

Theoretical Studies of Surface Enhanced Raman Scattering

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In 1974 Fleischmann and co-workers¹ noticed that high-intensity Raman spectra could be obtained when small molecules such as pyridine were adsorbed onto anodized silver electrode surfaces. The high intensities were originally attributed to the large number of molecules present on these highly roughened electrodes, but in 1977, Jeanmaire and Van Duyne² and Creighton and Albrecht³ discovered that an intrinsic surface enhancement effect was actually much more important in the observed spectra. Estimates of the enhancement per molecule due to this effect were placed at 10^5 - 10^6 or more.^{2,3} This marked the beginning of what we now call surface enhanced Raman spectroscopy (SERS), and its discovery has precipitated an avalanche of experimental and theoretical work aimed at understanding why there is an enhancement effect, what the spectra mean, and how this enhancement effect shows up in other spectroscopic, photophysical, and photochemical processes. In this Account we describe the basic theory behind SERS with the goal of understanding the basic enhancement mechanisms and what they tell us about the interaction of molecules with metals in the presence of a radiation field.

Although the reader can consult a number of excellent reviews⁴ for further details, some of the most important experimental facts about SERS are the following.

(1) First and foremost, the magnitude of the SERS enhancement for pyridine on optimally anodized electrodes is generally agreed to be in the range 1 - 3×10^6 at 515 nm.^{4a,5} One of the key uncertainties in determining this value, the surface coverage, has now been measured by double potential step chronocoulometry^{4a,5} in electrochemical measurements and by a variety of methods⁶ in UHV studies.

(2) Ag, Cu, and Au and their alloys are the substrates that produce the largest SERS enhancement.⁴ Originally it was thought that enhancements on Ag were a factor of 10 larger than on Cu, and Cu a factor of 10 larger than Au (see ref 7 and references therein), but more recent studies in which roughness, frequency, coverage, and electrode potential have all been carefully optimized^{15,8} indicate that the peak enhancements on all three metals are comparable to within a factor of 2. SERS has also been observed on Li and Na⁹ and has been reported on many other metallic and nonmetallic substrates.^{4d} These results (except for the alkalis) are still the subject of much experimental controversy, in part because of difficulties in making SERS, coverage,

potential modulation, and surface roughness measurements on the same system.

(3) The excitation frequency dependence of the enhancements is a complex function of both surface roughness and substrate dielectric properties. The most important difference between Ag and either Cu or Au is a rapid falloff in Cu or Au SERS intensities relative to Ag above 2 eV. This seems to be correlated with a rapid rise in the imaginary part of the Cu or Au dielectric constant above 2 eV due to interband transitions.⁷ The dependence of enhancement on roughness leads to different excitation profiles for different surface preparations, with anodized Ag electrodes giving a nearly flat dependence of enhancement on frequency (to within a factor of 10 or less) in the visible region⁷ and Ag colloids¹⁰ or arrays of posts¹¹ showing a peak enhancement at a frequency that depends on the shape of the metal particles in the colloid or array.

(4) SERS can and has been observed in a variety of different interfacial environments, including solid/liquid (aqueous and nonaqueous systems¹² and colloidal suspensions¹⁰), solid/UHV,^{10c,13,14} solid/air,^{9a,10c,14} and solid/solid (tunnel junctions^{10c,15} and thin film

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George C. Schatz was born in Watertown, NY, in 1949. He received a B.S. in Chemistry at Clarkson College in 1971 and a Ph.D. in Chemistry at CalTech in 1975. After spending a year as a Research Associate at MIT, he joined the Chemistry Department at Northwestern University as Assistant Professor in 1976. He was promoted to Associate Professor in 1980 and to Professor in 1982. This research is divided between studies of surface spectroscopy and photochemistry and studies of gas phase reaction dynamics and collisional energy transfer.

“sandwiches”^{10c,16}). The overall magnitude of the enhancements does seem to depend on environment (with solid/liquid enhancements larger than solid/UHV, for example), but few of the estimated enhancements are considered reliable to better than a factor of 3 so the effect of environment has not yet been fully worked out.

(5) For many substrates and interfacial environments, an optimum roughness scale can be identified. For Ag, surface roughness in the form of spheroidally shaped particles with diameters in the range of 10–100 nm appears optimal.^{4c} Results for Au and Cu are less clear, and there is at least one report for Au that suggests that relatively smooth surfaces (at the ≥ 25 -nm scale) give optimum enhancements.^{5,8}

(6) SERS can be observed for a wide variety of adsorbed molecules.^{2,4a} The magnitude of the enhancements are roughly molecule independent except for resonant Raman scatters.^{4a} There are, however, several features in the SERS spectra that suggest that chemical interactions between the molecule and substrate are important. Many spectra¹⁷ show metal–molecule stretch modes, for example, and the spectra of pyridine on different metals show somewhat different intensity patterns for different modes.¹⁸ Some of the SERS spectra of normal Raman scatterers show intensity patterns that are apparently characteristic of resonant Raman scattering.¹⁹

(7) Other optical processes have been observed (or are believed) to show surface enhancements, including harmonic generation²⁰ (second, third, fourth), photochemistry,²¹ and photoemission.²²

The development of a theoretical description of the above observations has a somewhat confusing history that has been reviewed in several places.⁴ It is possible, however, to make two statements that encompass nearly all of current thinking about SERS mechanisms. First, it appears certain that the *electromagnetic* interactions between adsorbate and substrate play a significant role (at least a factor of 10^2) in the observed enhancements. Indeed, the dependence of the enhancements on substrate dielectric properties and surface roughness is very easily explained with use of electromagnetic interactions. Second, the *chemical* interactions between adsorbate and substrate are thought to play at least some role in SERS, but whether chemical effects cause only small ($< \text{factor of } 10$) modulations in intensity patterns or whether they are responsible for a larger contribution ($\geq 10^2$) to the overall 10^6 enhancement factor is still uncertain. Let us now discuss in a general way what these statements mean.

The term “electromagnetic interaction” is taken to mean any interaction between the molecule and substrate in either the presence or absence of the electromagnetic field that leads to a change in spectral in-

tensities without requiring electronic overlap between the molecule and substrate. This is unambiguously defined only when the separation between the molecule and substrate is large enough so that the overlap is negligible. In general there are two broad classes of electromagnetic interactions: (1) those that occur even in the absence of the radiation field and (2) those that turn on only when the radiation field is on. The second class of interactions is best understood at present and can be divided into several enhancement effects (although it should be noted that they are not truly distinct). The first to be recognized,^{23–25} and probably the most thoroughly studied,^{26–31} is the enhancement in the local field experienced by the molecule due to excitation of surface plasmons in the metal particles making up the substrate. The surface plasmons are associated with collective excitations of the surface conduction electrons in metal particles. At the plasmon frequency, the metal surface becomes highly polarizable, leading to very large field induced polarizations and thus large fields local to the surface. Since the Raman intensity is proportional to the square of the applied field at the molecule, enhancement in the scattered intensity results. A closely related enhancement is also associated with excitation of surface plasmons by the Raman emitted photons. Both of these enhancements depend on substrate roughness and electronic structure since the frequency of the surface plasmon resonances depends on these parameters. They are largely molecule independent as are all of the electromagnetic mechanisms, and they are long-ranged effects since the dipole fields induced in polarizable metal particles vary as the inverse cube of the distance to the center of the particle.

Several other sources of enhanced local fields can also contribute to field-dependent electromagnetic interactions, including (1) enhancements associated with high curvature features on the surface (the “lightning rod” effect³²), (2) enhancements associated with polarization of the surface by the fields arising from induced dipoles in adsorbed molecules (the image effect^{7,33–35}), and (3) Fresnel reflection effects. The last of these contributes at most a factor of 10 or so to the overall enhancement effect and arises even for flat metal surfaces. The lightning rod effect can in principle cause very large enhancements (10^6 or greater³²) for molecules adsorbed on the tips of needles or in pores. It is probably much less important (less than a factor of 10) for the surfaces that have actually been studied. Unlike the other

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field-induced electromagnetic effects, the image effect becomes important only very close to the surface. This makes it impossible to separate it from chemical effects, and because of this, many of the original predictions^{5,33-34} of large (10^6) enhancements due to the image effect are probably inaccurate.

Let us now turn our attention to the electromagnetic interactions that are present even when the field is off. The prime example of this refers to the interaction of the oscillating dipole and/or quadrupole field of the vibrating adsorbed molecules with the surface electrons. Such fields would be expected to modulate the metal surface dielectric properties (especially at frequencies close to the surface plasmon frequency where the metal is highly polarizable), leading to Raman shifted reflection of light from the surface. This mechanism is sometimes called the "Raman reflectance" mechanism as a result and estimates of its importance³⁵⁻³⁷ have varied widely since it, like the image field mechanism, is most important when the adsorbed molecules are too close to the surface to ignore chemical effects. We will say more about it in the section on molecular orbital studies of surface enhancement effects.

The term "chemical interaction" refers to contributions to the enhancement that require overlap between the adsorbate and substrate. Chemical interactions are necessarily short ranged, and most SERS mechanisms that invoke chemical interactions postulate the importance of a surface-related resonant electronic state in producing the enhancement. In the recent literature³⁷⁻⁴¹ several groups have implicated adsorption-induced charge-transfer states as providing the resonant intermediate. A useful model due to Otto^{40a} considers SERS to involve electron-hole pair excitation by the incident radiation field followed by transfer of the excited electron to an adsorbate-localized charge-transfer excited state where interaction with the molecular vibration occurs such that subsequent migration of the electron to recombine with the hole leads to emission of a Raman shifted photon. Otto and Furtak^{40b} have also suggested that special sites of atomic scale roughness may play an important role in facilitating this charge transfer enhancement mechanism. Estimates of the contribution of charge-transfer states of SERS have been in the $10-10^3$ range,^{37-39,41} and reasonable correlation of the qualitative predictions of this idea (selection rules, metal dependence) has been noted. In addition, some evidence for the existence of charge-transfer excited states has been seen in ELS data.⁴² Unfortunately the above-mentioned estimates are all very crude, so the quantitative importance of the charge-transfer model is still not clear.

The possibility that the surface plasmon states may serve as resonant intermediate in SERS has also been suggested,^{24,43,44} but no estimate of the importance of

this has been made since the matrix element coupling the adsorbate electronic ground state with the surface plasmon excited state is quite difficult to evaluate. At large separations (outside the chemical region), this mechanism is the quantum analogue of the image effect.

Another type of chemical interaction refers to changes in the surface electronic state density through chemical interaction with the adsorbate. When the molecule vibrates, this will cause modulation in the surface optical properties, just as in Raman reflection. In fact, this mechanism is what Raman reflection becomes when the adsorbate is in contact with the surface. This illustrates an important point, namely, that the chemical and electromagnetic enhancement mechanisms are not readily separable, and any theory that attempts to separate them will probably fail in one or more limits. It is not possible to distinguish the contributions of different mechanisms cleanly in the experimental results either, and it is partly for this reason that estimates of enhancement contributions due to different mechanisms are so uncertain.

Because of this problem of interdependence of different mechanisms, one important goal of theoretical investigations is to develop a global model of surface enhancement effects, one in which all mechanisms are present and allowed to interact. Obviously this is a rather formidable task, but there has been a few attempts in this direction⁴ and in the section on molecular orbital studies we describe them. Before describing the general enhancement models, however, let us turn our attention to the very popular mechanism of local field enhancement via surface plasmon excitation.

The Electrodynamics of Small Spheroidal Particles

An often-studied model^{4f} of surface-enhanced processes consists of a single metal spheroid, small compared to the wavelength of light, onto which are adsorbed the molecules of interest. Chemical interactions between these molecules and the metal are ignored as are all interactions between different molecules, and the problem then is to solve Maxwell's equations to determine the field $\mathbf{E}(\omega)$ experienced by each molecule when the whole system is irradiated by an electromagnetic field at frequency ω . In doing this, we also make the simplifying approximation that the field enhancement for the Raman emitted photon can be calculated by using the same expression for the field \mathbf{E} as the incident photon but evaluated at the scattered frequency ω' .²⁹ The SERS enhancement factor is then proportional to $|\mathbf{E}(\omega)|^2|\mathbf{E}(\omega')|^2$. At first glance, this model seems easy to solve. If the spheroid is small compared to the wavelength of light, one expects that Maxwell's equations can be replaced by Laplace's equation. If we ignore the influence of induced dipoles in the molecules on the polarization of the spheroid (i.e., neglect image effects), then we need only be concerned with solving Laplace's equation for the spheroid with the surrounding medium replaced by an effective dielectric constant. This can be done by standard procedures using spheroidal coordinates, and the resulting fields $\mathbf{E}(\omega)$ and $\mathbf{E}(\omega')$ are then easily evaluated. There are, however, a number of problems in this development

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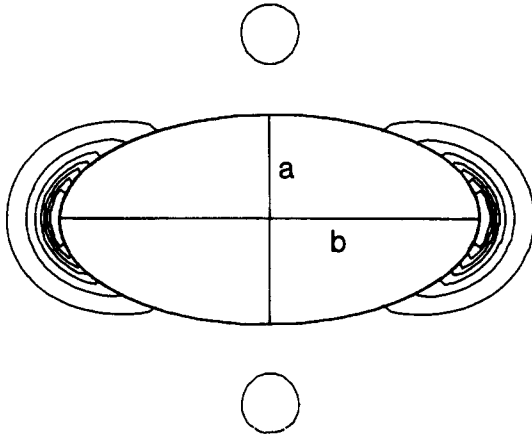


Figure 1. Contours of constant $|\mathbf{E}|^2$ for a prolate spheroid having $b/a = 2$ and using Ag dielectric constants from ref 43 at $\hbar\omega = 3.00$ eV. In determining $|\mathbf{E}|^2$, the effects of surface scattering, dynamic depolarization, and radiation damping have been included with $b = 280$ Å. Only contours outside the spheroid are plotted, and the contour values are at $|\mathbf{E}|^2/E_0^2 = 0.1, 13.9, 27.7, 41.5, 55.4, 69.2, 83.0,$ and 96.8 . (The maximum value of $|\mathbf{E}|^2/E_0$ is 124.9). The largest contour is located at the spheroid tip and the smallest is associated with two small depressions located along the a axis.

that have prevented accurate results from being obtained until very recently. These problems include the following: (1) including for surface scattering effects in the spheroid dielectric constants, (2) including for radiation damping and dynamic depolarization effects, and (3) performing the appropriate surface and orientation averaging to include for the contributions of molecules distributed over the whole spheroid. Let us now illustrate how this model works and how the above problems influence the results.

If we assume that the spheroid is prolate, with a major axis $2b$ and a minor axis $2a$ (see Figure 1) and that the electromagnetic field E_0 is applied along the b axis, then the resulting field at the surface of the spheroid is given by⁴⁵

$$|\mathbf{E}|^2 = E_0^2 \left[|1 - \zeta|^2 + \frac{2Re(1 - \zeta)\zeta^*\eta^2}{Q_1(\zeta_0^2)(\xi_0^2 - \eta^2)} + \frac{\zeta^2\eta^2}{Q_1(\xi_0)^2(\xi_0^2 - 1)(\xi_0^2 - \eta^2)} \right] \quad (1)$$

where the parameter $\zeta = (\epsilon_i - \epsilon_0)/(\epsilon_i + \chi\epsilon_0)$ is a function of the dielectric constants ϵ_i and ϵ_0 inside and outside the spheroid, respectively, and

$$\chi = -1 + 1/[(\xi_0^2 - 1)Q_1(\xi_0)] \quad (2)$$

ξ_0 in eq 1 and 2 equals $(1 - a^2/b^2)^{-1/2}$ and Q_1 is a Legendre function (of the second kind):

$$Q_1(\xi_0) = \frac{1}{2} \xi_0 \ln [(\xi_0 + 1)/(\xi_0 - 1)] - 1 \quad (3)$$

η in eq 1 is a spheroidal coordinate⁴⁶ that can be used to specify location on the surface. It is related to the usual polar angle θ via

$$\eta = \cos \theta [(\xi_0^2 - 1)/(\xi_0^2 - \cos^2 \theta)]^{1/2} \quad (4)$$

Let us assume that $\epsilon_0 = 1$ (vacuum) and that ϵ_i is given by the free-electron Drude model expression

$$\epsilon_i = 1 - \frac{1}{\omega} \frac{\omega_p^2}{\omega + i\gamma} \quad (5)$$

with ω_p being the bulk plasmon frequency and γ being the plasmon width. Then it is easy to show that $|\mathbf{E}|^2$ maximizes when $Re(\epsilon_i + \chi\epsilon_0) = 0$ or when (assuming $\omega_p \gg \gamma$)

$$\omega = \omega_{res} \simeq \omega_p/(1 + \chi)^{1/2} \quad (6)$$

Since χ varies from 2 to ∞ as the spheroid changes from spherical to needlelike, the resonance frequency ω_{res} varies from $\omega_p/2^{1/2}$ to 0 over the same range. This illustrates the sensitivity of peak frequency to spheroid shape.

The peak field is also sensitive to shape, as one can see by evaluating (1) at $\eta = \pm 1$ (i.e., at the tips) with (5):

$$|\mathbf{E}|^2 = E_0^2 \frac{\omega_p^2}{\gamma^2} \{ [1 - 1/(Q_1(\xi_0)(\xi_0^2 - 1))]2/(1 + \chi) \} \quad (7)$$

Notice the factor ω_p^2/γ^2 . This depends on the intrinsic dielectric properties of the metal and acts to favor metals with high plasmon frequencies and small widths (i.e., Ag, Li, etc.). The factor in braces in (7) depends on the shape of the spheroid and equals $4/3$ for a sphere and becomes infinite for a truly needlelike spheroid. From this one might surmise that the highest enhancements will be obtained from the most needlelike spheroids, but in fact this will be true only if all the molecules are located on the tips. This is evident from Figure 1 where $|\mathbf{E}|^2$ for Ag using dielectric constants from ref 47 is plotted. When a more realistic average over all locations on the surface is performed, one finds

$$\langle |\mathbf{E}|^2 \rangle = E_0^2 \frac{\omega_p^2}{\gamma^2} \left\{ \left[1 + \left(\frac{2}{Q_1(\xi_0)} + \frac{1}{Q_1(\xi_0)^2(\xi_0 - 1)} \right) \times \left(\frac{-(\xi_0^2 - 1)^{1/2} + \xi_0^2 \sin^{-1}(1/\xi_0)}{(\xi_0^2 - 1)^{1/2} + \xi_0^2 \sin^{-1}(1/\xi_0)} \right) \right] / (1 + \chi) \right\} \quad (8)$$

The quantity in braces in (8) equals 2 for a sphere and decreases to zero as the spheroid becomes infinitely prolate. If we generalize this formula to describe oblate spheroids (by replacing ξ_0 by $i\xi_0$ therein), we find that the quantity in braces maximizes at 2.44 when the spheroid is *infinitely* oblate. Thus the highest average enhancement for a metal whose dielectric constant is given by eq 5 is obtained for *oblate* spheroids! Although many real metals (i.e., Ag) have dielectric constants sufficiently different from (5) that the highest average enhancement is obtained for moderately prolate shaped spheroids, this analysis does illustrate how important it is to perform an average over the surface in estimating enhancements. In addition, it shows that the average

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enhancement can be much smaller than the peak ($\eta = \pm 1$) enhancement.

Another question of importance in the evaluation of eq 1 concerns the dependence of $|\mathbf{E}|^2$ on the size of the particle for a given b/a . At first glance it looks like $|\mathbf{E}|^2$ depends only on b/a and hence not on size for fixed b/a , but two effects make this conclusion seriously in error. First, the scattering of the conduction electrons off the particle surfaces significantly alters the particle dielectric properties for particles smaller than the conduction electron mean free path. Second, radiation damping and dynamic depolarization effects substantially reduce induced dipoles in particles larger than a few percent of the wavelength of light.

Surface scattering for spheroids was recently studied by Kraus and Schatz,⁴⁸ who found that it is best to consider that this modifies the plasmon width factor γ to

$$\gamma \rightarrow \gamma + v_F/L_{\text{eff}} \quad (9)$$

where v_F is the Fermi velocity and L_{eff} is an effective distance that depends on the shape of the spheroid. Somewhat different expressions are obtained for L_{eff} depending on whether the electron motions are treated classically or quantum mechanically. The classical expression is just the average chord length and is

$$L_{\text{eff}} = \frac{4}{3}b[(\xi_0^2 + 1)]/[(\xi_0^2 - 1)^{1/2} - \sin^{-1}(1/\xi_0) + (\xi_0^2 - 1)^{3/2} \ln(1 - 1/\xi_0^2)][\xi_0^2(\xi_0^2 - 1)^{-1} \sin^{-1}(1/\xi_0) + 1/(\xi_0^2 - 1)^{1/2}]^{-1} \quad (10)$$

Note that this expression reduces to $L_{\text{eff}} = b$ for $b = a$ (a sphere) and to $L_{\text{eff}} = (16/3\pi)a$ for $b \gg a$ (for needles). Thus L_{eff} is determined by the shorter dimension of the spheroid, and the v_F/L_{eff} contribution to the effective width can damp out plasmon resonance behavior whenever the smaller dimension of the spheroid is small compared to the mean free path. For the noble and alkali metals, this typically becomes important for particles smaller than 200 Å.

The terms *radiation damping* and *dynamic depolarization* refer to corrections to the LaPlace equation approximation to Maxwell's equations that are necessary because of finite particle size and less than infinite wavelength. Radiation damping is a well-known effect⁴⁹ that arises from emission by the dipole induced in the spheroid. Dynamic depolarization is a much more poorly understood effect⁵⁰ that is due to interference between radiation emitted at different locations on the spheroid.

The literature on radiation damping and dynamic depolarization effects is somewhat confusing in that originally Wokaun et al.⁵¹ included just the radiation damping effect in treating the electrodynamics of spheroids and concluded that particle sizes of 1000 Å or more were needed before it would be important. Later, Barber et al.⁵² used exact numerical solutions to Maxwell's equation for a spheroid to show that signif-

icant size-dependent damping could happen for particles larger than 100 Å. Analogous exact results for spheres have been found by Kerker and co-workers.²⁹ Meier and Wokaun⁵² then reexamined the phenomenological LaPlace equation treatment and found that the Maxwell equation and LaPlace equation results could be reconciled for spheres by adding the dynamic depolarization term to the LaPlace result. Zeman and Schatz⁵³ have since shown that this can be generalized to spheroids and that the Barber et al. result can be reproduced within the LaPlace equation framework by adding in a dynamic depolarization term.

To describe the Meier and Wokaun⁵⁰ argument in the present context, we note that the LaPlace equation electric field at large distance from the spheroid reduces to a dipole field with an induced dipole moment given by

$$\mu_{\text{ind}} = \alpha_0 E_0 \quad (11)$$

where the polarizability α_0 is

$$\alpha_0 = \frac{1}{3}\zeta \left(\frac{\xi_0 f^3}{Q_1(\xi_0)} \right) \quad (12)$$

and $f = (b^2 - a^2)^{1/2}$.

Inclusion of radiation damping and dynamic depolarization into this treatment leads to a dipole expression for the field at large distance where

$$\mu_{\text{ind}} = \alpha_0(E_0 + E_{\text{rad}}) \quad (13)$$

and E_{rad} is the sum of a radiation damping field and a dynamic polarization field. A reasonable approximation to E_{rad} can be obtained by averaging the fields associated with a distribution of radiating dipoles over the volume of the spheroid (evaluating each field at the center of the spheroid). Following the procedure of ref 50, we find that in the sphere limit

$$E_{\text{rad}} = \left(\frac{k^2}{b} + i\frac{2}{3}k^3 \right) \mu_{\text{ind}} \quad (14)$$

where $k = \omega/c$. The second term in this expression is the usual radiation damping field while the first term in the dynamic depolarization field. Although eq 14 is rigorous only for spheres, its generalization to spheroids⁵³ leads to an expression that is essentially the same. Substitution of (14) into (13) leads to a corrected expression for the induced dipole moment, which is given by

$$\mu_{\text{ind}} = \left(\frac{\alpha_0}{1 - \alpha_0 k^2/b - i\frac{2}{3}k^3 \alpha_0} \right) E_0 \quad (15)$$

Note that the radiation damping term leads to a $k^3 \alpha_0$ contribution while the dynamic depolarization term varies as $\alpha_0 k^2/b$. Evidently for particle sizes on the order of one-tenth of the wavelength of light, the dynamic depolarization term will dominate and will cause the induced dipole moment to be damped and the plasmon resonance frequency to shift as the particle size increases.

The effect of radiation damping and dynamic depolarization can be approximately included in the field enhancement in eq 1 by dividing the factor ζ by the

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denominator in (15). If this is combined with the surface scattering formula from eq 9 and 10 using eq 5 and still assuming $kb \ll 1$ and $\omega_p \gg \gamma$, one can derive the following expression, which gives the optimal particle radius b for a sphere:

$$(\gamma + \nu_F/b) = \frac{2}{3} \frac{\omega_p^6 b^5}{\nu_F c^4} \quad (16)$$

If we take $\omega_p = 4$ eV and $\gamma = 0.1$ eV (roughly the values needed for Ag), then (6) predicts an optimal radius of 87 Å. Somewhat larger sizes are obtained (~ 200 Å) when measured dielectric constants are used and prolate spheroidal particles are considered. These sizes are somewhat larger than were estimated in ref 52, but the latter calculations did not include for surface scattering effects and thus overestimated enhancements for small particles. The magnitude of $\langle |E|^2 \rangle$ at the optimal size and frequency is in the range 100–300 for Ag, which indicates a maximum SERS enhancement of 10^2 – 10^4 (depending on frequency shift). The fact that these optimized estimates are still much less than 10^6 is one of the stronger indications that additional mechanisms are involved in SERS.

Molecular Orbital Studies of Surface Enhancement Effects

The treatment of surface-enhanced optical processes by molecular orbital methods remains one of the most difficult challenges in modern quantum chemistry. Perhaps the key problem is the necessity of simultaneously describing the electronic properties of the (microscopic) adsorbed molecule and of the (macroscopic) substrate surface. Two simplifying models can be imagined: (1) a single molecule (or a regular array of molecules) on a flat perfect crystal surface and (2) a single molecule on a small (but still macroscopic) metal cluster. The first model is in principle amenable to treatment by band structure methods, although at present the closest to this that has been accomplished for calculating Raman intensities are jellium/RPA studies of induced dipoles (usually point dipoles) near semiinfinite flat surfaces.^{54,55} Semiempirical molecular orbital methods have also been used to study resonant Raman scattering associated with adsorbate-induced charge-transfer states³⁸ and with surface plasmons.⁴³ All of these studies have been useful in sorting out contributions to SERS and other processes that can arise on flat surfaces. Unfortunately the relation of these results to experiment is still not very clear in part because experimental observations of SERS on flat surfaces are still in dispute.^{5,56}

The second model, that of a molecule on a cluster, is more easily related to experiment, especially to SERS observations for colloidal systems and for metal island films, but the problems associated with accurately calculating spectroscopic properties for this model are quite formidable. The smallest metal particles for which SERS has been observed so far are Cu colloidal particles with a root mean square average radius of 50 Å.⁵⁷ These particles contain tens of thousands of at-

oms, which puts them out of range (by factors of 100–1000) of current electronic structure programs. It is possible of course to consider smaller clusters in such calculations, but clusters which are too small may be dominated by surface scattering.

One approach to using the second model on small clusters in a way that provides potentially meaningful conclusions about large clusters has recently been studied by Pandey and Schatz.^{37,58} In this approach, time-dependent Hartree-Fock (TDHF) methods have been used to calculate Raman intensities for small molecules (H_2 , CO, N_2) adsorbed onto small simple metal clusters (two to six atoms of Li, Na, Al). In these calculations the excited metal orbitals are given width factors that are characteristic of macroscopic metal clusters, thus forcing the clusters to have polarization properties that are like the macroscopic cluster. As might be expected, the Raman intensities are found to be large at frequencies that correspond to resonant excitations in the metal cluster. This is analogous to the excitation of surface plasmons in macroscopic systems, and in fact at large separations between molecule and cluster, the TDHF calculation reduces to the electromagnetic model.

As the molecule/cluster separation is shortened, the calculated Raman enhancements increase to values of 10^3 – 10^6 (depending on system) at the equilibrium adsorption geometry, and they can get even larger at shorter distances. Although it is impossible to uniquely decompose the enhancements into contributions from different mechanisms except at large separations, certain general trends can be identified (see ref 37 for a more detailed discussion) on the basis of a naturally occurring separation of the frequency-dependent polarizability derivative expression into three terms. One of these involves electron-electron interactions induced by the applied field and includes the induced polarization effects that are important in the electromagnetic model. This is the most important mechanism at long range and it also contributes significantly at equilibrium. The second contribution arises from modulation of the resonant cluster orbital energies by the vibrating adsorbate. This has both long- and short-range components (both electromagnetic and chemical) and for some systems makes the largest contribution to the Raman enhancements near equilibrium. In many respects this contribution is similar to the Raman reflection mechanism mentioned earlier. The third contribution is associated with modulation of the transition dipole matrix elements by vibration of the adsorbate. This is most important when chemical effects such as charge transfer cause the dipole matrix elements between the ground state of the molecule and the resonant excited state of the cluster to be strongly coupled to adsorbate vibration. As a result, this contribution is important only at short distances between adsorbate and cluster, but in this limit it is sometimes the most important contributor to the Raman intensity.

Several features of the results of these molecule/cluster TDHF calculations bear a strong resemblance to what is seen in SERS and other experiments. For

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CO and N₂ adsorbed onto lithium clusters, the CO Raman intensity is always substantially higher ($\sim 10^2$) than N₂. This agrees with observations for CO and N₂ on Ag.⁹ The TDHF calculations indicate that the difference between these two molecules is in how effectively they modulate the cluster orbital energies. The large dipole moment derivative of CO and the stronger chemical interaction associated with CO adsorption both cause substantially larger modulation by CO which leads to larger polarizability derivatives and therefore Raman intensities. It is also found that in comparing Raman intensities for a variety of molecules on different metals that the Raman enhancement varies as the inverse fourth power of the metal-cluster excited-state width. This seems to correlate with what is seen experimentally and it also provides a simple basis for estimating enhancements on metals not yet studied. Another important result from these calculations refers to the variation of molecular excited-state energies with molecule/cluster separation. The TDHF calculations indicate that only ionic (i.e., charge transfer) states show much variation with separation and that these can become relatively low lying certain circumstances. This agrees well with ELS observations.³⁸

Despite the apparently good correlation between the molecule/cluster calculations and observations, it should be emphasized that the molecule/cluster calculations

are still at a relatively primitive stage since only very small clusters have been treated to date. The generalization of these calculations to treating more relativistic size systems will require substantial simplifications in the TDHF technology.

Concluding Remarks

It should be clear from the preceding sections that the theoretical description of surface-enhanced optical processes is still incomplete. Some aspects, such as the contribution of electromagnetic interactions, are well understood conceptually and have been the subject of several quantitative calculations. Other aspects, such as the importance of chemical interactions, have only been subject to qualitative studies. Perhaps at the crudest level of development are attempts to develop a general theory for the interaction of molecules, metal surfaces, and radiation fields. Even with this somewhat primitive level of understanding, however, theory has and continues to play an important role in the evolution of SERS technology and in the development of other surface enhanced optical processes.

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