k}_t$, there will be secondary reflected and transmitted waves induced by the surface roughness (2.7), having tangential wave vectors $\vec{k}_t+\vec{g}$. For negative $\epsilon(\omega)$, all waves inside the metal are decaying waves in the $z$ direction, but outside the metal, the variation $\exp(-ik_{gz}z)$ of the secondary wave is determined by the relation $k_{gz}^2+(\vec{k}_t+\vec{g})^2=\omega^2/c^2$. For the existence of a bound transverse surface-plasmon wave solution in which the secondary field proportional to $\xi_g$ decays both inside and outside the metal, one must have $K_g^2>\omega^2/c^2$, where $\vec{K}_g=\vec{k}_t+\vec{g}$ is the tangential wave vector of the secondary wave. For $K_g^2<\omega^2/c^2$, one simply gets a secondary diffracted wave outside the metal, which we do not consider here. Thus, for $K_g>\omega/c$, the solution of (2.3) and (2.5) can be written in the form

$$\begin{aligned}\vec{E}=&e^{i\vec{k}_t\cdot\vec{r}_\parallel}[\vec{E}_i e^{ik_z z}+\vec{E}_r e^{-ik_z z}]\\ &+\vec{E}_g e^{i\vec{K}_g\cdot\vec{r}_\parallel}e^{\Gamma_g z}\quad \text{if } z<\xi\,,\end{aligned} \tag{2.12}$$

$$\vec{E}=\vec{E}_t e^{i\vec{k}_t\cdot\vec{r}_\parallel}e^{-\gamma z}+\vec{E}_g' e^{i\vec{K}_g\cdot\vec{r}_\parallel}e^{-\gamma_g z}\quad \text{if } z>\xi\,. \tag{2.13}$$

Here,

$$\vec{K}_g=\vec{k}_t+\vec{g}\,,\quad \Gamma_g=(K_g^2-\omega^2/c^2)^{1/2}\,, \tag{2.14}$$

$$\gamma^2=k_t^2-\frac{\omega^2}{c^2}\epsilon(\omega),\quad \gamma_g^2=K_g^2-\frac{\omega^2}{c^2}\epsilon(\omega)\,, \tag{2.15}$$

and the condition (2.6) is satisfied separately by all the three waves outside and the two waves inside the metal. While applying the continuity of the expressions (2.11) at $z=\xi$, one has to expand expressions of the type

$$\begin{aligned}e^{i\vec{k}_t\cdot\vec{r}_\parallel}e^{ik_z\xi}\simeq e^{i\vec{k}_t\cdot\vec{r}_\parallel}(1+ik_z\xi)=e^{i\vec{k}_t\cdot\vec{r}_\parallel}&\\ +ik_z\xi_g e^{i\vec{K}_g\cdot\vec{r}_\parallel},\ \text{etc.},&\end{aligned} \tag{2.16}$$

and equate the spatial Fourier components varying as $\exp(i\vec{k}_t\cdot\vec{r}_\parallel)$ and $\exp(i\vec{K}_g\cdot\vec{r}_\parallel)$, separately on both sides. Together with the condition (2.6), this procedure immediately leads to a set of algebraic coupled equations to determine all the amplitudes in the solution given by (2.12) and (2.13).

Since it is more convenient to write the complete solution in terms of respective $s$- and $p$-polarized components of the amplitudes, we split them as

$$\begin{aligned}\vec{E}_i&=E_i^s(\hat{k}_t\times\hat{z})+E^p_{i_\parallel}\hat{k}_t+E^p_{iz}\hat{z}\,,\\ \vec{E}_r&=E_r^s(\hat{k}_t\times\hat{z})+E^p_{r_\parallel}\hat{k}_t+E^p_{rz}\hat{z}\,,\\ \vec{E}_t&=E_t^s(\hat{k}_t\times\hat{z})+E^p_{t_\parallel}\hat{k}_t+E^p_{tz}\hat{z}\,,\\ \vec{E}_g&=E_g^s(\hat{K}_g\times\hat{z})+E^p_{g_\parallel}\hat{K}_g+E^p_{gz}\hat{z}\,,\\ \vec{E}'_g&=E'^s_g(\hat{K}_g\times\hat{z})+E'^p_{g_\parallel}\hat{K}_g+E'^p_{gz}\hat{z}\,,\end{aligned}\tag{2.17}$$

where, because of the condition (2.6)

$$\begin{aligned}&E_{iz}=E^p_{iz}=-\frac{k_t}{k_z}E^p_{i_\parallel}\,,\quad E_{rz}=E^p_{rz}=\frac{k_t}{k_z}E^p_{r_\parallel}\,,\\ &E_{tz}=E^p_{tz}=\frac{k_t}{-i\gamma}E^p_{t_\parallel}\,,\quad E_{gz}=E^p_{gz}=\frac{K_g}{i\Gamma_g}E^p_{g_\parallel}\,,\\ &E'_{gz}=E'^p_{gz}=\frac{K_g}{-i\gamma_g}E'^p_{g_\parallel}\,.\end{aligned}\tag{2.18}$$

The complete solution can then be specified by

$$E_r^s=\frac{(k_z-i\gamma)}{(k_z+i\gamma)}E_i^s\,,\quad E_t^s=\frac{2k_z}{(k_z+i\gamma)}E_i^s\,,\tag{2.19}$$

$$E^p_{rz}=\frac{(\epsilon k_z-i\gamma)}{(\epsilon k_z+i\gamma)}E^p_{iz}\,,\quad E^p_{tz}=\frac{2k_z}{(\epsilon k_z+i\gamma)}E^p_{iz}\,,\tag{2.20}$$

$$E_g^s=E'^s_g=-\frac{\omega^2}{c^2}\,\frac{2i\xi_gk_z(1-\epsilon)}{k_t(\Gamma_g+\gamma_g)}\times\left(\frac{\gamma(\hat{k}_t\times\hat{K}_g)_z}{(\epsilon k_z+i\gamma)}E^p_{iz}+\frac{ik_t(\hat{k}_t\cdot\hat{K}_g)}{(k_z+i\gamma)}E^s_i\right),\tag{2.21}$$

$$E^p_{gz}=\frac{2(\xi_gK_g)k_z\gamma_g(1-\epsilon)}{k_t(\epsilon\Gamma_g+\gamma_g)}\times\left(\frac{(\gamma\vec{k}_t\cdot\vec{K}_g+\epsilon k_tK_g/\gamma_g)}{(\epsilon k_z+i\gamma)}E^p_{iz}-\frac{ik_t(k_t\times K_g)_z}{(k_z+i\gamma)}E^s_i\right),\tag{2.22}$$

$$E'^p_{gz}=-\frac{\Gamma_g}{\gamma_g}E^p_{gz}+\frac{2(\xi_gK_g)k_zK_g}{\gamma_g(\epsilon k_z+i\gamma)}E^p_{iz}\,.\tag{2.23}$$

Note that the $p$-polarized secondary field $\vec{E}^p_g$ and $\vec{E}'^p_g$ can become quite large if

$$\mathrm{Re}(\epsilon\Gamma_g+\gamma_g)=0\tag{2.24}$$

which determines the surface-plasmon dispersion relation. Note also that when $\hat{k}_t\times\hat{g}\neq 0$, the surface plasmon can be excited resonantly by both $p$- and $s$-polarized incident waves. However, for $\vec{g}$ parallel to $\vec{k}_t$, only a $p$-polarized incident wave leads to the resonance.

The structure of the enhancement of the surface-plasmon field amplitude, $E^p_{gz}$, outside the metal may be examined further by analyzing its coefficient

$$\frac{\gamma_g(1-\epsilon)}{\epsilon\Gamma_g+\gamma_g}=\frac{\gamma_g(1-\epsilon)(\epsilon\Gamma_g-\gamma_g)}{\epsilon^2\Gamma_g^2-\gamma_g^2}=\frac{\gamma_g(\epsilon\Gamma_g-\gamma_g)}{\left[\dfrac{\omega^2}{c^2}\epsilon_1-K_g^2(\epsilon_1+1)-i\left(K_g^2-\dfrac{\omega^2}{c^2}\right)\epsilon_2\right]}\,,\tag{2.25}$$

where $\mathrm{Re}\gamma_g$, $\Gamma_g>0$. It has a resonance structure at the surface-plasmon frequency determined by the dispersion relation

$$f(K_g,\omega)\equiv\frac{\omega^2}{c^2}\epsilon_1(\omega)-K_g^2[\epsilon_1(\omega)+1)]=0\,.\tag{2.26}$$

The resonant enhancement of the field is proportional to

$$\frac{\tau_s}{(df/d\omega)_{\rm res}}=-\frac{1}{\Gamma_g^2\epsilon_2}=\frac{c^2}{\omega^2}\,\frac{(\epsilon_1+1)}{\epsilon_2}\,,\tag{2.27}$$

where $\tau_s$ is the lifetime of the surface-plasmon. At exact resonance, the coefficient (2.25) becomes

$$\frac{\gamma_g(1-\epsilon)}{(\epsilon\Gamma_g+\gamma_g)}\to\left(\frac{-2\gamma_g^2}{-i\Gamma_g^2\epsilon_2}\right)_{\rm res}=\frac{2\epsilon^2}{i\epsilon_2}\tag{2.28}$$

and it can become quite large for $\epsilon_1\ll-1$ and $\epsilon_2\ll|\epsilon_1|$. Note, however, that for rough surfaces with absorbed molecules, the effective $\epsilon_2$ near the surface can be much greater than its bulk value. In a simple theory, this additional contribution to $\epsilon_2$ varies as the square of the roughness amplitude.

## III. MODULATION OF THE INDUCED SURFACE DIPOLE MOMENT

The field distribution obtained in the preceding section for the case of a single spatial Fourier component of the surface roughness immediately allows us to calculate the classical induced surface charge density. To the lowest order in the amplitude $\xi$, (1.1), (2.12), (2.13), and (2.18) to (2.23) lead to

$$n_s(\vec{r},\omega)=-\frac{1}{4\pi e}\vec{\nabla}\cdot\vec{E}=\sigma_s(\vec{r}_\parallel,\omega)\delta(z-\xi)\,,\tag{3.1}$$

$$\sigma_s(\vec{r}_\parallel,\omega)=\sigma^P_{so}e^{i\mathbf{k}_t\cdot\mathbf{r}_\parallel}+(\sigma^P_{sp}+\sigma^S_{sp})e^{i\mathbf{K}_g\cdot\mathbf{r}_\parallel}\,,\tag{3.2}$$

$$\sigma^P_{so}=-\frac{1}{4\pi e}\,\frac{2k_z(1-\epsilon)}{(\epsilon k_z+i\gamma)}E^P_{iz}\,,\tag{3.3}$$

$$\sigma^P_{sp}=\sigma^P_{so}\xi_gK_g\left(\frac{K_g}{\gamma_g}-\frac{(\gamma\gamma_g\hat{k}_t\cdot\hat{K}_g+\epsilon k_tK_g)}{k_t\gamma_g}\,\frac{(\Gamma_g+\gamma_g)}{(\epsilon\Gamma_g+\gamma_g)}\right),\tag{3.4}$$

$$\sigma^S_{sp}=-\frac{1}{4\pi\epsilon}\,\frac{2k_z(1-\epsilon)}{(\epsilon k_z+i\gamma)}E^s_i\xi_gK_g(\hat{k}_t\times\hat{K}_g)_z\frac{(\Gamma_g+\gamma_g)}{(\epsilon\Gamma_g+\gamma_g)}\,.\tag{3.5}$$

Here, $\sigma^P_{so}$ corresponds to the usual induced surface charge density for a flat surface, and $\sigma^P_{sp}$ and $\sigma^S_{sp}$ correspond to the surface-plasmon charge densities induced in the presence of roughness by the *P*- and *S*-polarized incident light, respectively. Both $\sigma^P_{sp}$ and $\sigma^S_{sp}$ contain resonance denominators corresponding to the resonant excitation of surface plasmons, and for reasonable values of $\xi_g K_g$, they can become much larger than the nonresonant $\sigma^P_{so}$ from the flat surface.

The $\delta$-function structure of $n_s(\vec{r},\omega)$ in (3.1) is a direct consequence of our classical step-function model (2.5) for the variation of $\epsilon(\omega)$ at the metal-vacuum interface. In reality, outside the metal, $\epsilon$ decays smoothly to 1 on the length scale determined by $(\hbar^2/2m\Phi_B)^{1/2}$, where $\Phi_B = U_B - \epsilon_F$ is the barrier potential measured from the Fermi energy. Similarly, inside the metal, apart from the Friedel oscillations and the oscillations due to the periodic potential in the bulk, at high frequencies the variation of $n_s(\vec{r},\omega)$ is essentially governed near the surface[21,22] by the scale length $v_f/\omega$. At low frequencies, it is determined by the length $q_{\rm FT}^{-1} = (\epsilon_F/6\pi n e^2)^{1/2}$. As a rough estimate, in the frequency region of interest we may use an interpolated expression, $q_{\rm FT}(\text{bulk}) + 2\omega/v_f$, for the inside decay coefficient, close to the surface. In the presence of adsorbed molecules, we therefore replace the $\delta$ function in (3.1) by a phenomenological model function $F(\vec{r},\vec{R}_m)$. This is specified by

$$\delta(z-\xi) \rightarrow F(\vec{r},\vec{R}_m) = \begin{cases} A\exp\left(2\int_\xi^z dz\,K_{\rm out}(\vec{r},\vec{R}_m)\right), & z<\xi \\ A\exp\left(-2\int_\xi^z dz\,K_{\rm in}(\vec{r},\vec{R}_m)\right), & z>\xi \end{cases} \tag{3.6}$$

where $A$ is determined by the normalization integral

$$\int_{-\infty}^{\infty} dz\,F(\vec{r},\vec{R}_m) = \int_{-\infty}^{\infty} dz\,\delta(z-\xi) = 1\,. \tag{3.7}$$

Here

$$K_{\rm out}(\vec{r},\vec{R}_m) \simeq \left(\frac{2m}{\hbar^2}[\Phi_B + \Phi_{\rm out}(\vec{r},\vec{R}_m)]\right)^{1/2}, \tag{3.8}$$

$$K_{\rm in}(\vec{r},\vec{R}_m) \simeq \{\tfrac{1}{2}m\omega^2[\epsilon_F + \Phi_{\rm in}(\vec{r},\vec{R}_m)]\}^{1/2} + \tfrac{1}{2}q_{\rm FT} \tag{3.9}$$

are the decay coefficients outside and inside the metal, respectively, in the presence of additional potential energies $\Phi_{\rm out}$ and $\Phi_{\rm in}$ arising from partial atomic charges $Z_j e$ in the molecule.

Explicitly, outside the metal one has

$$\Phi_{\rm out}(\vec{r},\vec{R}_m) = -\sum_j Z_j e^2 \left(\frac{1}{|\vec{r}-\vec{R}_{jm}|} - \frac{1}{|\vec{r}-\vec{R}_{jm}+2\hat{z}(R_{jz}-\xi)|}\right), \tag{3.10}$$

where the second term represents the image term. Similarly, $\Phi_{\rm in}(\vec{r},\vec{R}_m)$ is represented by the first term (3.10), with an additional screening factor so that it decays exponentially as $\exp[-q_{\rm FT}(z-\xi)]$ away from the surface. Here, $q_{\rm FT}$ is the Thomas-Fermi wave vector. In the presence of molecular vibrations of frequency $\omega_0$, the atomic positions $\vec{R}_{jm}$ can be expanded around their equilibrium positions as

$$\vec{R}_{jm} = \vec{R}_j + \delta\vec{R}_j e^{i\omega_0 t} + \delta\vec{R}_j^{\,*} e^{-i\omega_0 t}\,. \tag{3.11}$$

This allows us to expand $\Phi_{\rm out}$, $\Phi_{\rm in}$, $K_{\rm out}$, and $K_{\rm in}$, and hence $F(\vec{r},\vec{R}_m)$ to terms linear in $\delta\vec{R}$. In order to simplify the algebra, we parametrize the static equilibrium parts of $\Phi_B + \Phi_{\rm out}$ and $\epsilon_F + \Phi_{\rm in}$ by effective constant values $\Phi_0$ and $E_F \simeq \epsilon_F$, respectively. It then leads to

$$F(\vec{r},\vec{R}_m) = F_0(\vec{r}) + F_1(\vec{r})\,e^{i\omega_0 t} + F_1^*(\vec{r})\,e^{-i\omega t}\,, \tag{3.12}$$

where, outside ($z<\xi$) and inside ($z>\xi$) the metal, one finds

$$F_0(\text{out}) = Ae^{2K_0(z-\xi)}, \quad F_0(\text{in}) = Ae^{-2K_i(z-\xi)}\,, \tag{3.13}$$

$$A = \frac{2K_0K_i}{K_0+K_i}, \quad K_0 = \left(\frac{2m}{\hbar^2}\Phi_0\right)^{1/2}, \quad K_i = \frac{\omega}{v_f} + \frac{q_{\rm FT}}{2}\,, \tag{3.14}$$

$$F_1(\text{out}) \cong A\left(\frac{K_0}{\Phi_0}\right)\int \frac{d^3q}{(2\pi)^3} H'_{\rm out}(\vec{q})\,e^{i\vec{q}\cdot\vec{r}_\parallel}\,e^{2K_0(z-\xi)} \times\left(\frac{2K_0}{iq_z(2K_0+iq_z)} - \frac{e^{iq_z(z-\xi)}}{iq_z}\right), \tag{3.15}$$

$$F_1(\text{in}) \cong A\left(\frac{K_i}{\Phi_0}\right)\int \frac{d^3q}{(2\pi)^3} H'_{\rm in}(\vec{q})\,e^{i\vec{q}\cdot\vec{r}_\parallel}\,e^{-(2K_i+q_{\rm FT})(z-\xi)} \times\left(\frac{(2K_i+q_{\rm FT})}{iq_z(2K_i+q_{\rm FT}-iq_z)} - \frac{e^{iq_z(z-\xi)}}{iq_z}\right), \tag{3.16}$$

$$H'_{\rm out}(\vec{q}) = \sum_j \delta\vec{R}_j\cdot\vec{\nabla}_j\left(\frac{4\pi Z_j e^2}{q^2}\,e^{-i\vec{q}_\parallel\cdot\vec{R}_j} \times\left(e^{-iq_z(R_{jz}-\xi)} - e^{iq_z(R_{jz}-\xi)}\right)\right), \tag{3.17}$$

$$H'_{\rm in}(\vec{q}) = \sum_j \delta\vec{R}_j\cdot\vec{\nabla}_j\left(\frac{4\pi Z_j e^2}{q^2}\,e^{-i\vec{q}_\parallel\cdot\vec{R}_j}\,e^{-iq_z(R_{jz}-\xi)}\right). \tag{3.18}$$

The surface dipole moment varying with Stokes frequency $\omega - \omega_0$ may now be obtained by evaluating the expression

$$\vec{p}_s(\omega - \omega_0) = -e \int d^3r(\vec{r} - \hat{z}\xi)\sigma_s(\vec{r}_{\parallel}, \omega)F_1(\vec{r}) . \tag{3.19}$$

Note that because of the normalization condition (3.7), the components of the full instantaneous surface dipole moment in $x$ and $y$ directions are independent of molecular coordinates $\vec{R}_m$, and hence the modulated dipole moment (3.19) should be nonvanishing only in the $z$ direction. The approximate forms (3.15) and (3.16) for $F_1$ are indeed consistent with this result. Thus, corresponding to the surface-plasmon charge density in (3.2), we find

$$\begin{aligned}\vec{p}_{sp}(\omega - \omega_0) &= \hat{z}\sum_j \left(\frac{\partial\beta_{zz}}{\partial\vec{R}_j}\right) \cdot \delta\vec{R}_j[-4\pi e(\sigma^S_{sp} + \sigma^P_{sp})] \\ &= \hat{z}\sum_j \left(\frac{\partial\beta_{zz}}{\partial\vec{R}_j}\right) \cdot \delta\vec{R}_j(E'_{gz} - E_{gz}) ,\end{aligned} \tag{3.20}$$

where the derivative of the surface polarizability $\beta_{zz}$ is given by

$$\begin{aligned}\frac{\partial\beta_{zz}}{\partial\vec{R}_j} \cong -Z_j e^2\left(\frac{2K_0K_i}{K_0+K_i}\right)\frac{\partial}{\partial\vec{R}_j}\Bigg(\frac{K_0}{\Phi_0}\int\frac{dq_z}{2\pi}\,\frac{e^{i\vec{K}_g\cdot\vec{R}_j}(e^{-iq_z(R_{jz}-\xi)} - e^{-iq_z(R_{jz}-\xi)})}{2k_0(2K_0+iq_z)^2(K_g^2+q_z^2)} \\ +\frac{K_i}{\epsilon_F}\int\frac{dq_z}{2\pi}\,\frac{e^{i\vec{K}_g\cdot\vec{R}_j}e^{-iq_z(R_{jz}-\xi)}}{(2K_i+q_{\mathrm{FT}})(2K_i+q_{\mathrm{FT}}-iq_z)^2(K_g^2+q_z^2)}\Bigg) .\end{aligned} \tag{3.21}$$

The first term in (3.21) comes from the induced surface charge density outside the metal whereas the second term is due to the induced charges inside the metal.

In order to get an estimate of relative significance of different terms in (3.21) we can consider here the effect of a single effective molecular charge of magnitude $Z_{\mathrm{eff}}e$ and vibration amplitude $\delta\vec{R}$, with an equilibrium distance, $a$, from the surface $z = \xi$. With $K_g \ll K_0, K_i$, we then get

$$\left(\frac{\partial\beta}{\partial\vec{R}}\right) = -\frac{Z_{\mathrm{eff}}}{4}\left(\frac{2me^2}{\hbar^2K_0^3}\right)\left(\frac{K_i}{K_0+K_i}\right) \times\left(\vec{I}_0 + \frac{K_iK_0^4\vec{I}_i}{k_F^2(K_i+q_{\mathrm{FT}}/2)^3}\right) , \tag{3.22}$$

where $k_F$ is the bulk Fermi wave vector, and where for vibrations in the $z$ direction we have

$$I_{0z} = e^{-2K_0a}(1+2K_0a) - (K_g/K_0)e^{-K_ga} , \tag{3.23}$$

$$I_{iz} = e^{-K_ga}/2 , \tag{3.24}$$

whereas for vibrations in the $x$-$y$ plane, we find

$$\vec{I}_{0_{\parallel}} = -i\frac{K_g}{K_0}[e^{-2K_0a}(1+K_0a) - e^{-K_ga}]\hat{K}_g , \tag{3.25}$$

$$\vec{I}_{i_{\parallel}} = -i(e^{-K_ga}/2)\hat{K}_g . \tag{3.26}$$

Since for most metals, at optical frequencies, $K_i + q_{\mathrm{FT}}/2$ and $k_F$ are approximately of the same order, (3.23) implies that for small molecular distances the dominant contribution comes from the first term in (3.23), when the vibrations are in the $z$ direction and the effective barrier height $\Phi_0 \ll \epsilon_F$, i.e., when $K_0 \ll K_i + q_{\mathrm{FT}}/2$. However, for large molecular distances and for vibrations parallel to $\hat{K}_g$, the contribution from the second term in (3.22), arising from the modulation of surface charges inside the metal, starts dominating the first term due to the modulation of the tunneled charge density outside the metal.

## IV. INTENSITIES OF STOKES SCATTERING

Now that we have a knowledge of the classical field distribution due to the light incident on a rough metal surface and also of the modulated-surface dipole moment, we are in a position to calculate both the direct CFE contribution and the MSDM contribution to the enhancement of Stokes scattering. If we agree to include the effect of the metal surface on the scattered Stokes field from the molecule in a separate exercise, the CFE contribution arising from the modulation of the molecular polarizability tensor $\overleftrightarrow{\alpha}$ by the enhanced surface-plasmon field can be calculated in the standard way. For each molecule, the scattered power per steradian due to this can be written in the usual form

$$\frac{dP_{sp}}{d\Omega}(\mathrm{CFE}) = \frac{\omega^4}{8\pi c^3}\left|\hat{e}_s \cdot \sum_j \frac{\partial\overleftrightarrow{\alpha}}{\partial\vec{R}_j} : \delta\vec{R}_j\vec{E}_g^P e^{-\Gamma_g|R_{jz}|}\right|^2 , \tag{4.1}$$

where $\hat{e}_s$ is the unit polarization vector of the scattered wave and $\vec{E}_g^P\exp(-\Gamma_g|R_{jz}|)$ is the enhanced surface-plasmon field at the molecular site. This result has to be modified by changing $\hat{e}_s$ to $\hat{e}_s \cdot \overleftrightarrow{G}_S$ to take account of the conversion of the near-zone Stokes field by the rough metal surface into the additional radiation field outside the metal. In general, the calculation of the near-zone Stokes field and its reflection and conversion to the outgoing radiation field by the metal surface is quite involved. However, for the case of a sinusoidal grating this additional tensorial enhancement factor $\overleftrightarrow{G}_S$ depends strongly on the angle of scattering, and except at those angles where the surface-plasmon field can couple out resonantly from the grating, it is still of order 1. In comparison to this, for an isolated molecule in the absence of the metal surface, one has the well-known result

$$\frac{dP}{d\Omega}(\text{isolated})=\frac{\omega^4}{8\pi c^3}\left|\hat{e}_s\cdot\sum_j\frac{\partial\overleftrightarrow{\alpha}}{\partial\vec{R}_j}:\delta\vec{R}_j\vec{E}_{\text{inc}}(\vec{R}_j,\omega)\right|^2 . \tag{4.2}$$

Thus, the net enhancement due to CFE can be written essentially as

$$F_{sp}(\text{CFE})\cong\left|\vec{E}_g^P e^{-\Gamma_g a}/\vec{E}_{\text{inc}}\right|^2|G_S|^2 , \tag{4.3}$$

where $a$ is the effective distance of the molecule from the metal surface, and where the expression for $\vec{E}_g^P$ in terms of $\vec{E}_{\text{inc}}$, $\epsilon_1(\omega)$, $\epsilon_2(\omega)$, and the roughness parameter $\xi_g K_g$ is given explicitly by (2.22) and (2.18).

Similarly, the expression for the modulated-surface dipole moment in terms of the derivative of the surface polarizability $\beta_{zz}$ immediately allows us to obtain the MSDM contribution to the Stokes power. For each molecule, we find

$$\frac{dP_{sp}}{d\Omega}(\text{MSDM})=\frac{\omega^4}{8\pi c^3}\left|(\hat{e}_s)_z\sum_j\left(\frac{\partial\beta_{zz}}{\partial\vec{R}_j}\right)\cdot\delta\vec{R}_j(E_{gz}'^P-E_{gz}^P)\right|^2 , \tag{4.4}$$

where $(\partial\beta_{zz}/\partial\vec{R}_j)$ is given by (3.21) or in a simplified form by (3.22)–(3.24). Compared to an isolated molecule, the enhancement due to MSDM then is of the order of

$$F_{sp}(\text{MSDM})\cong\left|\frac{\partial\beta_{zz}/\partial\vec{R}}{\partial\alpha_{si}/\partial\vec{R}}\right|^2\left|\frac{E_{gz}'^P-E_{gz}^P}{\vec{E}_{\text{inc}}}\right|^2 , \tag{4.5}$$

where in terms of $\sigma_{sp}^P$ and $\sigma_{sp}^S$ defined by (3.4) and (3.5)

$$E_{gz}'-E_{gz}=-4\pi e(\sigma_{sp}^P+\sigma_{sp}^S) . \tag{4.6}$$

The expression (4.5) contains two types of factors, one corresponding to the field enhancement arising from the resonant excitation of surface plasmons $[\text{Re}(\epsilon\Gamma_g+\gamma_g)=0]$, and the other corresponding to the ratio of the derivatives of the surface polarazibility and the molecular polarizability. The field-enhancement part is very similar to the CFE enhancement $F_{sp}(\text{CFE})$ of (4.3). However, if $(\partial\beta/\partial\vec{R})\gg(\partial\alpha/\partial\vec{R})$, the MSDM contribution can have an additional large enhancement factor as compared to the CFE contribution. A comparison of the expressions (4.1) and (4.4) also shows that the polarization properties of the MSDM contribution are quite different than that of the CFE contribution, which in turn may allow, in suitable cases, to separate them out experimentally.

On the *macroscopic* level, for spatially varying fields, Raman scattering arises from the modulation of the optically induced polarization in the system, which has the form

$$\vec{P}=\overleftrightarrow{\chi}\cdot\vec{E}+\overleftrightarrow{\vec{\beta}}':\vec{\nabla}\vec{E} , \tag{4.7}$$

where the second term is usually quite small in the bulk. However, near a metal surface,[22] $\vec{\nabla}\cdot\vec{E}$ is nonzero, and the normal component of $\vec{E}$ varies rapidly on the scale of a few Å. Our additional short-range MSDM contribution, in fact, comes from such a term on the *microscopic* level, with the dominant component of $\vec{P}$ having the symmetry determined by $\hat{n}\cdot\beta':\hat{n}\hat{n}$. Here $\hat{n}$ is the local normal unit vector for the arbitrary surface.

To investigate the relative importance of $F_{sp}(\text{CFE})$ and $F_{sp}(\text{MSDM})$, we use the simplified form of $(\partial\beta/\partial\vec{R})$ given by (3.22)–(3.26). Since $(\partial\alpha/\partial\vec{R})$ is of the order of $a_0^2$ where $a_0$ is the Bohr radius, we plot $[(\partial\beta/\partial\vec{R})/Z_{\text{eff}}a_0^2]^2$ in Figs. 2 and 3 as a function of the effective molecular distance, $a$, from the metal surface, for different values of the barrier heights $\Phi_0$. Other parameters are taken for Ag, with $\omega\cong 4\times10^{15}\ \text{sec}^{-1}$. Figure 2 corresponds to vibrations in the $z$ direction, whereas Fig. 3 is for the molecular vibrations in the $x$-$y$ plane in the direction of $\vec{K}_g$. Note the strong enhancement of $(\partial\beta/\partial\vec{R})_z$ for low barrier heights, when the distance $a$ is small. Using the same parameters, and with the incident angle $\theta_i=25°$, $\xi_g K_g\cong 0.2$, $\vec{K}_g\parallel\vec{k}_t$, and $\partial\alpha/\partial R\cong Z_{\text{eff}}a_0^2$, Fig. 4 shows the full enhancement factor $F_{sp}(\text{MSDM})$ at the exact surface-plasmon resonance for vibrations in the $z$ direction. Figure 5 gives a similar plot for $F_{sp}(\text{CFE})$ for compari-

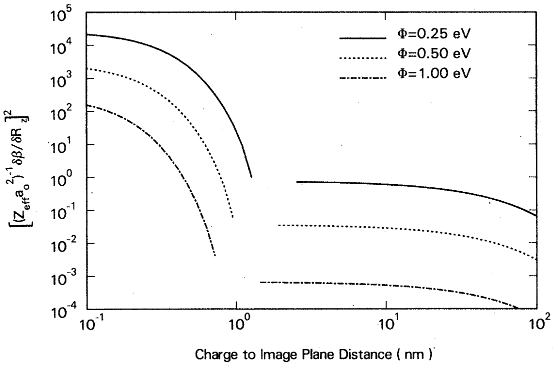

FIG. 2. A plot of the square of the surface polarizability derivative $\partial\beta/\partial R_z$ (in units of $Z_{\text{eff}}a_0^2$, $a_0$ = Bohr radius) against effective charge to image plane distance, $a$, for the molecule, for various effective barrier heights $\Phi_0$ (see text). This corresponds to molecular vibrations perpendicular to the $z=0$ plane. The minima due to interference between the short-range ($\sim e^{-2K_0 a}$) and the long-range ($\sim e^{-K_g a}$) terms in expression (3.23) have not been shown explicitly.

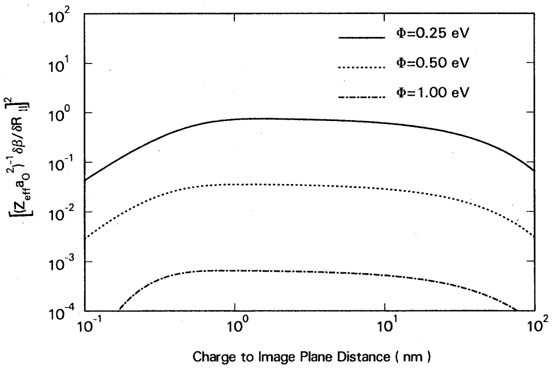

FIG. 3. Square of the surface polarizability derivative $\partial\beta/\partial R_{\parallel}$ (in units of $Z_{\text{eff}}a_0^2$) versus effective charge to image plane distance $a$, for various effective barrier heights $\Phi_0$. Note that there is no short-range enhancement in this case, corresponding to molecular vibrations in the $x$-$y$ plane.

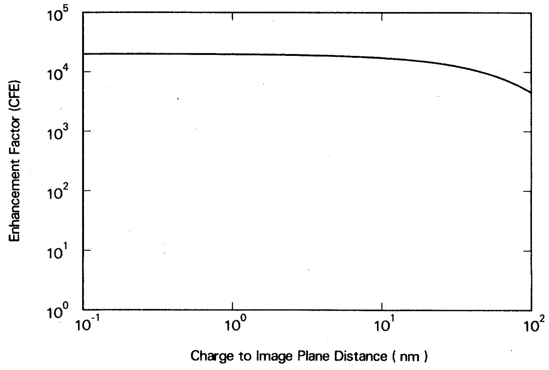

FIG. 5. The classical field enhancement factor $F_{sp}$(CFE) as a function of effective charge to image plane distance $a$, at exact surface-plasmon resonance for Ag, with incident photon energy 2.34 eV, grating periodicity 800 nm, $\vec{g}\|\hat{k}_t$, and $\xi_g K_g = 0.2$. The result is for those scattering angles for which the Stokes field surface conversion factor $G_S \cong 1$. For $\xi_g K_g \ll 1$, the enhancement factors $F_{sp}$(CFE) and $F_{sp}$(MSDM) vary as $\xi_g^2 K_g^2$. However, plotted enhancement factors in Figs. 4 and 5 are overestimates since smooth thin-film optical constants (Ref. 25) were used: rough, doped surfaces are more lossy than clean smooth ones.

son, with scattering angles such that $|G_S^2| \simeq 1$. For low barrier heights and small distances, $F_{sp}$(MSDM) is much larger than $F_{sp}$(CFE). However, at large distances $F_{sp}$(CFE) gives the dominant contribution.

For Cu, Ag, and Au, the frequency dependence of the enhancement factor $F_{sp}$(CFE) at exact surface-plasmon resonance is plotted in Fig. 6, using available bulk optical constants for each case. The result is for an 800-nm grating periodicity, with $\vec{g}\,\|\,\hat{k}_t$ and $G_s \cong 1$. Except for minor differences, one gets very similar curves for the frequency dependence of $F_{sp}$(MSDM). It is clear that the maximum enhancement is smaller in Au and Cu than in Ag. In all these metals, enhancement decreases rapidly when the surface-plasmon mode ceases to exist.

Before we conclude this section, it is important to point out that while comparing expressions (4.4) and (4.2), the vibration amplitudes $\delta\vec{R}_j(t)$ were tacitly assumed to be approximately the same for isolated molecules and molecules adsorbed at the metallic surface. Since in the Raman process under consideration, $\delta\vec{R}_j(t)$ is inversely

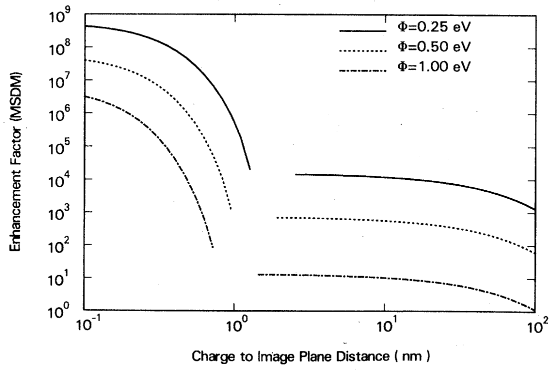

FIG. 4. The enhancement factor $F_{sp}$(MSDM) due to the modulation of the induced surface dipole moment, as a function of effective charge distance $a$, at exact surface-plasmon resonance. The results are for Ag, for various effective surface barrier heights $\Phi_0$, with molecular vibrations perpendicular to the $z=0$ plane, 2.34 eV incident photon energy, 800-nm grating periodicity, $\vec{g}\|\hat{k}_t$, and $\xi_g K_g = 0.2$. For definiteness, smooth thin-film optical constants[25] for Ag have been used and the isolated molecular polarizability derivative $\partial\alpha/\partial R_z$ is taken to be $Z_{\text{eff}}a_0^2$ ($a_0$ = Bohr radius).

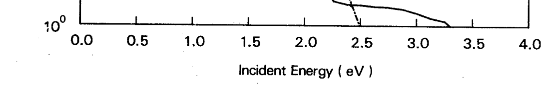

FIG. 6. Relative variation of classical field enhancement factors $F_{sp}$(CFE) for Cu, Ag, and Au as a function of incident photon energy, for an 800-nm grating periodicity. Again, we have assumed exact surface-plasmon resonance conditions, smooth thin-film optical constants, and $G_S = 1$. Similar frequency dependence is obtained for $F_{sp}$(MSDM).

proportional to the square root of the molecular vibration frequency $\omega_0$, this implies that we are assuming only small changes in the ion-ion interaction in the molecule and the corresponding force constants, even in the presence of additional electronic charge density due to the tunneling of the conduction electrons. The induced charge density [given by (3.1), as modified by (3.6)], associated with the induced surface dipole moment, is oscillating rapidly with the incident light frequency, $\omega$, to affect the screening of the ion-ion interaction in the molecule. But our model also implies additional nonresonant static electronic charge density at the molecular site, due to the tunneling. Can this change the force constants and vibration frequencies appreciably? Experimentally, one finds very small vibration frequency shifts, as observed by using Raman spectroscopy. This is also true for observations involving inelastic electron-tunneling spectroscopy, where a theoretical model[20] similar to ours is used for conduction electron-molecule interaction to analyze the intensities. Whereas, the additional tunneled electron density between the molecule and the surface is important in determining the equilibrium distance of the molecule from the metal surface, in shifting the molecular electronic levels, and in giving the metal-molecule coupling, we believe it does not lead to any drastic changes in the screening of the already short-range ion-ion interaction *inside* the molecule. Similarly, except for any accidental resonance with respect to the incident light frequency, the intrinsic electron polarizability of the molecule should not change by a very large factor, due to shifts in its electronic energy levels. However, to establish the theoretical validity of our model on a firmer ground, it would be necessary to perform a self-consistent calculation of all these effects simultaneously.

## V. DISCUSSIONS

In the preceding sections we have developed a phenomenological model to calculate the intensity of Stokes-scattered light from molecules adsorbed at a rough metal surface, when transverse surface plasmons are excited resonantly by the incident light. While we explicitly derived the expressions for the scattering intensity when only one spatial Fourier component of surface roughness is present, in the linear theory under consideration, the complete expression can be obtained readily by a simple superposition of our results for different periodicities $\vec{g}$. For the resonant excitation of the surface plasmons of frequency $\omega$, only a narrow band of spatial components will in fact contribute to the enhanced intensity. However, for random surface roughness, unlike the case of a sinusoidal grating, the scattered intensity will no longer be a strong function of the incident angle $\theta_i$, since there will always be a finite possibility of finding an appropriate $\vec{g}$ for resonant excitation of the surface plasmons of frequency $\omega$ and wave vector $|(\omega/c)\sin\theta_i \hat{k}_t + \vec{g}|$. Of course, the corresponding roughness amplitude $\xi_g$ has to be appreciable for a large enhancement.

We would like to emphasize here that our linear approximation for calculating induced secondary fields near a metal surface will break down when the Fourier amplitude $\xi_g$ of the surface roughness becomes large compared to the wavelength of light. As $\xi_g$ increases, we must correct for the depletion of the fundamental Fresnel fields of Sec. II, and for the creation of higher-order secondary waves with wave vectors $\vec{k}_t \pm 2\vec{g}$, $\vec{k}_t \pm 3\vec{g}$, etc. Since in the lowest approximation this correction is of the order $\xi_g^2 K_g^2$, with increasing $\xi_g K_g$ the amplitude of the surface-plasmon fields of Sec. II will saturate according to the expression $\xi_g K_g/(1 + B\xi_g^2 K_g^2)$, where $B$ is of the order 1. Thus, our surface-plasmon model predicts a resonant enhancement of the Raman cross section varying as $\xi_g^2 K_g^2$, for $\xi_g K_g \ll 1$, with a maximum for $\xi_g K_g \cong 1$. For $\xi_g > c/\omega$, one has to consider exact geometrical shapes of the bumps on the metal surface to calculate the field distribution. However, the problem can be tackled only for very simple shapes and isolated bumps.[12,23]

Apart from the introduction of standard phenomenological quantities such as the molecular polarizability $\tilde{\alpha}$, bulk metallic density $n$, and the complex dielectric function $\epsilon(\omega)$, in our model we also introduced the effective surface barrier heights $\Phi_0$ for the conduction electron tunneling to the molecular site and the effective partial ionic charges in the molecule and their positions with respect to the metal surface. This was necessary because, for distances comparable to the molecular size, the interaction of the induced metallic charge density with the molecule could not be treated using classical methods involving the concept of a point molecular polarizability and a sharp cutoff for the metallic dielectric function. In this sense, our additional contribution due to the modulation of surface polarizability is related to the classical calculation[4,6] of the enhancement of the molecular polarizability $\tilde{\alpha}$ due to the presence of the metal surface. But our calculation shows that this additional polarizability contribution has a symmetry different from that of $\partial\tilde{\alpha}/\partial\vec{R}$, and that for the first few monolayers it depends considerably on the surface barrier height $\Phi_0$, i.e., on the overlap of the induced surface charge density with the molecular charges. It has already been recognized by most workers that to explain large enhancements of the Raman cross sections, both the classical field enhancement (our CFE contribution) and the polarizability enhancement may be necessary.

It should be noted that in our model, there is a finite MSDM contribution even in the absence of surface roughness, if we keep the first term in (3.2) for the induced surface charge density. This is related to a similar contribution already discussed earlier by McCall and Platzman.[8] It can indeed become appreciable for small $\Phi_0$, but in the absence of resonant field enhancement in this case, it is not enough to explain observed Raman cross sections.

Our quantitative results for the scattering intensity can be tested experimentally in a variety of ways. In fact, many of the crucial predictions of our model (e.g., dependence of the intensity on the incident scattering angle $\theta_i$, frequency $\omega$, and grating amplitude $\xi_g$) are consistent[16] with the experimental observations of Tsang *et al.*[2,16] on tunnel junction grating structures. Nevertheless, for a direct quantitative check it will be necessary to do extensive controlled experimentation on molecules adsorbed on a single thick sinusoidal grating[24] of different metals. This is now underway. Reliable values for the other phenomenological parameters have also to be obtained independently for the same samples. Smooth thin-film optical constants used here from the available data[25] may not be completely relevant for a rough metal surface with adsorbed molecules.

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