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NONLOCAL ELECTRODYNAMIC EFFECT ON THE ENHANCEMENT FACTOR FOR SURFACE ENHANCED RAMAN SCATTERING

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The electromagnetic enhancement factor for surface enhanced Raman scattering is reexamined taking into account the nonlocal dielectric response of the substrate surface. Surface roughness is represented typically by a spherical island and nonlocal effect is introduced via a simple phenomenological model which makes possible a closer quantitative comparison with experiments. It is found that the nonlocal effect can lead to significantly lower values for the enhancement factor compared to the results calculated in the literature ignoring this effect. A sample calculation shows that, for scattering frequencies much below the surface plasmon frequency of the substrate, the nonlocal correction decreases the enhancement effect by up to 10%; and for frequencies close to the surface plasmon frequency, the difference could be by orders of magnitude. Possible experimental observation of this effect is discussed.

Keywords: A. surfaces and interfaces, D. optical properties, E. inelastic light scattering.

1. INTRODUCTION

SINCE the first discovery of the surface enhanced Raman scattering (SERS) from pyridine molecules adsorbed at roughened silver electrode in 1974 [1], it is now well established that the underlying mechanism for this effect includes factors of both electromagnetic (EM) and chemical origin [2]. While the EM mechanism refers mostly to the huge local EM field arising from resonant coupling of the surface plasmon excitation with radiation in the presence of surface roughness, the chemical effect refers to the modification of the transition dipole of the admolecule due to charge transfer process between the molecule and the substrate. For strongly chemisorbed systems, a recent experiment has reported that SERS can be maintained even at highly elevated temperatures [3]. Moreover, for a specific molecule–substrate system, the "individual weight" of these two mechanisms is not always clear and easily quantified, although it is generally believed that for most systems, the EM effect should play a more dominant role in comparison with the chemical effect [4]. This problem has recently become more interesting since the SERS effect has now been observed for a large variety of molecule–substrate systems, including even nonmetallic substrates [5].

Experimentally, the difficulty in quantifying the EM effect is due mainly to the problem in characterizing the substrate in terms of its morphology and stability. It is well known that chemically roughened electrodes and vacuum deposited metal films are of poor reproducibility and durability. Although experiments performed in ultrahigh vacuum can provide *in situ* surface characterization and other roughening methods (e.g. the "sandblasted method" [6]) can provide more durable surface structure, yet most of these roughened structures are quantified statistically in terms of certain mean deviations from a "flat reference", rendering comparisons with theoretical results mostly qualitative or at best quanti-

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tative to the limit of orders of magnitude comparison. An alternative approach is to impose a more defined surface structure such as a grating or an island substrate, as that prepared by depositing a metal film on underlayers of gas-evaporated Si particles [7], yet theoretical calculations for such a surface morphology are quite complicated and are often restricted to macroscopic phenomenological approaches. In addition, further approximations such as perturbation in terms of the roughness parameter or some sort of "dielectric averaging procedure" are often needed to make the calculation feasible [8], thus making a quantitative comparison between theory and experiment more difficult. However, modern technology using microlithographic [9] and scanning tunneling microscope (STM) techniques has now made possible the preparation of well characterized, stable substrate surface with very simple geometry, so that comparison with theoretical calculations can be made more exact. For example, one can think of using the STM to deposit arrays of mounds of silver atoms on non-metallic substrates, with the sizes of mounds controllable down to tens of angstroms by adjusting the field strength of the STM tip. These mounds can then be spaced out to an extent that the SERS signal observed will be mainly affected from isolated single substrate islands.

Hence it is now meaningful to theoretically investigate very detailed microscopic surface effects to facilitate a thorough and quantitative understanding of the mechanisms behind SERS. One of these is referred to as the nonlocal dielectric response of the substrate which has already been studied previously in the literature in this regard [10, 11]. Here, the nonlocal effect refers to the microscopic nature of the surface electrons which invalidates the treatment of the surface as a sharp geometrical profile, as is done in many electromagnetic theories in the explanation of SERS [8, 12, 13]. In the work of Weber and Ford [10], random (Gaussian-distributed) surface roughness was considered following the "effective surface current" method of Kretschmann [14], perturbative calculation to the lowest order of the roughness parameter was then carried out which led to an overall enhancement (gain) ratio expressible in terms of the results for the case of a flat surface. Nonlocal effect was then introduced into the flat surface result via the Kliewer–Fuchs formalism for the reflectance from a flat boundary [15]. Results were reported that the NL effect is important for molecule–surface distances below about 20 Å resulting in a *reduction* of the "enhancement factor" up to 100-fold. However, aside from being perturbative, their result for the "roughness enhancement factor" depends on the Gaussian parameters in the distribution function and that detailed quantitative comparison between the local and nonlocal theories were not reported. Thus it would be difficult to design a SERS experiment to study the calculated NL results as reported in [10]. In other studies of the NL effects [2] such as the work of Fuchs and Barrera [11], only the problem of a molecular dipole at a flat boundary was treated without much reference to SERS. More sophisticated theories have been formulated recently which go beyond the level of modeling the substrate as a single particle with local dielectric response [16–18]. In the work of Dignam and coworkers [16, 17], model for a "diffuse surface" was achieved by applying results from density functional theory, with the calculated SERS and phonon-induced scattering intensities depending on certain parameters fitted to the surface electron density of the spherical jellium. In addition, substrates modeled as coated and interacting particles were also considered in their work. In the work of Stockman and collaborators [18], fractal cluster substrates were considered with enhancement ratio calculated with respect to the case of a substrate containing "nonaggregated monomers". Moreover, it seems that the unique role of the NL dielectric response of the substrate on the various factors in the SERS experiments has not been highlighted in these previous works. Hence, it is our interest in this communication to study in detail the NL effects on SERS for a clearly defined surface structure representing the surface roughness. We shall present a simple phenomenological model accounting for the diffuse nature of the surface and the results will depend only on the electronic and optical parameters of the substrate material. Our results will provide an estimate on the error in earlier similar calculations in the literature ignoring the NL effects [13] as well as a detailed comparison with future experimental results using substrates prepared by the "STM-doping" technique as elaborated in the above.

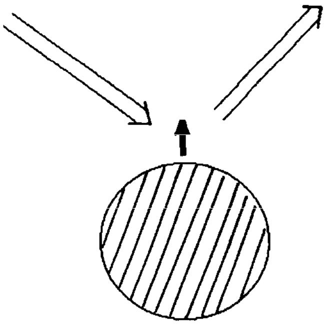

Fig. 1. Configuration of the problem.

2. THEORETICAL MODELING

We consider here the simplest surface structure of an isolated spherical island [13] (Fig. 1) and calculate in detail the NL effect on the SERS signal. Following the semiclassical approach of Gersten and Nitzan (GN) [13], which is valid when both the radius of the island (a) and the molecule–surface distance (d) are much smaller than the scattering wavelength (λ), the Raman cross section (at frequency ω) 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

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

where α_n^s is the nth-pole polarizability of the sphere given by

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

and the $G_\perp$ function for a radially oriented ($\perp$) molecular dipole is given by

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

We have assumed a radial molecular orientation since it is known that maximum SERS signal could be obtained in this configuration [2, 13]. We further assume the molecule to be located in vacuum and ϵ the dielectric function of the substrate sphere. The enhancement ratio (R) is defined to be the ratio of σ_{RS} in equation (1) to the same quantity in the absence of the substrate sphere. Thus we obtain

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

In order to introduce the nonlocal effect into R, we notice from equations (3) and (4) that the dependence of R on the dielectric response of the substrate is completely characterized by the multipolar polarizability of the sphere. Thus the NL effect on SERS could be accounted for if one knows how α_n^s is modified by this NL effect. To this end, we apply the model published by Fuchs and Claro [19] which introduces nonlocality into α_n^s by assuming the existence of a fictitious surface charge on the sphere to "smooth" the electric field at the boundary, so that the boundary is now in effect "smeared" out and quantum (wave) nature of the surface electrons could be accounted for. By introducing certain "additional boundary condition", a phenomenological expression for the NL multipolar polarizability could be obtained as [19]

$$\alpha_n^s(\omega) = \frac{n(\xi_n-1)}{n(\xi_n+1)+1}a^{2n+1}, \tag{5}$$

with

$$\xi_n(\omega) = \left\{\frac{2}{\pi}(2n+1)a\int_0^\infty \mathrm{d}k\frac{j_n^2(ka)}{\epsilon(\mathbf{k},\omega)}\right\}^{-1}, \tag{6}$$

where j_n is the spherical Bessel function, and the nonlocal response $\epsilon(\mathbf{k},\omega)$ is an input taken from microscopic many-body theories. Using the hydrodynamic model for $\epsilon(\mathbf{k},\omega)$ [20], equation (6) could be obtained analytically in terms of the modified Bessel functions as

$$\xi_n(\omega) = \left\{\frac{1}{\epsilon}+(2n+1)\left(\frac{a\omega_p}{\beta u}\right)^2 I_{n+1/2}(u)K_{n+1/2}(u)\right\}^{-1}, \tag{7}$$

where ϵ and ω_p are the Drude function and bulk plasmon frequency of the metal substrate, respectively, and the definitions for β and u can be found in [19].

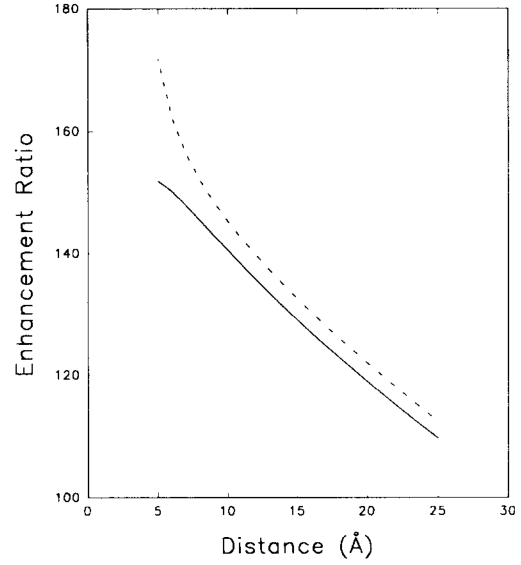

Fig. 2. Comparison of the SERS enhancement factor (R) as a function of molecule–surface distance (d) as calculated by the nonlocal (solid curve) and local (broken curve) theories, respectively. The radius of the sphere (a) is fixed at 500 Å and scattering frequency (ω) at 2.5 eV.

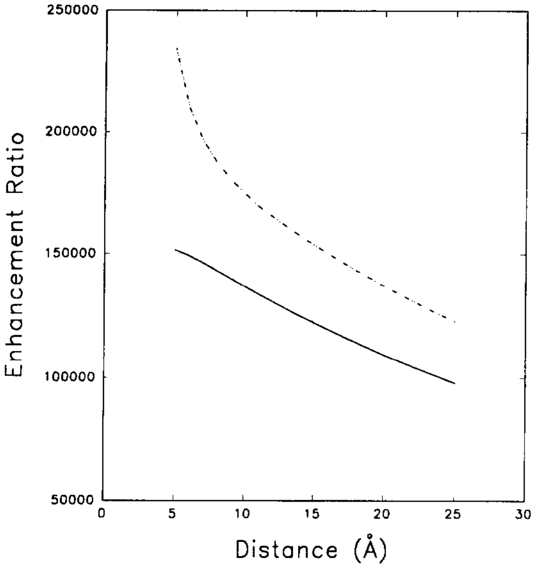

Fig. 3. Same as in Fig. 2 at frequency close to the surface plasmon frequency ($\tilde{\omega} = \omega/\omega_{sp} = 0.95$).

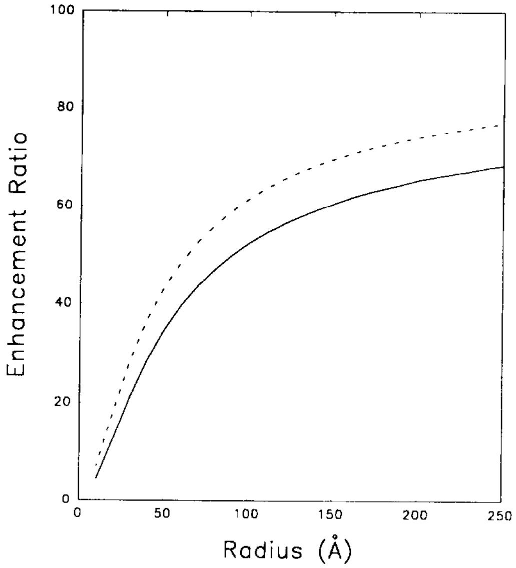

Fig. 5. R vs a for d fixed at 5 Å and $\tilde{\omega}$ at 0.1.

3. NUMERICAL RESULTS AND DISCUSSION

We have used equations (4)–(7) to study the NL effect on SERS. The substrate is assumed to be silver (Ag) throughout and the various data needed for computation could be found in our previous work [21]. Except for the comparisons with [17] made below, the molecular polarizability α in equation (4) is taken to be $10\,\text{Å}^3$ as in [13]. Numerical results for some sample calculations are shown in Figs. 2–5 with the values for various parameters listed in the figure captions. The NL results are shown as solid curves in all the graphs in comparison with the local (L) calculations which are shown by broken (dashed–double dotted) curves. Figure 2 shows the variation of the enhancement factor R with the molecule–surface distance d for a fixed scattering frequency ($\omega = 0.1\omega_{sp}$) and sphere radius a where $\omega_{sp} = \omega_p/\sqrt{3}$ is the surface plasmon frequency of the sphere. We see that while both the NL and L results show a relatively slow decrease with distances [13] and converge slowly to each other at far distances, the NL effect leads to a decrease in R from a few % up to 10%. This decrease due to NL effect persists in general for frequencies below ω_{sp} and becomes very significant for frequencies very close to ω_{sp} as shown in Fig. 3 for $\omega = 0.95\omega_{sp}$. Figure 4 shows R vs the normalized scattering frequency at fixed d and a. Note that here we choose a small value for a so that $a \ll \lambda$ for the whole range of our frequencies. We notice that the resonance in the SERS frequency spectrum is slightly blue-shifted by the NL effect and the EM enhancement can be orders of magnitude smaller according to the NL calculation for frequencies close to ω_{sp}. Figure 5 shows the result as a function of the sphere radius at a fixed molecule–surface distance of 5 Å. For a fixed molecule–substrate configuration, it is well established that there exists an optimal roughness which leads to the maximum SERS signal. This has been predicted theoretically in case of substrate with both grating and statistically roughened structures [22] and has been observed from island surfaces [7]. However, for the GN model, this optimal radius (which maximizes R) is not obtainable unless the molecule is very close to the surface ($d \lesssim 2$ Å in this case), for the existence of an optimal a in this model arises purely from the "image

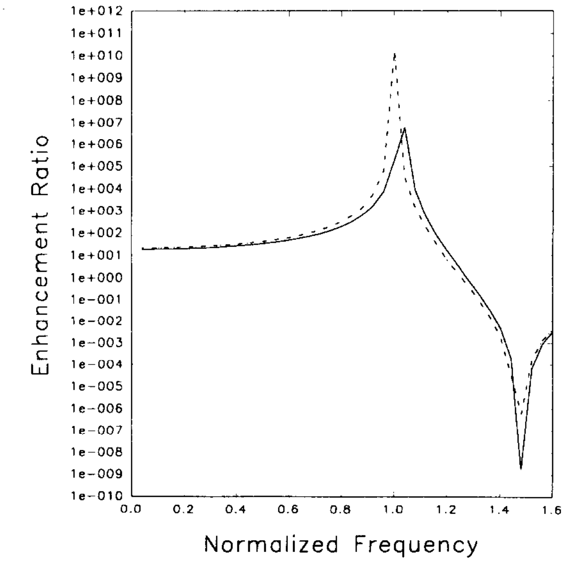

Fig. 4. R vs normalized scattering frequency ($\tilde{\omega} = \omega/\omega_{sp}$) for d fixed at 10 Å and a at 50 Å.

enhancement factor" [i.e., the factor $(1 - \alpha G_{\perp})^{-1}$ in equation (4)] which becomes almost unity for a slightly larger value of d [13]. Moreover, results at such short distances from the surface are suspicious due to the crude nature of the present model, hence we cannot have a conclusive result for the NL effects on the optimal roughness within this model. We also note that the $a \to \infty$ limit is unreasonable and this is due to the restriction $a \ll \lambda$ in the GN model as discussed above.

In order to access better the accuracy of the present simple model, we have calculated the dipolar nonlocal polarizability (α_1^s) of the substrate sphere as well as the SERS signal for the CO–silver system and compared the results with those obtained in the recent work by Dignam and coworker [17] using density functional theory to account for the diffusive nature of the spherical surface. Since the present work does not account for the coverage and the anisotropic effects, we shall use the radial molecular polarizability and set it equal to 2.6 Å^3 [17]. Figure 5 shows the results for α_1^s vs normalized frequency for a sphere with $a = 25$ Å. When compared with Fig. 3 of [17], we see that the "small features" there cannot be reproduced here due to the negligence of the phonon-induced effects which were included in the previous work [17]. In addition, the present model also yields values for α_1^s up to 30% smaller due to the complete account for the nonlocal effects in both the solution of the boundary value problem [19] involving the molecule–sphere interaction and in the wave-vector dependence of the substrate dielectric response. Figure 6 shows the SERS intensity spectra obtained in the present model which should be compared with those shown in Fig. 2 of [17] for two values of the radius of the sphere. We have normalized our results with respect to those in [17] for the 50 Å sphere at the frequency $\omega = \omega_{sp}$. Again, we see the previous "small features" are not obtained in the present calculation and the present model gives slightly less spectral widths compared to those obtained in [17].

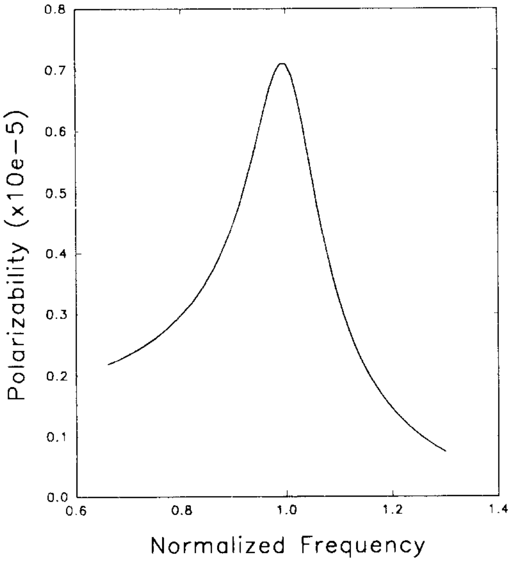

Fig. 6. Nonlocal dipole polarizability (in Å^3) as a function of normalized frequency according to the present model (to be compared with Fig. 3 of [17]).

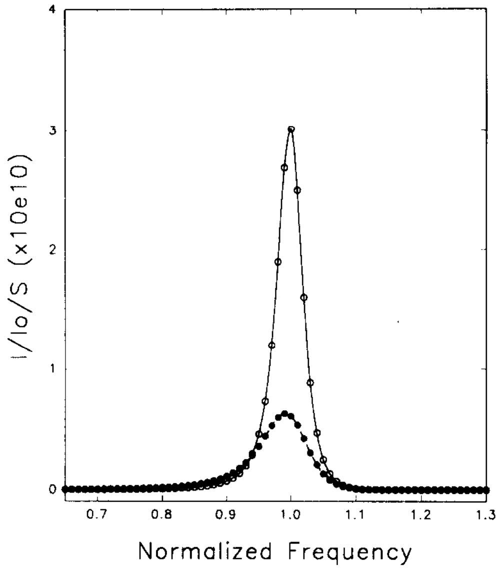

Fig. 7. Normalized SERS intensity per sphere cross-section area ($S = \pi a^2$) as a function of the normalized frequency (to be compared with Fig. 2 of [17]). The open-circle curve is for $a = 50$ Å and the filled-circle one for $a = 25$ Å.

4. CONCLUSIONS

In this communication, we have shown via a model calculation explicitly and quantitatively the importance of the NL effect in the complete understanding of the EM mechanism responsible for SERS. Although this effect was previously mentioned in the literature [2] and studied theoretically using perturbative approach [10], to our knowledge it has not been precisely quantified for a well-defined substrate geometry as is done in our present work. Moreover, the recent and more sophisticated work of Dignam and coworkers [16, 17] has modeled the diffusive nature of the surface using a density functional approach but in a certain sense, it remains a local description since the nonlocal effects were not accounted for in solving the boundary value problem concerning the interaction between the molecule and the substrate sphere. As discussed above, it is now possible to prepare a substrate with well defined and well separated islands on glass with the help of a STM. Hence we believe that the present calculations are verifiable by studying SERS from physisorbed molecules at these islands. Possible extension of the present model would be to generalize the NL calculation for an ellipsoidal particle as has been done in the local theory [13]. However, since this new technique of island preparation using STM could produce particles (of small sizes) which are very close to perfect spheres via annealing of the substrate, the present calculation can indeed be checked against future experiments. The more quantitative understanding of the EM effect in SERS will become useful, especially since SERS is now possible from substrate even of non-metallic nature as cited above [5].

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