

SURFACE SCIENCE LETTERS

**ELECTROMAGNETIC EFFECTS IN THE SURFACE ENHANCED RAMAN
SCATTERING FROM A MOLECULE AT A LIQUID Hg SURFACE**

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In a previous publication the image enhancement effect and the enhanced radiation due to near field excitation of surface roughness were calculated for a finite-size molecule above a metal described by a nonlocal dielectric relation [Phys. Rev. Letters 44 (1980) 1774]. When applied to a roughened Ag surface these calculations led to a predicted Surface Enhanced Raman Scattering (SERS) gain of $\sim 10^3$ due to each effect, yielding an overall gain $\sim 10^6$, in agreement with experiment. Here these calculations are extended to the case of a liquid Hg surface, the roughness corresponding to thermally excited ripples. The SERS gain due to image enhancement is reduced to ~ 10 , due primarily to the ~ 24 times greater electron scattering rate in Hg over that in Ag. The roughness gain is reduced to ~ 2 at room temperature, due to the difference between the ripplon spectrum and that of the boss-like surface structures assumed for the solid surface. The predicted overall SERS gain for Hg is ~ 20 , far less than reported in recent observations [R. Naanan et al., J. Phys. Chem. 84 (1980) 2692]. The discrepancy raises serious questions about the electromagnetic explanations of SERS.

In a recent paper we discussed the image enhancement effect and power radiation above a smooth metal surface, including the effects of nonlocal response of the metal and finite molecular size [1]. The image enhancement effect was found to be much reduced below that predicted for a point polarizable molecule above a local metal, both finite size and nonlocality being important. Treating the molecule as a polarizable point above a nonlocal metal, as has been done now by several authors [1–5], still overestimates the enhancement. Using parameters appropriate for Ag it was shown that the image enhancement gain for surface enhanced Raman scattering (SERS) could reasonably be expected to be as large as 10^3 . In an earlier paper we showed how the coupling out of the near field of the dipole by a suitably roughened surface could lead to an additional gain as large as 10^3 , the combined effects giving a net gain of order 10^6 , in agreement with the observations on roughened Ag surfaces [2]. Recently SERS gains as large as 10^4 – 10^6 have been reported for

molecules adsorbed on liquid-Hg surfaces [6], and we wish to report here the extension of our calculations to this case. The principle differences between a liquid-Hg surface and a roughened Ag surface, from our point of view, are the much increased electron scattering rate in Hg and the fact that a liquid surface is not roughened. In the next section we describe the results of our calculation of the smooth-surface image enhancement gain for Hg. We find that this gain for the dielectric-sphere model is reduced below that for Ag by about two orders of magnitude. In the third section we calculate the coupling out of the near field by the roughness associated with capillary wave fluctuations on the liquid surface. The result is a predicted roughness gain of ≈ 2 . The net predicted gain is ≈ 20 . The conclusion is that the experimental results for liquid-Hg surfaces cast serious doubt on the electromagnetic explanations of SERS.

In ref. [1] the nonlocal response of the metal surface is described by the semi-classical infinite-barrier model with the bulk metal response given by the Lindhard dielectric relation extended to include the effects of finite electron scattering rate and a phenomenological core polarization. The necessary parameters of this model are the plasma frequency ω_p , the Fermi momentum k_F , the Fermi velocity v_F , the electron scattering rate ν , and the core polarization term ϵ_b . For the case of Hg we determine the first three parameters assuming an electron density corresponding to two electrons per atom and a mass equal to the free electron mass, giving

$$\hbar\omega_p = \hbar(4\pi n e^2/m)^{1/2} = 10.6 \text{ eV}, \quad (1a)$$

$$k_F = (3\pi^2 n)^{1/3} = 1.34 \times 10^8 \text{ cm}^{-1}, \quad (1b)$$

$$v_F = \hbar k_F/m = 1.55 \times 10^8 \text{ cm s}^{-1}. \quad (1c)$$

We determine the last two parameters by fitting the optical data in the visible region, giving $\epsilon_b = 2$, $\hbar\nu = 1.37 \text{ eV}$ [7].

Again in ref. [1], the finite molecular size is characterized by the multipole polarizabilities. There it is argued that a reasonable simple physical model of the molecule for the calculation of these polarizabilities is that of a dielectric sphere. In this case the parameters to be fitted are the usual (dipole) polarizability α , of the molecule and the molecular radius a .

In fig. 1 we plot the image enhancement gain for molecules above a smooth non-local metal surface as a function of the distance d of the molecular center from the surface. The applied electric field has been taken perpendicular to the surface, the parallel orientation gives similar results. The solid curves are for Hg, the dashed curves are for Ag. For the point-dipole model the principle differences are a broadening and consequent reduction of the maximum of the gain peak for Hg, due to the increased electron scattering rate ($\nu_{\text{Hg}} \approx 24\nu_{\text{Ag}}$), and a shift of the peak to smaller distances, due to the smaller core-polarization term. For the dielectric sphere model the radius has been arbitrarily chosen to be $a = 1.6 \text{ \AA}$. In both cases the gain peak is shifted to just outside the molecular radius, i.e. the molecule is nearly touching the surface at maximum gain. As shown in ref. [1], the zero point

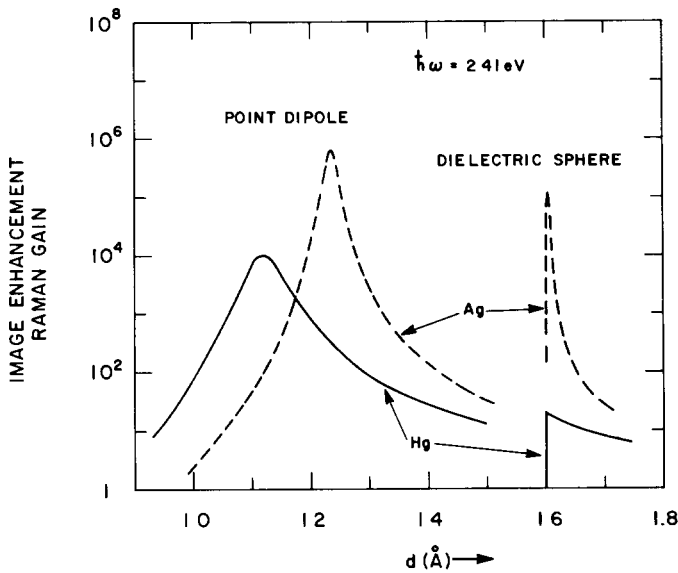


Fig. 1. Smooth-surface image enhancement gain plotted versus the spacing of the molecule from the metal surface. The gain is calculated according to eq. (75) of ref. [1]. The curves on the right are for a 1.6 Å radius sphere, those on the left for a point-dipole molecule. In both cases the free molecular polarizability is $\alpha = 11.3 \text{ \AA}^3$, corresponding to pyridine adsorbed in an upright orientation. The frequency shown is the pump frequency, a Raman shift of 1000 cm^{-1} was assumed.

motion of the molecule against the surface requires that the gain peak must be averaged over distances $\Delta d \approx 0.1 \text{ \AA}$. For the Ag surface the averaging substantially reduces the peak gain but still leaves a gain $\approx 10^3$. For the Hg surface, because of the large width of the gain peak, the reduction is less, but the peak gain is itself small so the gain ≈ 10 . We conclude, therefore, that the smooth surface image enhancement gain for Hg is about two orders of magnitude below the value for Ag.

In this connection we should comment upon a calculation by Efrima and Metiu of the image enhancement gain for a point-dipole molecule above a metal described by its local optical dielectric constant $\epsilon(\omega)$ [8]. They gave numerical results which indicated comparable gains for Hg and Ag and which were noted in ref. [6]. In fact for this model, because of the large imaginary part of $\epsilon(\omega)$ for Hg, the gain for Hg is 2–3 orders of magnitude below that for Ag (the exact value depends upon assumptions about positional averaging). This discrepancy apparently arose from a misreading of a confusing figure in ref. [7].

In ref [2] we calculated the power emitted by roughness features on a solid metal surface which are driven by the local field of the dipole. Although the liquid Hg surface is on the average smooth, on the time scale of the optical field there will be fluctuations of the surface associated with capillary waves (ripples) and pho-

nons. As we shall show below, these fluctuations are predominantly long-wavelength and low-amplitude. We therefore use a slightly different formulation from that of ref. [2], where the roughness was viewed as corresponding to boss-like surface structures. A similar formulation for small amplitude surface structures has been given by Aravind and Metiu [9]. The current density associated with fluctuations of the surface is [10]

$$\mathbf{j}(\mathbf{r}) = -i\omega \frac{\epsilon(\omega) - 1}{4\pi} \mathbf{E}(\boldsymbol{\rho}) u(\boldsymbol{\rho}) \delta(z), \quad (2)$$

where $\mathbf{E}(\boldsymbol{\rho})$ is the smooth-surface dipolar field just within the metal, $\epsilon(\omega)$ is the optical dielectric constant of the metal, $u(\boldsymbol{\rho})$ is the surface height above the mean, and

$$\mathbf{r} = \boldsymbol{\rho} + z\hat{z}. \quad (3)$$

The medium above the surface has been taken to be vacuum. The source of the fields is an oscillating dipole $\boldsymbol{\mu}$ with time dependence $\exp(-i\omega t)$ placed just above the surface. Since the time scale of the surface fluctuations is slow compared with the optical frequency ω , we neglect the time dependence of the height $u(\boldsymbol{\rho})$. The field and current have therefore the same time dependence $\exp(-i\omega t)$ which is not displayed in (2). As in ref. [2], we argue that when the dipole is near the surface the field $\mathbf{E}(\boldsymbol{\rho})$ is localized in the near zone. This means that for optical emission, for which the wavelength is long, the current (2) is pointlike and corresponds to an effective dipole,

$$\boldsymbol{\mu}_{\text{eff}} = \frac{\epsilon(\omega) - 1}{4\pi} \int d\boldsymbol{\rho} \mathbf{E}(\boldsymbol{\rho}) u(\boldsymbol{\rho}), \quad (4)$$

placed at the surface. If for simplicity we assume the field applied to the molecule is perpendicular to the surface, then for a molecule close to the surface $\mathbf{E}(\boldsymbol{\rho}) \approx E_z(\boldsymbol{\rho})\hat{z}$ and $\boldsymbol{\mu}_{\text{eff}}$ is oriented perpendicular to the mean surface. In this case the optical power radiated is

$$P_{\text{rough}} = \frac{1}{2} \omega \langle \boldsymbol{\mu}_{\text{eff}}^* \boldsymbol{\mu}_{\text{eff}} \rangle \text{Re} \int_0^{\omega/c} dp \frac{p^3}{q_1} (1 + r_{12}^p), \quad (5)$$

where in the integrand

$$q_1 = (\omega^2/c^2 - p^2)^{1/2}, \quad (6)$$

and r_{12}^p is the Fresnel reflection coefficient for P-polarized light. In eq. (5) we have omitted the power radiated into surface plasmons since on Hg, unlike Ag, the damping of these modes is so strong that only a negligible fraction of them will be successfully reradiated by roughness before being absorbed in the metal. The brackets $\langle \dots \rangle$ indicate the statistical average over the roughness. The power directly radiated by the molecular dipole is given by the same formula (5) with $\boldsymbol{\mu}_{\text{eff}}$ replaced

by μ and no statistical average. The roughness gain is therefore

$$G_{\text{rough}} = 1 + \langle \mu_{\text{eff}}^* \mu_{\text{eff}} \rangle / |\mu|^2 \tag{7}$$

The statistical average in (7) can be written, using (4),

$$\langle \mu_{\text{eff}}^* \mu_{\text{eff}} \rangle = \left| \frac{\epsilon(\omega) - 1}{4\pi} \right|^2 \int d\mathbf{p} \int d\mathbf{p}' E_z(\mathbf{p})^* E_z(\mathbf{p}') \langle u(\mathbf{p}) u(\mathbf{p}') \rangle \tag{8}$$

The height correlation has been calculated by Loudon using the fluctuation dissipation theorem and the equations of hydrodynamics [11]. The result is

$$\langle u(\mathbf{p}) u(\mathbf{p}') \rangle = \frac{kT}{(2\pi)^2} \int d\mathbf{p} \exp[i\mathbf{p} \cdot (\mathbf{p} - \mathbf{p}')] \left(\frac{1}{\alpha p^2} + \frac{1}{2\rho_0 v_a^2 p} \right), \tag{9}$$

where k is Boltzmann's constant, T the absolute temperature, α the surface tension, ρ_0 the fluid density, v_a the velocity of sound in the fluid, and the integration is over the surface wave vector. This result follows from eqs. (64) and (67) of ref. [11] with a factor of 2 to account for the reality of our $u(\mathbf{p})$. The first term in the integrand of (9) is the contribution of ripples, the second is that of acoustic waves and is in general smaller. The dipolar field just below the surface is

$$E_z(\mathbf{p}) = \frac{i\mu}{2\pi} \int d\mathbf{p} \exp(i\mathbf{p} \cdot \mathbf{p}) \frac{p^2}{q_1} (1 + r_{12}^P) \exp(iq_1 d), \tag{10}$$

where again q_1 is given by (6). Using this and (9) in (8) we find for the roughness gain

$$G_{\text{rough}} = 1 + kT \left| \frac{\epsilon(\omega) - 1}{4\pi} \right|^2 \int d\mathbf{p} \left(\frac{1}{\alpha p^2} + \frac{1}{2\rho_0 v_a^2 p} \right) \frac{p^4}{|q_1|^2} \times |1 + r_{12}^P|^2 \exp[i(q_1 - q_1^*) d] \tag{11}$$

The integral is dominated by the contribution from large p where we can use the quasistatic approximation [1], $q_1 \approx ip$, and the asymptotic ($p \rightarrow \infty$) value of the reflection coefficient, $r_{12}^P \approx (\epsilon_b - 1)/(\epsilon_b + 1)$ [2]. Then

$$G_{\text{rough}} \approx 1 + \pi kT \left| \frac{\epsilon(\omega) - 1}{4\pi} \right|^2 \left| \frac{2\epsilon_b}{\epsilon_b + 1} \right|^2 \left(\frac{1}{2\alpha d^2} + \frac{1}{4\rho_0 v_a^2 d^3} \right) \tag{12}$$

Numerical data for Hg are [11] $\alpha = 0.55 \text{ J/m}^2$, $\rho_0 = 13.6 \times 10^3 \text{ kg/m}^3$, $v_a = 1.5 \times 10^3 \text{ m/s}$. As in the second section, fitting the optical data gives $\epsilon_b = 2$ and $\epsilon(\omega) = -12.6 + 8.3i$. Using $d = 1.6 \text{ \AA}$ we find at room temperature $G_{\text{rough}} \approx 2.4$.

We can understand the smallness of this result in terms of the mean amplitude of the surface fluctuations and their correlation length. Using (9) and dropping the acoustic wave contribution we find for the mean square height of the fluctuating surface

$$\langle u^2 \rangle = \frac{kT}{2\pi\alpha} \ln \frac{p_{\text{max}}}{p_{\text{min}}} \tag{13}$$

where p_{\max} and p_{\min} are, respectively, the maximum and minimum surface wave vector. Similarly, the correlation length is

$$\xi \equiv \langle u^2 \rangle^{-1} \int_0^{\infty} d\rho \langle u(\rho) u(0) \rangle = \left(p_{\min} \ln \frac{p_{\max}}{p_{\min}} \right)^{-1}$$

Choosing $p_{\max} \approx 1 \text{ \AA}^{-1}$ and $p_{\min} \approx \omega/c \approx 10^{-3} \text{ \AA}^{-1}$, we find at $T = 300 \text{ K}$,

$$\langle u^2 \rangle^{1/2} \approx 1 \text{ \AA}, \quad \xi \approx 150 \text{ \AA}. \quad (15)$$

We see therefore that the surface fluctuations associated with ripples have a correlation length which is long compared with their mean height. This is in contrast with the roughness observed on solid Ag surfaces, for which the correlation length is comparable to the mean height. Note that p_{\max} and p_{\min} have been introduced only for this discussion of the surface fluctuation profile, they do not appear in the expression (12) for G_{rough} . If we were to choose a Gaussian form for the height correlation, as in refs. [2] and [9], and fit the parameters of the Gaussian with the values (15), the resulting gain would be much smaller. The correlation (9) is far from Gaussian.

The two electromagnetic effects, image enhancement gain and near field excitation of surface roughness, which we have earlier shown could account for the SERS effect on roughened Ag surfaces, cannot account for the observations of SERS on liquid-Hg surfaces. Other electromagnetic effects which have been proposed as explanations for the SERS effect, for example resonances of a Maxwell-Garnett surface composite [12] or resonant excitation of surface roughness features [13,14], are even more clearly incapable of explaining the effect on Hg surfaces. We conclude that the observations of SERS on liquid Hg surfaces raise serious questions about the electromagnetic explanations of the effect.

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