Collective Theory for Surface Enhanced Raman Scattering

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We present an implementation of Maxwell's equations on adaptive meshes in order to study interaction of light with metal surfaces. For the first time it is possible to handle surfaces consisting of complex particles close enough to interact strongly. A fully retarded implementation allows treatment of large particles as well as small. By way of example we model a rough silver surface as an array of half-cylinders embedded in a silver surface. Very localized plasmon modes, created by strong electromagnetic coupling between touching metallic objects, dominate the surface enhanced Raman scattering response. [S0031-9007(96)00826-5]

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When a metal surface is rough on a nanometric scale, it contains very complex electromagnetic (EM) modes which have important consequences for incident light. These modes modify spectroscopic properties of an adsorbed molecule in a radical manner by changing the laser field incident on the molecule. The lifetime and emission intensity of its excited states are also altered [1]. Perhaps the most celebrated effect associated with these rough metal surfaces is the surface enhanced Raman scattering (SERS) [2]. In SERS, enhancements of up to 10^6 in the Raman signal can be obtained for molecules adsorbed on rough surfaces of copper, silver, and gold [3]. In this Letter we introduce for the first time a computational approach to the theory of SERS allowing investigation of metal particles of complex geometry that may be strongly electromagnetically coupled to many other particles. The theory includes a complete treatment of retardation effects, which are extremely important when particle size is comparable to the wavelength of light.

As an example we consider a rough silver surface modeled as an array of half-cylinders embedded in a silver surface. The acuteness of the angle of intersection of cylinders is varied by altering the intercylinder spacing thus altering the effective "roughness" of the surface.

Although the experimental technique is now well established and widely used to study excitation spectra of molecules, the relative importance of electromagnetic and molecular effects in producing enhancement is still a matter of debate [4]. Because chemisorption theory is not fully developed, theoretical effort has concentrated on electromagnetic effects. In studying electromagnetic contributions to enhancement, the first approaches treated only EM modes of isolated nanometer objects [5], but, as most of experimental works shows, SERS is a collective effect appearing in surfaces composed of closely interacting structures. Recently, more sophisticated treatments [6] have been aimed at including these interaction effects by taking a pair or a chain of small metallic spheres as a model of a rough surface. However, we believe that a quantitative theoretical understanding of the factors controlling this phenomenon is still lacking. Furthermore, the important question as to the nature of the EM modes responsible for SERS remains unanswered.

Our computational approach adds a powerful new theoretical tool with which to investigate SERS. We adapt methodology originally developed to analyze photonic materials [7,8]. This on-shell computational technique is ideally suited to study EM waves in complex media, particularly in metallic structures where the dielectric function depends strongly on frequency [9]. In contrast with other theories, we do not treat coupling between neighboring objects as a perturbation of the EM modes of isolated particles, allowing more realistic surface geometries to be studied. Inclusion of retardation enables us to analyze the SERS effect in surfaces comprising strongly coupled features of dimensions comparable to the wavelength of light, going beyond the scope of all previous *electrostatic* approaches to this problem.

It can be shown that, to a first approximation, EM enhancement of Raman signals depends on the total electric field at the molecule position, $\mathbf{E}(\mathbf{r}_m, \omega)$,

$$\rho(\mathbf{r}_m, \omega) = \left| \frac{\mathbf{E}(\mathbf{r}_m, \omega)}{E_{\mathrm{inc}}(\omega)} \right|^4, \tag{1}$$

where $\mathbf{r}_m$ is the location of the molecule, and $E_{\mathrm{inc}}(\omega)$ is the electric field associated with the incident plane wave.

In order to compute the electric fields shown in Eq. (1), we approximate the continuous fields by their values at a series of discrete points [8]. In the newest version of the formalism [10], it is possible to work with nonorthogonal and/or nonuniform meshes instead of square ones, adapting the computational mesh to the particular geometry of the system. For the case of EM waves interacting with metallic structures, we use a nonuniform mesh densely sampled where variation of the wavefields is rapid (at the surface of the objects) and less densely sampled elsewhere.

Assuming propagation of light along the z axis and the structure is N_z layers thick in this direction, it is possible to find a set of equations [8] relating EM fields at one side of the structure to those on the other side, constructing the EM

transfer matrix of our system. For SERS, knowledge of the EM transfer matrix allows us to calculate transmission and reflection matrices for an incident plane wave with momentum $\mathbf{k}$ and energy ω [11]. From these quantities we construct the total $\mathbf{E}$ field outside the surface as a sum of incident and reflected waves,

$$\mathbf{E}_{\text{total}}(\mathbf{r},\omega) = e^{i\mathbf{k}\cdot\mathbf{r}}\mathbf{E}_{\text{inc}}(\mathbf{k},\sigma,\omega) + \sum_{\mathbf{k}'\sigma'} e^{i\mathbf{k}'\cdot\mathbf{r}}\mathbf{E}(\mathbf{k}',\sigma',\omega)\hat{\mathbf{R}}(\mathbf{k},\sigma;\mathbf{k}',\sigma'), \tag{2}$$

where $\mathbf{E}_{\text{inc}}(\mathbf{k},\sigma,\omega)$ is the electric field associated with the incoming plane wave and the reflection matrix $\hat{\mathbf{R}}(\mathbf{k},\sigma;\mathbf{k}',\sigma')$ defines scattering of the incoming wave, momentum $\mathbf{k}$, and polarization σ, into an outgoing wave $\mathbf{k}'\sigma'$. $\mathbf{E}(\mathbf{k}',\sigma',\omega)$ is the electric field associated with this outgoing plane wave. Then we propagate the EM fields in real space through the structure, again using the EM transfer matrix, to obtain a detailed picture of electric fields surrounding the objects that comprise our system. The Raman enhancement is calculated from Eq. (1).

We model a rough silver surface as a chain of semicylinders placed upon a silver surface; see Fig. 1. Although the geometry of a rough silver surface in a SERS experiment is more complex, we believe that our model retains the fundamental physics of SERS in systems characterized by highly coupled features [3]. The dielectric function of silver as tabulated in [12] has been used in our calculations.

With this simple model we address some fundamental questions raised in the explanation of SERS: (i) Can we obtain a quantitative measure of EM interaction between neighboring metallic objects (varying d from $d > 2R$ to $d = 2R$)? (ii) What is the nature of the EM modes responsible for the huge enhancement? (iii) What is the effect of the roughness of the surface on enhancement of the Raman signal (varying d from $d = 2R$ to $d < 2R$)? (iv) How does the observed enhancement depend on dimensions of surface features measured relative to the wavelength of incident light?

Assuming that the Raman active molecules are adsorbed on the surfaces of the semicylinders, in Fig. 2 we use Eq. (1) to calculate the enhancement averaged over the surfaces of these cylinders. This is done for different values of the ratio $d/2R$ as a function of incident photon energy using $2R = l = 30$ nm, typical dimensions of the features present in SERS experiments [3].

An interesting point to notice in Fig. 2 is that, as stated in previous works with silver spheres [6], short range interaction between metallic features becomes important when objects are brought closer than $\approx$3 times the radius of individual semicylinders: note the small change in enhancement from $d = 4R$ to $d = 3R$. Below a separation of $d = 3R$ interaction grows rapidly.

Note that the shift to lower frequencies of the SERS maxima observed in most SERS experiments [3] is fully accounted for in our calculation: mutual interaction of particles produces absorption of light at very much lower energies than the original surface plasmon resonance at $\omega \approx 3.3$ eV. This EM coupling is essential for producing Raman enhancements as large as 10^5–10^6. In Fig. 2, we can see that the average enhancement grows from 10^3 for

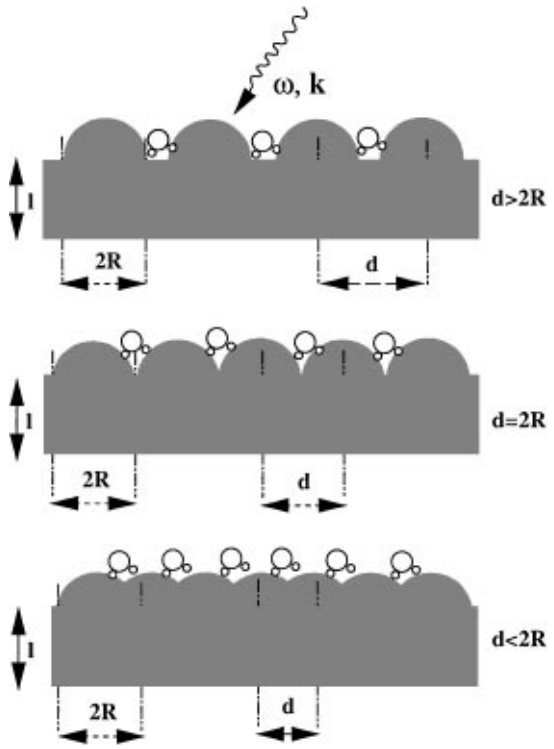

FIG. 1. Our model of a rough surface: a chain of silver semicylinders placed upon a silver slab with thickness $l = 2R$, where R is the radii of the semicylinders. For the calculations shown in Figs. 2 and 4, $2R = l = 30$ nm and d varies from values $d > 2R$ to $d < 2R$.

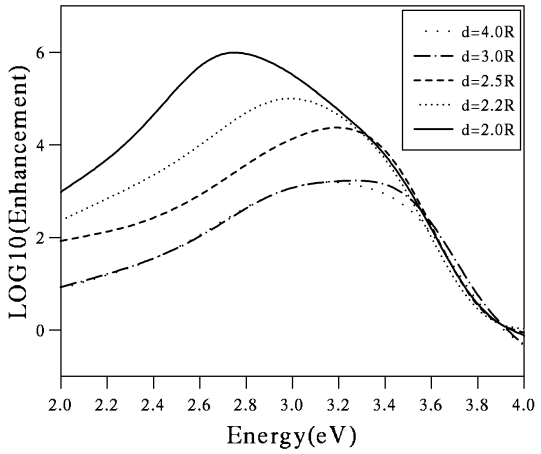

FIG. 2. The enhancement averaged over the surfaces of the semicylinders shown in Fig. 1, for different values of the ratio $d/2R$, with $2R = l = 30$ nm. d, the spacing between cylinders, varies from $4R$ to $2R$.

"isolated" cylinders growing to a maximum of 10^6 for the case $d = 2R$ where the cylinders are touching.

Using the transfer matrix technique we can map the electric field in real space, helping us to address the question about the nature of the particular plasmon modes responsible for the huge enhancement in SERS. Figure 3 shows a detailed picture of the **E** field generated by a plane wave normally incident on the system of Fig. 1 for the case of touching cylinders, $d = 2R$. We have evaluated the fields at $\omega = 2.7$ eV, the frequency of maximum enhancement. Also shown is $\nabla \cdot \mathbf{E}$, which gives the polarization charge induced by the incident photon.

Clearly the incident radiation is exciting a plasmon trapped between the semicylinders, creating a huge **E** field in this location. The plasmon obviously has a strong dipole component. This result gives quantitative support to the idea that SERS is a very local phenomenon occurring at crevices or in pores of the rough surface. Our calculations show that these localized resonant plasmon modes are able to produce enhancements as large as 10^7 in the Raman signal of the molecules adsorbed at these particular locations. Although such locations have been studied both experimentally [13] and theoretically [14,15] in the past, we believe that our fully converged electromagnetic theory can give new insights on this subject.

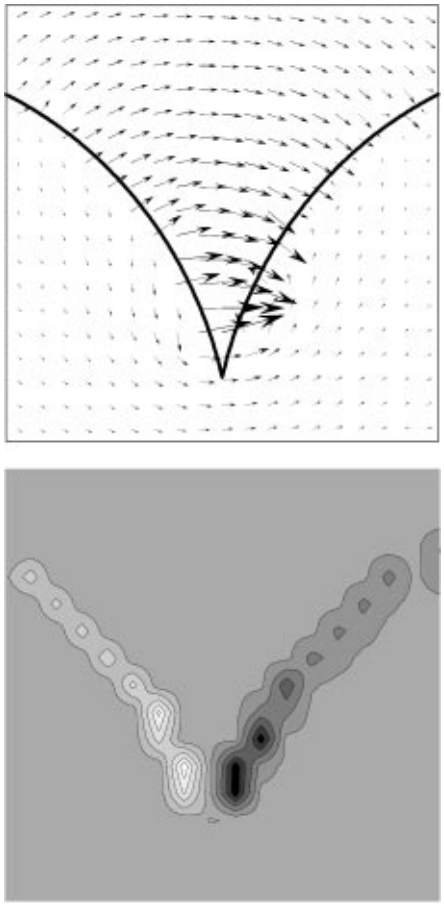

FIG. 3. A picture of the **E** field (upper figure) and its divergence (lower figure) generated by a normally incident plane wave at the frequency of maximum enhancement, 2.7 eV for $2R = d = l = 30$ nm: see the full curve in Fig. 2. The largest positive charge corresponds to white and the largest negative charge to black.

Within our model we can analyze the quantitative dependence of this localized plasmon mode on decreasing values of surface roughness, as defined by the sharpness of the angle with which the cylinders intersect. In Fig. 4 we show the local enhancement evaluated at crevices of the rough surface (instead of the averaged enhancement presented in Fig. 2) for different values of the ratio $d/2R$ with $d \leq 2R$ (see lower picture of Fig. 1). As we can see in this figure, the strength and frequency of this mode are very sensitive to geometry of the region where metallic features couple. With decreasing roughness, the maximum is blueshifted and enhancement strongly reduced. Hence, our results suggest that in a nonuniform rough surface in which different kinds of crevices coexist, the total measured enhancement will be governed by the Raman signal coming from molecules located at features that present maximum roughness. Moreover, our calculations help to explain why rough surfaces whose large scale features are quite different present strong similarities in the strength and frequency dependence of the observed enhancement [3].

Another interesting property we can analyze is the dependence of enhancement on dimensions of surface features measured relative to the wavelength of light, a question previously addressed only for the case of isolated spherical metallic objects [5]. In Fig. 5, we show the enhancement evaluated at the crevices of the rough surface as a function of scale in the case of touching semicylinders ($d = 2R$). Calculations for several different values of the radii are shown as functions of photon wavelength.

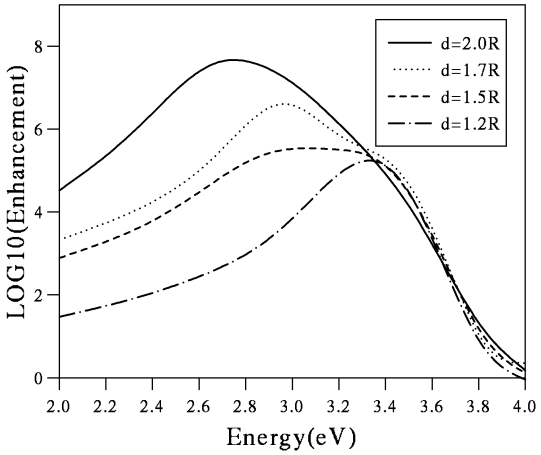

FIG. 4. The local enhancement evaluated at the crevices between the semicylinders shown in Fig. 1, for different values of the ratio $d/2R$, with $2R = l = 30$ nm. d, the spacing between cylinders, varies from $2R$ to $1.2R$. In this regime the cylinders intersect and roughness of the surface decreases.

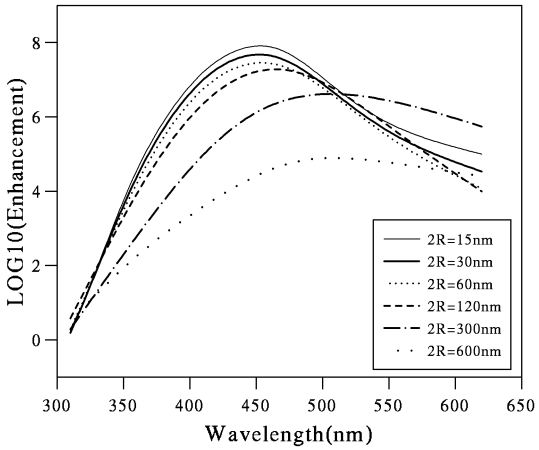

FIG. 5. The local enhancement of the Raman signal evaluated at the crevices between the semicylinders, in the case of ($2R = d = l$), as a function of the wavelength of the incident light and for different values of the radii, ranging from $2R = 15$ to 600 nm.

Some important conclusions can be drawn from these results. First, as in the case of isolated spheres, the SERS effect seems to be more important when dimensions of features are much smaller than the wavelength of light. In this limit, electrostatics governs the response,

$$\nabla \cdot \mathbf{D}(\mathbf{r}) = \nabla \cdot [\varepsilon(\mathbf{r})\mathbf{E}(\mathbf{r})] = 0\,, \qquad (3)$$

and therefore two surfaces simply related by a change of scale will exhibit the same local response, provided the scale of the structures is small enough to ensure the validity of the electrostatic approximation. This is the reason why the enhancement in Fig. 5 saturates and is almost independent of the particular dimensions of the metallic objects for the case of very small particles.

However, when dimensions of features are not much smaller than the wavelength of light, $100 < 2R < 300$ nm, the localized plasmon mode responsible for SERS in the strong coupling case appears to be more robust in frequency and strength than the EM mode present in isolated objects [5]. Only when dimensions of interacting structures are comparable or larger than the wavelength of incident light does retardation become more significant. First, current flowing to produce polarization has to overcome greater inductive resistance due to magnetic effects. Hence we expect a lowering of resonant frequencies: Figure 5 shows a clear shift of the maximum enhancement to longer wavelengths. The second effect is that radiative coupling becomes much stronger as dimensions approach wavelengths that can be radiated in the vacuum thus providing radiative damping of resonant features and therefore a strong reduction of the enhancement associated with these localized plasmon modes (see Fig. 5). This behavior is again in agreement with experimental evidence which seems to indicate that the SERS effect is only observed in surfaces whose features are smaller than the wavelength of light [16].

In conclusion, we have presented a new computational approach to SERS theory that can handle complex structures, and take account of strong electromagnetic coupling between them. Our results indicate in a quantitative way that SERS is produced by excitation of very localized plasmon modes located in regions where structures touch and interact strongly. Collective EM effects of this nature can explain enhancements of 10^5–10^6 in the Raman signal and their dependence on photon frequency. We have also analyzed the dependence of these EM modes on surface roughness and on dimensions of the metallic features. We believe that our results help answer some fundamental questions raised in the explanation of this phenomenon. We think that computational approaches, such as the one applied here, will allow a more quantitative comparison of theoretical predictions with experimental results emerging from uniform SERS-active surfaces which can now be synthesized [17].

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