THE ROLE OF SURFACE ROUGHNESS IN SURFACE ENHANCED RAMAN SPECTROSCOPY (SERS): THE IMPORTANCE OF MULTIPLE PLASMON RESONANCES

Uri LAOR [‡] and George C. SCHATZ [‡]
Department of Chemistry, Northwestern University, Evanston, Illinois 60201, USA

Received 20 April 1981, in final form 12 June 1981

The interaction of light with clusters and random distributions of metal hemispheroids on a perfect conducting flat surface is studied. Significant SERS enhancements are found to arise from multiple plasmon contributions to the surface electromagnetic fields.

1. Introduction

Ever since its discovery [1], surface enhanced Raman spectroscopy (SERS) has been the subject of much theoretical speculation concerning the origin of the observed factor of 10^6 intensity enhancement. Several mechanisms have now been proposed (ref. [2] contains a review) but much controversy currently exists concerning the relative importance of each. One mechanism which has recently received much study [3–7] and some though not universal experimental support [8,9] concerns the enhancements in surface electromagnetic fields which arise from roughness-induced excitation of surface plasmons. A simple model of this effect is obtained by considering the interaction of an electromagnetic field with a metal spheroid. Large fields at the surface of the spheroid can occur at zero frequency if the spheroid is sufficiently prolate. However, the ratio of major to minor axis (c/a) required in this model to explain the observed SERS intensities is quite large (c/a = 10–50) [3]. Alternatively, if the frequency dependence of the metal dielectric constant is included [4,5], a large intensity enhancement is obtained at frequencies close to the surface plasmon frequency of the hemispheroid. This frequency varies rapidly with c/a, but for metals like Ag, it occurs in the visible region (where most SERS experiments have been done) for c/a = 2–3 [4,5]. A single spheroid would, however, show a resonant variation of intensity with frequency which is not in agreement with many SERS experiments [1]. Most experiments do not refer to isolated spheroids, however, but to roughened surfaces which are better approximated as a random distribution of hemispheroids on a flat metal plane.

In this paper, we consider the electrodynamics of hemispheroidal random distributions in an attempt to assess more quantitatively the importance of the surface roughness enhancement mechanism. An important conclusion of this study is that much of the enhancement from these distributions is controlled by the low-frequency branches of multiple plasmon resonances which arise from clusters of only moderately prolate hemispheroids. Even for c/a ratios of 1.5–2.0, these cluster resonances cause significant local-field enhancements at frequencies well into the near infrared. These multiple resonances are a particular property of certain hemispheroid clusters and are not found in isolated spheroids or high-symmetry arrays. In addition, they are not predicted by effective medium theories such as Maxwell-Garnett theory [10]. For random distributions, we shall show that the near continuum of resonances arising from the contributions of many clusters leads to an intensity enhancement which has a frequency dependence which is similar to that observed in SERS experiments, but with an overall magnitude which is closer to 10^2 than 10^6. However, this lower figure agrees with estimates of roughness contributions to SERS made in recent electrochemical experiments [9].

[‡] On leave from Atomic Energy Commission, Nuclear Research Center–Negev, Beer-Sheva, Israel.
[‡] Alfred P. Sloan Fellow.

2. The origin of multiple plasmon resonances in clusters of hemispheroids

The electrodynamics of rough surfaces has been the subject of numerous theoretical studies [11]. Since we are primarily interested in bumps which are a few hundred Å in both diameter and height, we approximate the electrodynamic description using Laplace's equation. Our rough surface model consists of a distribution of hemispheroidal bosses (having arbitrary dielectric constants) on a flat perfectly conducting metal surface. Adrian [4] and Gersten and Nitzan [5] have studied this model for the special case of a single hemispheroid and they have shown the close relationship between the electrostatics of an isolated spheroid and that of a hemispheroid on a perfect conducting surface. Here we extend this work to consider many hemispheroids having randomly chosen locations, and c and a values. For such distributions we find that under certain conditions, the electrodynamics is dominated by the collective response of certain clusters of hemispheroids which are contained in the distributions In this section, we show how such clusters can exhibit multiple plasmon resonance effects.

Each of the hemispheroids in a cluster can be characterized using spheroidal coordinates [12]. Choosing the origin of the coordinate system at the center of the hemispheroid, with the z axis along the axis of revolution (assumed to be perpendicular to the perfect conducting flat surface), we define

$$\xi = (r_1 + r_2)/2f \tag{1}$$

and

$$n = (r_1 - r_2)/2f\,, \tag{2}$$

where $f = (c^2 - a^2)^{1/2}$ and r_1 and r_2 are the distances to the two foci of the ellipsoid of revolution whose upper half forms the hemispheroid under consideration These coordinates are appropriate for prolate ellipsoids; for oblate ones, f is replaced by $-if$ and ξ and $i\xi$ in the formulas to be derived.

If a constant field E_0 is applied to the hemispheroid along the z direction, solution of Laplace's equation leads to the following expression for the potential ϕ outside the hemispheroid (for $z \geqslant 0$)

$$\phi = E_0 \eta \xi f - E_0 f \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \chi\epsilon_2} \frac{\xi_0 \eta Q_1(\xi)}{Q_1(\epsilon_0)}\,, \tag{3}$$

where Q_1 is a Legendre function of the second kind [12], ξ_0 is the value of ξ at the hemispheroid surface, ϵ_1 is the hemispheroid dielectric constant and ϵ_2 is the dielectric constant of the medium (solution or vacuum) which is in contact with the hemispheroid The function χ is given by

$$\chi = -1 + (\xi_0^2 - 1)^{-1}\left[\tfrac{1}{2}\xi_0 \ln\left(\frac{\xi_0 + 1}{\xi_0 - 1}\right) - 1\right]^{-1} \tag{4}$$

and varies from 2 to ∞ as c/a varies from 1 to ∞. This expression for χ is equivalent to one previously given by Adrian [4].

In the limit $\xi \to \infty$ (i.e. for long distances from the hemispheroid or for a hemisphere), eq. (3) reduces to the simple point-dipole expression.

$$\phi = E_0 z + \mu z/R^3\,, \tag{5}$$

where R is the distance from the origin. The induced dipole moment μ is found to be proportional to E_0 (i.e. $\mu = \alpha E_0$) with an effective hemispheroid polarizability of

$$\alpha = \tfrac{1}{3} f^3 \frac{\xi_0}{Q_1(\xi_0)} \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \chi\epsilon_2}\,. \tag{6}$$

Now let us consider a cluster of N hemispheroids A simple technique for treating the interaction between hemispheroids is to include for their dipolar coupling. This approximation should be valid in the limit that the hemispheroids are adequately separated, or are close to being hemispheroidal. Although not all the problems of relevance to SERS satisfy these limits, this approximation should provide at least a qualitative picture.

The inclusion of higher multipoles in the interaction between two spheres has been studied quite recently by Aravind et al. [13]. Although they find that a large number of multipoles are required ($\approx$60) in order to converge the field when the spheres are quite close together, their results are qualitatively and sometimes quantitatively similar to what we obtain for the same system using the dipole approximation. For example, both they and we find that the field is larger between the two spheres than elsewhere when the applied field points at an angle of 45° relative to the intersphere axis. The magnitude of the field en-

hancements are not always the same, however, with differences of factors of 2 or more at some orientations when the spheres are close together.

The dipolar coupling between the ith hemispheroid, and all other ones is determined by

$$\mu_i = \alpha_i \left[E_0 + \sum_{j \neq 1}^{N} \frac{\mu_j}{R_{ij}^3} \right], \quad i = 1, \ldots, N, \tag{7}$$

where μ_i is the induced dipole moment on hemispheroid i, α_i is the polarizability of i [from eq. (6)], and R_{ij} is the separation between the centers of hemispheroids i and j. Eq. (7) assumes that all the hemispheroids are on a flat plane, with E_0 perpendicular to that plane. In that case, μ_j/R_{ij}^3 is just the perpendicular field arising from hemispheroid j evaluated at the location of i. The system of equations represented by eq. (7) can be rearranged to (in vector notation)

$$\boldsymbol{\mu} = \mathbf{D}^{-1} \boldsymbol{\alpha} E_0 , \tag{8}$$

where

$$D_{ij} = \delta_{ij} + (\alpha_i/R_{ij}^3)(1 - \delta_{ij}) \tag{9}$$

Cluster plasmon resonances are now identified by finding the frequencies ω for which the determinant of $\mathbf{D}$ vanishes. Because the α_i are complex in general, this will not usually happen for real frequencies. However, often the roots are quite close to the real axis, and in such circumstances, large μ_i can result, leading to large surface fields at the resonant frequencies.

The number of distinct resonances to be obtained for a given cluster depends on both its size and symmetry, as well as the width of the individual resonances. For high-symmetry clusters (one or two hemispheroids, an equilateral triangle, a square, etc.), the determinant of $\mathbf{D}$ vanishes at only one frequency, usually that associated with a collective in-phase polarization of all the hemispheroids in the cluster. For isolated clusters of no symmetry, the number of plasmon resonances can be as large as the number of members in the cluster though it is often the case that some resonances are too close in frequency to be resolved. When multiple resonances occur, those other than the highest-frequency one cause some of the hemispheroids to have induced polarizations with alternating signs (as determined by the eigenvectors of $\mathbf{D}$). Often the lower-frequency multiple resonances occur at frequencies which are well below the lowest single-hemispheroid resonant frequency of any member of the cluster.

To evaluate the surface fields needed for SERS intensity calculations using this model, one first calculates an effective local field E_{0i} for each cluster (using $E_{0i} = \mu_i/\alpha_i$). Then, derivatives of the second term in (3) (with E_{0i} replacing E_0) are used to evaluate the fields parallel to and perpendicular to the surface. These fields are then summed over all hemispheroids in the cluster, and integrated over the entire area of the surface (hemispheroids plus flat regions). The absolute square of this, multiplied by 16 (to include for effects of reflection from the flat surface [4]), gives an estimate of the parallel and perpendicular surface field enhancement contribution to SERS. This estimate ignores contributions to the enhancement from simultaneous excitation of plasmon resonances at both the incident and Stokes shifted frequencies. This is a small effect according to Adrian [4] because molecules located near hemispheroids which are in resonance at the exciting frequency will generally be off resonance at the scattered frequency. In addition, the process of averaging the local field enhancement over the entire surface (which was not done by Adrian) reduces the effect of coupling between molecular and hemispheroidal dipoles at the Stokes shifted frequency. The existence of multiple resonances does complicate this issue somewhat but we shall ignore this problem here. Our model also ignores contributions to SERS intensities from other mechanisms (image effects, resonant Raman coupling of the molecule to the plasmon states, adatom effects, etc.).

3. Numerical examples: hemispheroidal clusters and random distributions

To demonstrate the effect of multiple plasmon resonances on SERS intensities, we have calculated the local field enhancement factor of the previous section for clusters of 1, 2, 6 and 8 identical hemispheroids, each with $a = 25$ nm, $c = 61$ nm ($c/a = 2.44$), using dielectric constants appropriate for Ag surfaces [14] in contact with water ($\epsilon_2 = 1.8$ [4]). For the geometrical configurations pictured in fig. 1 (where each cluster resides in a square region, (500 nm)^2 in area), we obtain a perpendicular enhance-

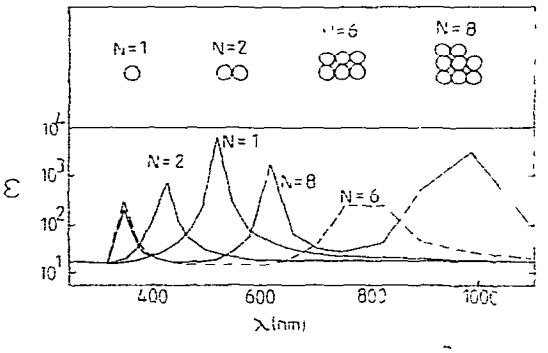

Fig. 1. Rough surface enhancement factor ϵ versus wavelength (λ) in nm for the four clusters of hemispheroids depicted in the top panel. These clusters contain $N = 1$, 2, 6 and 8 hemispheroids, each of which has $a = 25$ nm, $c = 61$ nm, and whose dielectric constant is taken to be that of silver [13]. Each cluster is located at the center of a square region $(500\ \text{nm})^2$ in area for the purpose of intensity calculations. The ϵ values were calculated at the wavelengths listed in ref. [13], and straight lines were used to connect these points in the figure. The lines for $N = 6$ have been dashed for greater visual clarity. Note that the ϵ versus λ curves for $N = 6$ and 8 show multiple resonances (two peaks for $N = 6$ and three for $N = 8$).

ment factor ϵ which is plotted against wavelength λ in fig. 1. For one hemispheroid, a single resonance is seen at $\lambda = 515$ nm, with a peak enhancement of $\approx 10^4$. This enhancement is smaller than has been estimated previously for single hemispheroids [4,5], because ϵ involves an average over the entire $(500\ \text{nm})^2$ region containing the hemispheroid. (The hemispheroid itself occupies less than 5% of the surface area.) A cluster of two hemispheroids (fig. 1) shifts the resonance to lower λ ($\lambda = 430$ nm) and decreases the peak intensity enhancement. This resonance involves a collective in-phase polarization of both hemispheroids, and leads to a resonant frequency which is similar to what would be obtained from a single less prolate hemispheroid. For six hemispheroids, two resonances are observed, one in phase at 350 nm, and one out of phase at $\lambda = 800$ nm. For eight hemispheroids, three resonances are observed (at $\lambda = 350$, 620 and 980 nm). Note that the longer-wavelength resonances are typically broader than the short-wavelength resonance, and that they can occur at longer wavelengths than the single-hemispheroid resonance (even well into the near infrared). The number of distinct resonances to be expected in a given situation is not always easy to predict (except for configurations of high symmetry) because often some roots of the secular equation overlap enough to cause resonant profiles to coalesce.

To demonstrate how clusters of spheroids cause important long-wavelength contributions to SERS, we now consider a random distribution of hemispheroids. A total of 68 hemispheroids were chosen with a and c values sampled randomly between 0 and 20 nm. These were spread randomly on a square region 100 nm in length and width, and periodic boundary conditions were used to extend this to an infinite planar array. Intensity enhancements were calculated as before for both Ag and Cu hemispheroids, and are depicted (for fields perpendicular to the surface) in fig. 2. Because of the finite sample of hemispheroids used in the primary square region, the calculated ϵ versus λ curves are somewhat bumpy. However, the general trend on Ag is clear in that a flat dependence on λ above 350 nm is obtained (300 nm is the flat surface plasmon frequency for Ag). The values of the enhancements on Ag are typically $\approx 10^3$, although somewhat higher values are observed in the near infrared due to the lower branches of multiple resonances. Since the value of ϵ for a perfectly smooth surface would be 16 according to our model, the maximum *roughness-induced* contribution to the SERS enhancement in fig. 2 is $\approx 10^2$. For Cu, ϵ values of ≈ 300 are observed for $\lambda > 600$ nm, and a factor of 5 decrease in ϵ occurs at $\lambda = 600$ nm.

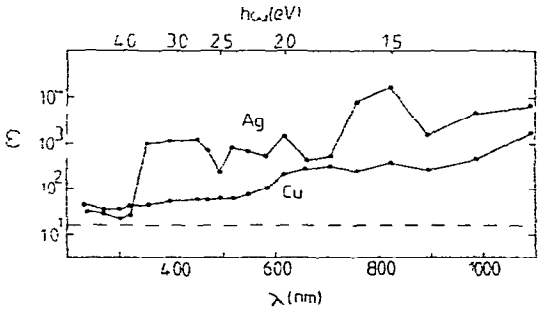

Fig. 2. ϵ versus λ for a random distribution of hemispheroids on a flat surface. Separate results for Ag and Cu are plotted, with the actual calculated points connected by straight-line segments. Top scale gives the energy $\hbar\omega$ (in eV) associated with each wavelength. The dashed line at $\epsilon = 16$ indicates the flat surface contribution to ϵ as discussed in the text.

4. Discussion

It is clear from the examples of the previous section that multiple plasmon resonances are important in determining the response of hemispheroid clusters and random distributions to radiation. The wavelength dependence of ϵ depicted in fig. 2 is qualitatively similar to that observed experimentally for both Ag and Cu [15], and demonstrates how the overlapping of resonances present in random distributions can lead to a relatively flat wavelength dependence below the flat surface plasmon frequency. Fig. 2 also demonstrates that realistic models of surface roughness *do not* account for the full factor of 10^6 enhancement observed in SERS experiments. The maximum enhancement from this mechanism is $\approx 10^2$ on both Cu and Ag. It is also the case that the factor of 5 drop in intensity in fig. 2 for Cu near 600 nm is smaller than the observed drop [15] by over an order of magnitude.

Acknowledgement

We acknowledge helpful discussion from R.P. van Duyne. This research was supported by Contract N00014-79-C-0794 from the Office of Naval Research.

References

[1] D.L. Jeanmaire and R.P. van Duyne, J. Electroanal Chem. 84 (1977) 1;
M.G. Albrecht and J.A. Creighton, J. Am. Chem. Soc. 99 (1977) 5215.

[2] T.E. Furtak and J. Reyes-Corona, Surface Sci. 93 (1980) 351.

[3] J.I. Gersten, J. Chem. Phys. 72 (1980) 5779.

[4] F.J. Adrian, Chem. Phys. Letters 78 (1981) 45.

[5] J.I. Gersten and A. Nitzan, J. Chem. Phys 73 (1980) 3023.

[6] S.L. McCall, P.M. Platzman and P.A. Wolff, Phys. Letters 77A (1980) 381.

[7] M Moskovits, J. Chem. Phys. 69 (1978) 4159,
E. Burstein, C.Y. Chen and S. Lundquist, Proceedings US–Japan Seminar, Solid State Commun 32 (1979);
M. Kerker, D.S. Wang and H. Chew, Appl Opt. 19 (1980) 4159;
P.K. Aravind and H. Metiu, Chem. Phys. Letters 74 (1980) 301.

[8] J.E. Rowe, C.V. Shank, D.A Zwemer and C.A. Murray, Phys. Rev. Letters 44 (1980) 1770.
D.A. Zwemer, C.V. Shank and J E. Rowe, Chem. Phys. Letters 73 (1980) 201.

[9] S.G. Schultz, M. Janik-Czachor and R.P. van Duyne, Surface Sci. 104 (1981) 419.

[10] J.C. Maxwell-Garnett, Phil. Trans. Roy. Soc. 203 (1904) 385, 205 (1906) 237.

[11] O. Hunderi, Surface Sci. 96 (1980) 1.

[12] M. Abramowitz and I.A. Stegun, Handbook of mathematical functions (Dover, New York. 1965) chs. 8 and 21.

[13] P.K. Aravind, A. Nitzan and H. Metiu, Surface Sci 110 (1981) 189.
P K Aravind, E. Hood and H. Metiu, Bull. Am. Phys. Soc. 26 (1981) 379.

[14] P.B. Johnson and R.W. Christy, Phys. Rev. B6 (1972) 4370.

[15] C.S. Allen, G.C. Schatz and R P. van Duyne, Chem. Phys. Letters 75 (1980) 201.