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Enhanced Raman Scattering by Adsorbates Including the Nonlocal Response of the Metal and the Excitation of Nonradiative Modes

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The enhanced Raman scattering from a molecule adsorbed on a metal surface is calculated by use of classical electrodynamics. The metal response function is modeled with a local interband term plus a nonlocal free-electron term. The important effects are the image enhancement of the effective dipole and the roughness coupling of the near fields of the dipole and its image. These combine to give estimated gains $\approx 10^6$.

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A number of molecules adsorbed on certain noble-metal surfaces show Raman scattering cross sections exceeding their nominal values by 10^5–10^6. Submicroscopic roughness is needed to observe the effect, and the dependence upon pump and Raman frequencies is weak.[1-8] The explanations for this surface-enhanced Raman (SER) effect which have been offered to date are not, in our opinion, sufficiently convincing regarding the treatment of the metallic response.[9-12] In this Letter we show that the SER effect can be understood in terms of the classical electromagnetic interaction of a dipole with the metal. We distinguish three aspects of this interaction: an enhanced effective polarizability due to image effects, strong emission into nonradiative surface waves, and surface-roughness–coupled emission driven by the near fields of the dipole and its image. The last two aspects are closely related since the near fields also couple into the nonradiative waves. Image effects have previously been considered by neglecting spatial dispersion in the metal response,[9,12] an approximation that is not valid, since the local field is evaluated at a point ~1 Å from the metal. We model $\epsilon(\omega,\vec{k})$ of the metal with a k-independent interband term plus a k-dependent free-electron term. We give an exact calculation for a point dipole above a smooth surface. We then show that finite molecular size and zero-point motion reduce the image enhancement, resulting in a maximum SER gain of $\sim 10^3$. Finally we show that the power radiated on a roughened surface is increased by a factor of $\sim 10^3$ over that on a smooth surface; thus an overall SER gain of $\sim 10^6$ can occur.

We consider a molecule a distance d from the metal in a medium of real dielectric constant ϵ_1. The molecule is oriented in the direction $\hat{z}$ normal to the metal surface and has polarizibility α. The applied electric field is $\hat{z}E_0\exp(-i\omega_0 t)$. The generalization to arbitrary orientations of the molecule and applied field is straightforward,[12] but the simple geometry we choose shows the essential features of our model.

The dipole induced at ω_0 is given by

$$\vec{\mu}(\omega_0) = \alpha(E_0 + E_r)\hat{z}, \tag{1}$$

where E_r is the reflected dipolar electric field, given by[13-15]

$$E_r = \mu(\omega_0)F(\omega_0,d), \tag{2}$$

$$F(\omega_0,d) = \int_0^\infty dp\, \frac{p^3}{\epsilon_1 q_1} r_{12} e^{-2q_1 d}, \tag{3}$$

$q_1 = (p^2 - \epsilon_1\omega^2/c^2)^{1/2}$, and r_{12} is the amplitude reflection coefficient for p-polarized light. Solving (1) and (2) for $\mu(\omega_0)$, we obtain

$$\mu(\omega_0) = [1 - \alpha F(\omega_0,d)]^{-1}\alpha E_0. \tag{4}$$

The dipole induced at the Raman shifted frequency ω_R by the molecular vibration will be proportional to $\mu(\omega_0)$ with the same proportionality constant c_R that would apply in the absence of the metal. As in (1), there is a reflected field term; so the dipole at ω_R must satisfy

$$\mu(\omega_\mathrm{R}) = c_\mathrm{R}\mu(\omega_0) + \alpha E_r(\omega_\mathrm{R}), \tag{5}$$

where $E_r(\omega_\mathrm{R})$ is given by (2) and (3) with ω_0 replaced by ω_R. The resulting dipole at ω_R is then

$$\mu(\omega_\mathrm{R}) = \frac{c_\mathrm{R}\alpha E_0}{[1 - \alpha F(\omega_0,d)][1 - \alpha F(\omega_\mathrm{R},d)]}. \tag{6}$$

The time-averaged total power *dissipated* at ω_R is

$$P_{\text{tot}}(\omega_R) = -\tfrac{1}{2}Rl[\dot{\vec{\mu}}(\omega_R)^* \cdot \vec{E}(\omega_R)], \tag{7}$$

where $\vec{E}(\omega_R)$ is the dipolar field evaluated at the dipole. The reflected field is given by (2) with ω_0 replaced by ω_R, and we obtain

$$P_{\text{tot}}(\omega_R) = \tfrac{1}{2}\omega_R |\mu(\omega_R)|^2 \,\text{Im}\int_0^\infty dp \frac{p^3}{\epsilon_1 q_1}(1 + r_{12}e^{-2q_1 d}). \tag{8}$$

In this formula, three major mechanisms for dissipation can be identified: $P_{\text{tot}} = P_{\text{photon}} + P_{\text{SP}} + P_{\text{DSM}}$, where P_{photon} is the radiated power corresponding to the range $0 < p < \epsilon_1^{1/2}\omega/c$; P_{SP} is the power emitted into surface plasmons, corresponding to the *pole* in r_{12} at $p \simeq [\epsilon_1\epsilon_2/(\epsilon_1+\epsilon_2)]^{1/2}\omega/c$ (here ϵ_2 is the local dielectric constant of the metal); and P_{DSM} is the power emitted into the *continuum* of driven surface modes, corresponding to the range $\epsilon_1^{1/2}\omega/c \ll p \lesssim d^{-1}$. For a smooth surface only the first mechanism is observed and the total Raman intensity is given by Eq. (8) with the upper limit of integration $p = \epsilon_1^{1/2}\omega/c$. Dividing this by the corresponding expression in the absence of the metal [$r_{12} = 0$ in (6) and (8)] gives the gain:

$$G_R = \frac{1}{|1-\alpha F(\omega_0,d)|^2}\,\frac{1}{|1-\alpha F(\omega_R,d)|^2}\left[1 + \frac{3c^3}{2\omega^3}\,\frac{1}{\epsilon_1^{3/2}}\,\text{Im}\int_0^{\epsilon_1^{1/2}\omega/c} dp\frac{p^3}{q_1} r_{12}e^{-2q_1 d}\right]. \tag{9}$$

In deriving (9) we have neglected several factors of order unity which have to do with averaging over molecular orientations and correcting the applied field and the radiated power for the metal reflectivity.

For the reflection coefficient, we use the result of Kliewer and Fuchs,[16]

$$r_{12}(p) = (q_1 - \epsilon_1 Z_{12})/(q_1 + \epsilon_1 Z_{12}), \tag{10}$$

where

$$Z_{12}(p) = \frac{2}{\pi}\int_0^\infty \frac{dq}{k^2}\left(\frac{p^2}{\epsilon_l} + \frac{q^2}{\epsilon_t - c^2k^2/\omega^2}\right), \tag{11}$$

$k^2 = p^2 + q^2$; and the nonlocal transverse and longitudinal dielectric functions of the metal are given by the Lindhard formulas modified for a finite relaxation time[17]:

$$\epsilon_t(\omega,k) = \epsilon_b(\omega) - \frac{\omega_p^{\,2}}{\omega(\omega+i\nu)}f_t, \tag{12}$$

$$\epsilon_l(\omega,k) = \epsilon_b(\omega) + \frac{(\omega+i\nu)3\omega_p^2 f_l/k^2 v_F^{\,2}}{\omega + i\nu[f_l/(f_l)_{u=0}]}, \tag{13}$$

where ω_p is the plasma frequency, ν^{-1} is the electron scattering time, v_F is the Fermi velocity, and f_t and f_l are given in Ref. 17. We have added a local term ϵ_b to represent the bound electron contributions. The optical $\epsilon_2(\omega)$ for Ag is fit in the region 450–700 nm by the $k=0$ limits of (12) and (13) by use of $\hbar\omega_p = 9.33$ eV, $\hbar\nu = 0.58$ eV, and $\epsilon_b = 3.6$.[18]

In the expression (9) for the smooth surface gain, the dominant factors are those associated with the image enhancement of the induced dipole. This enhancement will be large only when $\text{Im}(F) \ll \text{Re}(F) \cong \alpha^{-1}$ at both ω_0 and ω_R. In practice, the Raman shifts are small enough and the ω dependence is slow enough that $F(\omega_0,d) \cong F(\omega_R,d)$. The condition $Rl(F) = \alpha^{-1}$ thus determines the optimum d value, and $G_{R,\max} \approx [\text{Re}(F)/\text{Im}(F)]^4$ gives the gain at this distance.

In Fig. 1 we show computed results of F vs d for Ag at 633 nm with $\epsilon_1 = 1$. The solid curves

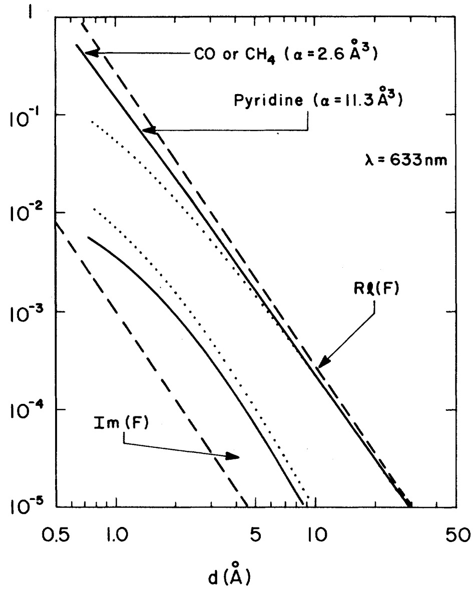

FIG. 1. The local-field function $F(\omega,d)$, Eq. (3), for Ag. The solid curves are calculated with spatial dispersion and an interband term, the dashed curves neglect spatial dispersion, and the dotted curves neglect the interband term.

correspond to the model described above; the arrows near the top indicate points at which $\mathrm{Re}(F) = \alpha^{-1}$ for CO or pyridine adsorbed in upright orientations.[19] The dashed straight lines are for the local limit,[12]

$$F_{\mathrm{loc}}(\omega, d) = (4\epsilon_1 d^3)^{-1}(\epsilon_2 - \epsilon_1)/(\epsilon_2 + \epsilon_1). \tag{14}$$

The dotted curves are obtained by treating the metal as a truly free-electron plasma with $\epsilon_b = 1$ and by adjusting ω_p and ν so that the $k = 0$ limit, $\epsilon_2(\omega)$, is reproduced. These curves show that much smaller SER gains will occur when $\epsilon_b = 1$. This results from the complete screening of the free-electron response at large p, giving $r_{12} \to (\epsilon_b - \epsilon_1)/(\epsilon_b + \epsilon_1)$, which equals zero if $\epsilon_b = \epsilon_1 (=1)$. For Cu and Au a sizable nonzero value for $\epsilon_b - 1$ is also required to fit the optical data, and calculations at 633 nm for these metals predict gains and optimum distances similar to those for Ag. At shorter wavelengths, however, the onset of d-band transitions in Cu and Au gives large values for $\mathrm{Im}(\epsilon_b)$, which significantly reduces the gains.

Numerical results are summarized in Table I. The local approximation gives maximum gains about 10^2 larger at $d = 1.5$ Å. Although the maximum gains shown are very large, they apply only to a point dipole, which is a rather serious restriction, considering that the d values of interest are comparable to molecular sizes. As a means of modeling the finite-size effects, we have extended the above calculations to treat a dielectric sphere of finite radius.[20] For spheres of radii 1.6–1.8 Å with $\alpha = 11.3$ Å^3, we find that the gain peaks when the sphere nearly (10^{-3} Å) touches the surface, the peak height is reduced by 10^{-1}–10^{-2}, and the peak width is (surprisingly) narrowed ($\sim 10^{-3}$ Å). This width is, in fact, much less than the zero-point motion of the molecule vibrating against the surface [$\sim (1-5)\times 10^{-2}$ Å]. The image enhancement gain must be further reduced by the ratio of the peak width to the zero-point motion. The overall effect of finite size is a reduction of the smooth-surface gains in Table I by a factor of 10^{-3}. Furthermore, we find there is no strong ω dependence in the gain.

The last two columns of Table I give the ratios of the power dissipated via surface plasmons and driven surface modes to the directly radiated power. These ratios are independent of the image effects and have no sharp d dependence. Clearly the driven surface modes dominate! The surface-plasmon contribution can be calculated using the local approximation for $r_{12}(p)$.[15,21] On the other hand, the contribution of the driven surface modes, which comes mainly from values of $p \lesssim d^{-1}$ in Eq. (8), is due primarily to electron-hole excitations, which are completely neglected in a local description.[22]

TABLE I. Computed results for pyridine on Ag. The parameters are $\epsilon_b = 3.6$, $\epsilon_1 = 1$, $\hbar\omega_p = 9.33$ eV, $\hbar\nu = 0.58$ eV, $v_F = 1.4\times 10^8$ cm/s, $k_f = 1.2\times 10^8$ cm^{-1}, $\alpha = 11.3$ Å^3, and a Raman shift of 1000 cm^{-1}. The last two columns give the ratios of the surface-plasmon and driven-surface-mode emission to free photon radiation.

$\hbar\omega_0$ (eV)	d (Å)	$G_{\mathrm{R,max}}$	$P_{\mathrm{SP}}/P_{\mathrm{photon}}$	$P_{\mathrm{DSM}}/P_{\mathrm{photon}}$
1.96	1.23	1.9×10^6	1.7	3.4×10^6
2.41	1.24	7.7×10^5	2.7	2.5×10^6
2.60	1.24	5.6×10^5	3.3	2.3×10^6

The fields associated with the driven surface modes are the near fields of the dipole and its image. The electron-hole excitations are effective at coupling power out of these near fields, but that power remains in the metal. Surface roughness provides a mechanism for coupling the power in the near fields directly into observable radiation.

We describe the surface roughness by a polarizability per unit area, $h(\vec{\rho})$, which has a Gaussian correlation $\langle h(\vec{\rho})h(\vec{\rho}\,')\rangle = \langle h^2\rangle \exp(-|\vec{\rho} - \vec{\rho}\,'|^2/a^2)$, with $\langle h^2\rangle^{1/2}$, $a \ll \lambda$.[23] The current density induced by the dipolar fields is

$$\vec{j}(\vec{r}) = -i\omega h(\vec{\rho}) E_z(\vec{\rho})\delta(z)\hat{z}, \tag{15}$$

where for brevity we consider only the normal component of $\vec{E}$. When the molecule is close to the surface, the electric field at the surface is localized in the near zero. This means that for the long-wavelength emission this current is pointlike and the power is given by analogy to (8) with $d = 0$:

$$P_{\mathrm{rough}} = \tfrac{1}{2}\omega_{\mathrm{R}} \int d^3\rho \int d^3\rho' \langle h(\vec{\rho})h(\vec{\rho}\,')\rangle E_z^*(\vec{\rho}\,') \,\mathrm{Im}\int_0^{p_{\max}} dp\,(p^3/\epsilon_1 q_1)(1 + r_{12}), \tag{16}$$

where $p_{\max}$ is chosen to be slightly above the surface-plasmon pole. Since $p_{\max} d \ll 1$, we see from (8) that

$$P_{\mathrm{rough}} = (P_{\mathrm{photon}} + P_{\mathrm{SP}})\,|\mu(\omega_{\mathrm{R}})|^{-2} \int d^3\rho \int d^3\rho' \,\langle h(\vec{\rho})h(\vec{\rho}\,')\rangle E_z^*(\vec{\rho}) E_z(\vec{\rho}\,'). \tag{17}$$

This is the power emitted into free photons and surface plasmons by roughness coupling of the near fields. The surface plasmons, being high-Q propagating modes, will ultimately be scattered into observable radiation by roughness and, hence, the total gain due to roughness is

$$G_{\mathrm{rough}} = (P_{\mathrm{photon}} + P_{\mathrm{SP}} + P_{\mathrm{rough}})P_{\mathrm{photon}}^{-1}. \tag{18}$$

The dipolar electric field on the surface is given by[14]

$$E_z(\vec{\rho}) = \frac{\mu(\omega_{\mathrm{R}})}{2\pi}\int d^3p\, e^{i\vec{\mathrm{p}}\cdot\vec{\rho}}\frac{p^2}{\epsilon_1 q_1}(1+r_{12})e^{-q_1 d}. \tag{19}$$

Using (17)–(19) with the Gaussian correlation, we find

$$G_{\mathrm{rough}} = \frac{P_{\mathrm{photon}} + P_{\mathrm{SP}}}{P_{\mathrm{photon}}}\left(1 + \frac{2\pi^2 a^2\langle h^2\rangle}{\epsilon_1^{\,2}}\int_0^\infty dp\,\frac{p^5}{q_1^{\,2}}\,|1+r_{12}|^2 \exp(-2q_1 d - \tfrac{1}{4}a^2p^2)\right). \tag{20}$$

If we now assume that $h(\vec{\rho}) = [(\epsilon_2 - \epsilon_1)/(\epsilon_2 + 2\epsilon_1)]\,\xi(\vec{\rho})$, with $\langle \xi^2\rangle = a^2$ and $a \gg d$ (which corresponds to boss-like surface structures), we find that $G_{\mathrm{rough}} = 2\times10^3$ for the parameters at 633 nm in Table I. Although the roughness coupling produces a sizable increase in the observed radiation, it is extremely inefficient (10^{-3} compared to the electron-hole excitations) at coupling energy out of the near fields.

We conclude that the SER gain on a highly roughened surface will be a product of two factors, the image enhancement and the roughness gain, each of which is ~10^3, resulting in an overall gain of ~10^6. The first factor requires direct contact of the molecule with the metal, while the second is long range, ~10^2 Å.

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