well-defined.) The second derivatives $\partial^2 U/(\partial X_i \, \partial X_j)$ of the internal energy U as a function of all the extensive variables X_i have been shown by Weinhold[31] to have the properties of a metric, which can be used to construct a distance $D(f, i)$ (shortest length) between states i and f.[32] The dissipated availability is then

$$\Delta A \geq D^2(\epsilon/\tau) \tag{12}$$

where ϵ is a mean relaxation time of the system, and τ is the duration of the process. For endoreversible systems the bound is strengthened to

$$\Delta A \geq L^2(\epsilon/\tau) \tag{13}$$

where L is the length of the actual path traversed from i to f. These expression give a direct measure of the cost of finite process time, in terms of internal relaxation times and equilibrium properties.

Concluding Remarks

In this *Account* we have pointed out the inadequacy of reversible thermodynamics to describe processes which proceed at nonvanishing rates and have pointed out a number of new methods to treat this situation. The primary goal has been to obtain bounds of performance which are more realistic than the reversible ones. Some of the finite-time procedures are generalizations of traditional quantities, like potentials and availability; others are entirely new, like the thermodynamic length.

Since the central ideas of reversible thermodynamics are retained in finite-time thermodynamics, we are continuing our attempts to generalize traditional concepts to include time. Especially important are connections to statistical mechanics and irreversible thermodynamics, e.g., investigating the finite-time content of Keizer's Σ-function[33] and processes far from equilibrium. The most exciting results emerging at the moment are applications of the thermodynamic length which seems to be able to simplify calculations on such diverse systems as lasers, separation by diffusion, and signal encoding.

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Electromagnetic Model for Surface-Enhanced Raman Scattering (SERS) on Metal Colloids

Milton Kerker

Department of Chemistry, Clarkson University, Potsdam, New York 13676

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The realization that Raman signals from pyridine adsorbed at *roughened* silver electrodes[1] are enhanced 10^5–10^6 over signals from dissolved pyridine[2,3] unleashed a torrent of investigations that has hardly abated.[4,5] Suitable substrates for adsorbed molecular species, in addition to the roughened electrodes on which this remarkable phenomenon was first observed, include colloidal metal particles, vacuum-deposited metal island films, matrix-isolated metal clusters, roughened surfaces of single crystals under ultrahigh vacuum, tunnel junction structures, smooth metal surfaces in the attenuated total reflection arrangement, metal-capped polymer posts, and holographic gratings. The initial observations of SERS for adsorbates on gold, silver, and copper have been extended to include aluminum, cadmium, lithium, nickel, palladium, platinum, and sodium.

Speculations to account for this surface-enhanced Raman scattering (SERS) immediately fell into two major categories. A purely physical mechanism was proposed in which the molecules were presumed to respond to gigantic electromagnetic fields generated locally by collective oscillations of the free electrons in small metal structures. In addition, so-called "chemical" mechanisms envisioned charge transfer between metal and adsorbate or else formation of a molecule–metal atom complex with consequent molecular resonances. Such specific molecular interactions may certainly play a role since different molecules on the same surface or different Raman bands of the same molecule may exhibit different SERS effects. Indeed, contributions to SERS from each of these two kinds of mechanisms, electromagnetic and chemical, are not mutually exclusive, yet the predominant current view is that the major contribution is electromagnetic and is due to the local field enhancement associated with resonant excitation

Milton Kerker is Thomas S. Clarkson Professor and Dean of Science at Clarkson University. Born in Utica, NY, in 1920, he received the AB, MA, and Ph.D. degrees from Columbia University after which he joined Clarkson's Chemistry Department in 1949. He has served since 1965 as co-editor of the *Journal of Colloid and Interface Science*. In addition to light scattering, a subject on which he has written a treatise, he is interested in the mechanics of aerosols and the history of science.
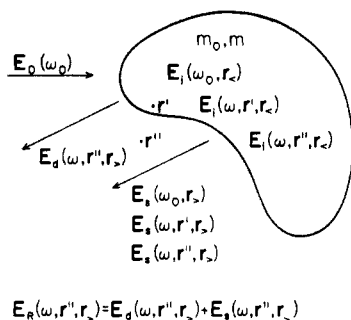
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$E_R(\omega,r'',r_>)=E_d(\omega,r'',r_>)+E_s(\omega,r'',r_>)$

Figure 1. Model for scattering by particle with refractive indexes m_0, m at incident and Raman circular frequencies ω_0 and ω. Raman dipoles at r' and r''. Incident, internal, and scattered fields at ω_0 are $E_0(\omega_0)$, $E_i(\omega_0)$, and $E_s(\omega_0)$. Raman internal and scattered fields due to dipoles at r' and r'' are $E_i(\omega,r')$, $E_s(\omega,r')$ and $E_i(\omega,r'')$, $E_s(\omega,r'')$, respectively. $r_<$ and $r_>$ denote positions inside and outside the particle, respectively.

of electron oscillations, otherwise termed surface plasmons.

Although the vast majority of experimental studies have utilized other substrates, colloidal particles are uniquely advantageous for theoretical analysis. Colloid optics is a venerable subject and in this Account we will expand upon classical light scattering theory in order to articulate a complete electromagnetic field theory of SERS. Not only does this predict the magnitude of the enhancement in agreement with measurements, but also it depicts the remarkable wavelength dependence of SERS upon the optical properties and the morphology of the colloidal particles. The model can be considered as prototypic of the other substrates for none of which has it been possible to derive a definitive theory. Indeed, a substrate such as a "roughened" surface cannot even be described deterministically even through it can be very crudely envisaged as comparable to a smooth surface covered with "colloidal bumps".

We will not discuss experiments with colloidal sols in this Account even though such experiments stimulated the theoretical research summarized here.[6] Our own early experiments[7-10] have been in agreement with some of the main features of the theory but there are areas which require clarification and continued work before a definitive Account can be presented.

Elastic and Inelastic Light Scattering

We first consider elastic light scattering, for which there is no frequency shift. When a particle, composed of a homogeneous medium characterized by a refractive index m_0 (Figure 1), is irradiated by an electromagnetic wave at frequency ω_0, there is a field outside the particle constructed by superposition of the incident field $E_0(\omega_0)$ plus a scattered field $E_s(\omega_0,r_>)$ and an internal field $E_i(\omega_0,r_<)$. These fields can be completely described in terms of the particle morphology and refractive index by appropriate matching at the particle boundary.[11]

In inelastic scattering by molecules, of which fluorescence and the Raman effect are examples, the frequency of the scattered light differs from that of the incident light. As a first approximation, the molecule is treated as a polarizable electric dipole which is excited at one frequency and reemits at some shifted frequency.

There are several important areas of experimental investigation where inelastically scattering molecules are embedded within small particles, particularly Raman microprobe analysis of colloids and flow fluorimetry of biological cells and chromosomes. A number of years ago we raised the following query regarding these experiments: How are inelastic signals affected by embedment of active molecules within small particles? The result has been to show that such signals do indeed depend upon the particle morphology, the refractive index of the particle, and the spatial distribution of the active molecules within the particle.

To understand why this is so, we turn again to Figure 1. An inelastic scattering molecule, located at some position r' within the particle, is excited by the radiation field at the incident frequency inside the particle[12] and it will radiate at the shifted frequency, ω, for which the refractive index is m. The Raman field $E_i(\omega,r',r_<)$ at the shifted frequency ω inside the particle is composed of a dipolar field plus an induced field necessary to satisfy the boundary conditions. The Raman scattered field outside of the particle, $E_s(\omega,r',r_>)$, is obtained from the solution of this boundary value problem. For an array of molecules it is necessary to add the results appropriately (coherently or incoherently) to correspond to the particular distribution of Raman active material within the particle.

We have formulated the theory and carried out numerical calculations for spheres,[13-16] concentric spheres,[17] cylinders,[18] and spheroids.[19,20] Some of the main predictions of the theory have been verified by experiments with fluorescent polymer latexes.[21-26]

Model for SERS

The path has been straightforward, at least conceptually, from the theory of elastic scattering by small particles to the above model of inelastic scattering by

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molecules embedded within small particles. Extension to the case where the active molecules are outside of the particle, including positions at the outer surface, corresponds to what one finds in SERS.

The molecule (Figure 1), once again presumed to behave as an electric dipole, is located at a position $\mathbf{r}''$ outside of the particle. The electric field outside the particle at frequency ω_0 is comprised of the field of the incident plane wave $\mathbf{E}_0(\omega_0)$ plus the scattered field $\mathbf{E}_s(\omega_0, r_>)$. This field excites the dipole located at $\mathbf{r}''$ to radiate at the Raman frequency. The Raman radiation field outside of the particle is comprised of the dipole field plus an induced field necessary to satisfy the boundary conditions. In this instance the induced field is the Raman scattered field for which the essential boundary value problem had been solved by us in another context.[27]

The enhancement is obtained by comparison of the Raman signal in the presence of the particle with that from a molecular dipole having the same polarizability as the surface-enhanced dipole but in the absence of the particle.

There is also an effect arising from the orientation of the various dipoles. In practice, our calculations have been performed by comparing Raman signals from a particle uniformly covered by dipoles whose axes are normal to the surface with a similar arrangement of dipoles in the solution. We assume that the absorption and emission dipoles are similarly oriented but uncorrelated in phase. In the case of spheroids, the particles are taken to be randomly oriented. There would be differences for different orientation of the dipoles at the surface, but we have not explored this in detail.

While these electromagnetic considerations provide the necessary framework for the model, they can be enriched by any specific chemical information available from either experiment or theoretical analysis. This may be done by incorporating that information into the Raman polarizability. The completely general solution for homogeneous spheres and the numerical results for that case will be discussed in the next section.

Calculation of SERS for Spherical Particles

Our calculations for spherical particles give the dependence of the angular distribution and polarization of the SERS upon the size and dielectric properties of the particle as well as on the orientation of the molecular dipoles and their distance from the surface. The mathematical analysis and more detailed calculations are given elsewhere.[28,29] The sampling of numerical results presented here is intended merely to illustrate some of the main physical features of the phenomenon. The optical constants of silver[30] are used because they exhibit the most striking effects. Indeed, that is why silver has been used in most of the experimental work. It should be borne in mind that values of these constants obtained from measurements on bulk samples may not be valid for small particles because of quantum size effects.[31] The Raman shift has been selected at
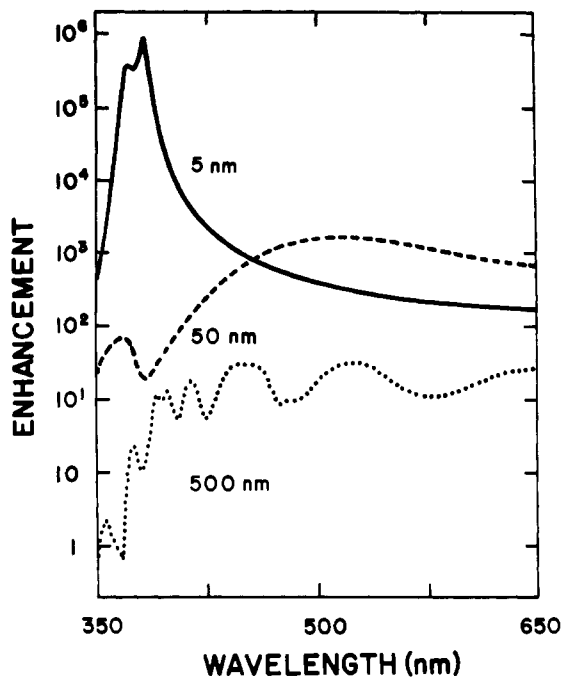
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Figure 2. SERS excitation profile for a monolayer on 5-, 50-, and 500-nm-radius Ag spheres in water for 1010 cm^{-1} Raman band.

1010 cm^{-1} to correspond to this much studied pyridine line. The upper value of particle radius $a = 500$ nm has been dictated by the computational time requirements rather than by any limitations of the theoretical analysis.

Figure 2 depicts the enhancement as a function of excitation wavelength, i.e., the excitation profile, for a monolayer at the surface of 5-, 50-, and 500-nm-radius silver spheres immersed in water. The magnitude of the double-peaked maximum for the 5-nm particle agrees with the largest measured values (10^5–10^6). For $a = 50$ nm, the enhancement maximum of 10^4 is much broader and is shifted to longer wavelengths. For the still larger particle, $a = 500$ nm, the enhancement oscillates in the 10–10^2 range throughout the visible.

The peak value of 10^6 occurs only at about 382 nm and only for particles with radii about 10 nm and smaller. The origin of this huge enhancement can be envisaged if we consider a very much simplified expression for the enhancement in the limiting case that the particle be very much smaller than the wavelength viz.

$$G = |(1 + 2g)(1 + 2g_0)|^2 \qquad (1)$$

$$g = \frac{m^2 - 1}{m^2 + 2} \qquad g_0 = \frac{m_0^2 - 1}{m_0^2 + 2} \qquad (2)$$

When much smaller than the wavelength, the particle behaves as if it were a polarizable dipole with polarizability $a^3 g$. In a formal sense excitation of the dipolar surface plasmon, which results in SERS, takes place whenever there is a resonance as the denominators of g and g_0 become small. This happens whenever m_0 and m approach the value $2^{1/2} i$. For silver in water resonance occurs at about 382 nm. Actually, these expressions do not blow up, even where $m^2 = -2$, because higher order terms contribute to both numerator and denominator of g, g_0 as $m^2 + 2$ becomes small.[28,29]

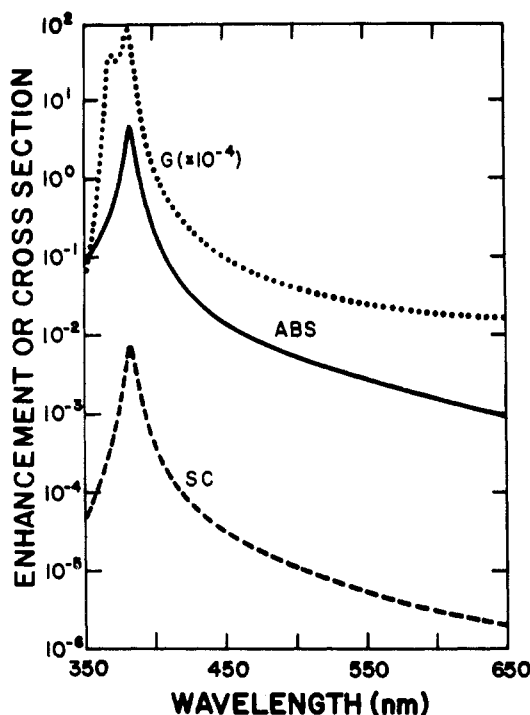(31) U. Kreibig and C. V. Fragstein, *Z. Phys.*, **224**, 307 (1979).

Figure 3. Comparison for 5-nm-radius Ag sphere in water of the SERS excitation profile (···) for 1010 cm⁻¹, absorption cross section (—), and scattering cross section (- - -).

The physical origin of the resonance can be understood in terms of the Drude model.[32] When the free electrons oscillate in phase with the electromagnetic field, the refractive index becomes a purely imaginary number. A small particle, now conceived to be a cavity of oscillating free electrons, will have a characteristic frequency at which it will resonate. For very small spheres this so-called dipolar surface plasmon is excited to resonance whenever $m = 2^{1/2} i$.

The enhanced electric fields associated with excitation of the dipolar surface plasmon also result in enhanced absorption and scattering as shown in Figure 3 where the SERS excitation profile, the absorption spectrum, and the scattering spectrum of a 5-nm-radius silver sphere in water are compared.[33] Note how each of these peaks is at precisely the same excitation wavelength.

For larger spheres there will, in addition to the dipolar mode, be a hierarchy of higher order modes all of which contribute to the various optical processes associated with the spherical particles. Any one of these may be resonantly excited at a particular frequency which depends upon particle size and optical constants. Actually, resonant excitation of a particular mode may result in very strong fields localized at radial positions inside the particle, thereby giving rise to strong absorption,[34] whereas resonant excitation of some other mode may give rise to strong fields localized just outside the particle surface, giving rise to SERS. Accordingly, for larger spheres the absorption and scattering spectra will be decoupled from the SERS excitation spectrum. This point should be emphasized. The absorption and scattering spectra are necessarily coupled with the

SERS excitation profile *only* when the particles are sufficiently small to be treated in the dipole limit.

SERS of Water

One challenge to the electromagnetic model has been the failure to observe SERS by water. The Raman cross section for water is so small that even a strongly enhanced signal from a monolayer would be difficult to detect, particularly in aqueous medium where it would have to be resolved from the signal due to the large quantity of bulk water. However, since the enhanced electromagnetic field extends somewhat from the surface, the number of water molecules contributing to the enhancement is greater than a monolayer and a SERS signal might be expected.

Yet another factor, the magnitude of the particular Raman shift, must be considered.[35] For Raman bands of very low wavenumber, the polarizability factors g_0 and g at the excitation and Raman frequencies are both within the resonance band and enhancements as high as 10^7 are predicted. For a Raman band of about 1000 cm⁻¹, one of these frequencies will have migrated toward the edge of the resonance band and the enhancement drops to about 10^6. It is this double resonance which gives rise to the double peak in the excitation profile for the 5-nm particle in Figure 2. The principal water band is so large (3500 cm⁻¹) that the Raman coupled emission is outside of the resonance band of the particle for the incident radiation and the enhancement drops to no more than about 10^5.

This effect may be responsible for very intense low-wavenumber Raman bands that have been observed.[36,37] Also Pockrand[38] has noted that the OH stretching vibrations of adsorbed water and the CH stretching modes of pyridine and ethylene are quite weak relative to the other Raman bands. The electromagnetic model seems to provide a simple explanation of these observations. Thus, when the incident radiation is tuned into the frequency range where the dipolar surface plasmon is excited, the Raman shifted radiation is less enhanced, the greater the Raman shift. This follows because for larger Raman shifts only the incident or the Raman shifted frequency can be tuned into the dipolar surface plasmon. The other frequency is too far removed from the resonant condition.

By considering both of these effects, the falloff with distance and the frequency shift, we have shown quantitatively that the failure to observe enhanced Raman signals from the layer of water surrounding colloid particles is due to the enhanced signal being overwhelmed by the signal from the bulk water.[35]

Dipole–Dipole Interaction

The model for SERS which we have considered up to now treats the interaction of only a single molecular dipole with a colloidal particle. Yet experimental studies have indicated that for submonolayer surface coverage, the enhancement also depends upon the extent of the coverage[38,39] which suggests possible di-

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SERS on Metal Colloids

pole–dipole interactions. It should be possible to treat this aspect electromagnetically. A first approach to analyzing the effect of surface coverage may be made by considering the mutual interaction of two Raman scattering molecular dipoles in the vicinity of a spherical particle and we have formulated this three-body problem using a self-consistent technique.[40]

However, calculations, carried out for silver spheres in water, indicate no appreciable interaction when the dipoles are separated by a distance of 0.4 nm or greater. For a separation of 0.2 nm there is about a 15% decrease in the Raman signal and this effect increases sharply for still closer distances of approach. However, such close approaches are unlikely for the centers of real molecules. Of course this two-body treatment oversimplifies the many-body interactions that occur in real systems and so one must look to an extension of the model to the many-body problem before the effect of submonolayer coverage on SERS can be estimated definitively. Yet for low surface coverage the Raman signal strength should correlate with surface coverage.

Spheroids

The most striking feature of SERS is that the gigantic enhancement occurs over a narrow wavelength region and that for spheres much smaller than the wavelength this excitation profile parallels a sharp band in the absorption and scattering spectra (Figure 3). These effects are sensitive to particle morphology and we now extend the model to prolate spheroids. The treatment is restricted to the limit that the particle be small compared to the wavelength. An ellipsoidal particle radiates as if it were a polarizable dipole with polarizability $(abc)g_i$ where

$$g_i = \frac{(m^2 - 1)}{3[1 + (m^2 - 1)P_i]} \qquad i = a, b, c \qquad (3)$$

and the depolarization factor P_i depends upon the values of the three semiaxes of the ellipsoid: a, b, and c.[11] For a sphere the triply degenerate values of $P_i = {}^1/_3$ so that resonance, as we have already seen, occurs whenever $m^2 = -2$. For an ellipsoid there may be three distinct absorption bands corresponding to the three values of P_i; for a spheroid there may be two bands, one of which will be doubly degenerate.

This dependence of the optical absorption of small particles on shape has been known for a long time. As the shape of an equivolume silver sphere is changed to increasingly elongated prolate spheroids, the triply degenerate absorption band at 382 nm for the sphere splits into two bands, which depend upon the two semiaxes of the spheroids, one of these at a lower wavelength and a doubly degenerate one at a higher wavelength.[33] For a 3 to 1 axial ratio, the longer wavelength band has shifted to 580 nm. In the parlance of the resonance model, there is a dipolar surface plasmon resonating at each of these wavelengths.

It is not surprising that there is a similar effect upon the SERS excitation profile. We have utilized the same physical model as for spheres but because of the added mathematical complexities, have only obtained a result valid for particles which are small relative to the wavelength.[33] Somewhat similar results were also obtained by Gersten and Nitzan[41] and by Adrian.[42] A
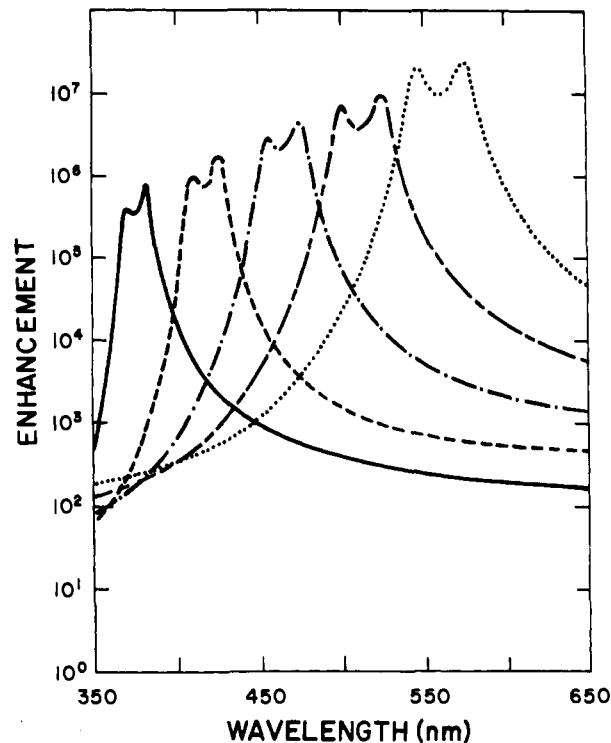
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Figure 4. SERS excitation profiles for monolayer on a very small Ag prolate spheroid in water with axial ratios 1 (—), 1.5 (– – –), 2.0 (·–·), 2.5 (———), and 3.0 (···). Raman shift is 1010 cm⁻¹.

typical calculation is shown in Figure 4, where the excitation profile for a silver particle in aqueous medium in plotted as a sphere is deformed into an increasingly elongated equivolume spheroid. The molecular dipoles are assumed to form a monolayer and to be oriented normal to the surface, and the particles are assumed to be randomly oriented. Not only does the strongly enhanced band shift but the enhancement itself increases by an order of magnitude. The longer wavelength branch of the bimodal peak occurs at the same wavelength as the corresponding peak in the absorption spectrum. The separation of the two modes in the SERS band equals the Raman shift, in this instance 1010 cm⁻¹

Concentric Spheres

In this case a particle of radius b is comprised of two regions, a spherical core of radius a and an outer concentric spherical shell. The Raman active molecules are taken to be outside the sphere. For the limiting case that the particle is small compared to the wavelength the enhancement is given by eq 1 where the polarizability factor of the particle is

$$g = \frac{(m_2^2 - 1)(m_1^2 + 2m_2^2) + q^3(2m_2^2 + 1)(m_1^2 - m_2^2)}{(m_2^2 + 2)(m_1^2 + 2m_2^2) + q^3(2m_2^2 - 2)(m_1^2 - m_2^2)} \qquad (4)$$

and m_1^2 and m_2^2 are the refractive indices of the core and spherical shell regions relative to the medium and $q = b/a$.[11,43] A similar expression holds for g_0.

There are two possibilities for exciting strong resonances: either the spherical shell is composed of a

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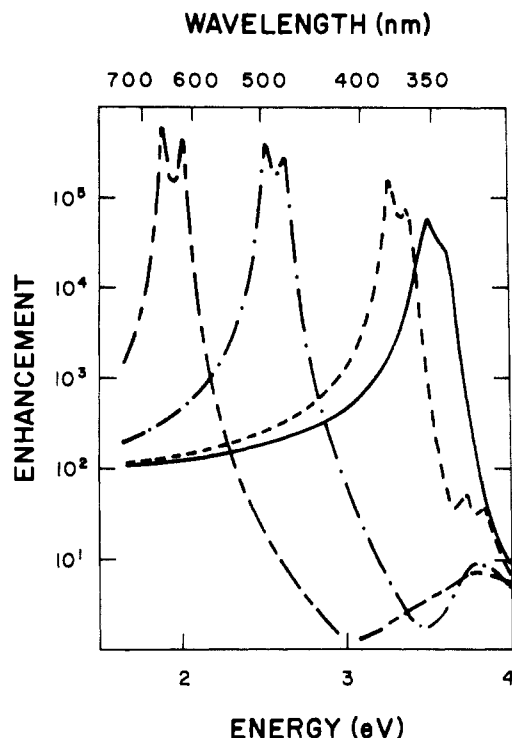(43) A. L. Aden and M. Kerker, *J. Appl. Phys.*, **22**, 1242 (1951).

WAVELENGTH (nm)

700 600 500   400   350

ENERGY (eV)

Figure 5. SERS excitation profiles for monolayer on a very small concentric sphere in air with silver shell and core with relative dielectric constant 2.25. Curves correspond to radial ratios q = 0 (—), 0.50 (---), 0.80 (·--·), and 0.90 (— — —). Raman shift is 1010 cm^{-1}.

plasma such as silver and the core is a dielectric material or the reverse where the core is a plasma. Some SERS excitation profiles[44] are illustrated in Figure 5 for the former case. The dependence of the SERS excitation profile upon the particular morphology is once again apparent. Furthermore, the SERS depends not only upon the dielectric constant of the metallic region but also upon that of the dielectric regions within the particle and of the external medium. In Figure 5 the external medium has been taken as air rather than water. This increases the relative dielectric constant of silver by the factor 1.77 which has the effect of lowering the enhancement substantially. Similar effects occur when the core of the particle is a metallic plasma and the outer shell is a dielectric.

Electrooptic Effects

It has been known since the initial studies of SERS of adsorbates on metal electrodes that the applied voltage has a pronounced effect. This may be due to alteration of surface morphology, to adsorption–desorption of adsorbed species, or to chemical reactions. In addition, there will be a redistribution of conduction electrons upon modulation of the potential which will be manifested as an altered dielectric constant in the surface region. This in turn affects the optical properties. Such an electroreflectance effect is well-known on electrode surfaces. We ask whether this effect may sensibly modify the absorption and elastic scattering by colloidal metal spheres and especially whether it will also modify the SERS. Colloidal particles are usually charged so that one might expect that the outer shell of such metal particles might comprise a region of altered dielectric constant.

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We have used a model by McIntyre and Aspnes[45] to calculate the depletion of conduction band electrons from a surface due to imposition of a voltage of 0.8 V. The SERS excitation profiles[46] were calculated by using the concentric sphere model outlined above. Depending upon the thickness selected for the layer from which electrons were depleted, there was significant broadening and splitting of the peak enhancement. However, the magnitude of the effect is particularly sensitive to the specific model used to calculate the depletion of electrons and no significant effect on SERS was found when models other than McIntyre and Aspnes were used.[47]

Active Molecules in a Spherical Shell

In this case the active molecules are treated as electric dipoles embedded within the dielectric spherical shell which coats the metallic core, rather than as a monolayer dangling out into the medium external to the particle. The field within the dielectric shell at the incident frequency which stimulates the Raman dipole must first be calculated, and the boundary value problem posed by a dipole radiating from within the dielectric shell is then solved.[17,48] Two interesting examples for which there may be significant experimental implications have been explored.

The first of these was stimulated by reports of measured enhancement of luminescence by dye molecules adsorbed on metal island films.[49] When it is recognized that fluorescence and the Raman effect can be treated similarly only in the most simplistic sense and that quenching, energy transfer, and other decay channels for fluorescence may intervene, the present model still provides a possible condition for enhancement of fluorescence. Indeed, assuming a coating of rhodamine B[50] on silver, enhancement of fluorescence as high as 10^4 was obtained. The shape of the emission spectrum itself was only moderately different from that of the pure dye.

In the second example, the metallic particle is coated with a dielectric region within which the Raman active molecules are embedded. We ask in this case whether the SERS excitation profile might not be shifted and whether the peak enhancement itself might not be affected. Indeed, that is the case.

Excitation of the dipolar surface plasmon requires that the denominator of the polarizability factor g in eq 4 become very small. For a concentric sphere this will occur for the roots for the denominator of g set equal to zero. When m_1^2 is complex, as it is for metals, the root for m_2^2 will also be complex. Yet there are roots with complex m_1^2 for which the real part of m_2^2 is positive yet the imaginary part is very small. In such cases we surmise that a nonabsorbing purely dielectric material whose dielectric constant equals the real part of such a root might show a strong enhancement.

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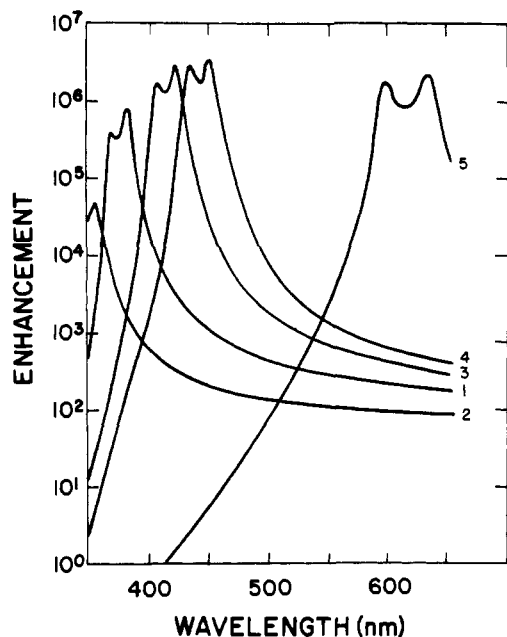
Figure 6. SERS excitation profile for dielectric coated silver sphere in water with radial ratios $q = 0.5$ and coating dielectric constant (1) 1.77 (water), (2) 1 (air), (3) 3.06, (4) 4.0, and (5) 11.6. Raman shift is 1010 cm^{-1}. Raman dipoles form a monolayer on the Ag surface.

Figure 6 depicts the SERS excitation profiles for such dielectric-coated Ag spheres in water with $q = 0.5$ and coating dielectric constants $m_2^2 = 1, 3.06, 4.0$, and 11.6.[51] In this case the Raman dipoles have been located at the interface between the silver core and the dielectric coating. There is a fivefold increase in the peak enhancement and a shift of the peak to longer wavelengths as m_2^2 increases from 1.77 (pure silver in water) to 4.0.

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Further increases in m_2^2 result in continued wavelength shift of the peak enhancement but not its magnitude. The excitation profile also depends sensitively upon the thickness of the dielectric layer as well as the actual distribution of the dipoles within the layer.[51]

Concluding Remarks

The classical electromagnetic model of colloid optics which is extended here to encompass SERS is able to account for the major experimental features of that phenomena. The electromagnetic field near a small metal particle is strongly enhanced at frequencies for which the incident radiation excites resonant surface plasmons within the particle. SERS occurs because of the coupling of the excitation of a Raman active molecule by this incident field with a similar resonance which occurs upon reradiation at the Raman shifted frequency.

The perturbation of electromagnetic fields near the surfaces of small particles is a sufficiently general phenomenon to affect other optical processes. Indeed, the methods of this *Account* may be extended to include four-wave mixing,[52,53] coherent anti-Stokes Raman scattering (CARS),[54] and double resonance at dielectric surfaces.[55]

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Picosecond Studies of Organic Photoreactions

John D. Simon and Kevin S. Peters*†

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

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Interest in the molecular motions associated with reactions in solution has sparked a rapid growth in the application of picosecond laser technology to the study of organic photochemical systems. Frequently, fast photochemical dynamics are discussed in terms of a

Kevin Peters received his B.S. from the University of Oklahoma. After obtaining his Ph.D. from Yale University in 1975, studying with Professor Ken Wiberg, he continued for a year as a postdoctoral fellow for Professor Fred Richards. He then began his work in picosecond spectroscopy during a postdoctoral appointment with Professor M. Applebury and Dr. Peter Rentzepis. In 1978 he was appointed to the faculty at Harvard University. He is currently Associate Professor of Chemistry at the University of Colorado. He is an Alfred P. Sloan Fellow and a Henry and Camille Dreyfus Teacher-Scholar.

John Simon received his B. A. from Williams College. Studying with Kevin Peters, he received his Ph.D. from Harvard in 1983. He is currently a postdoctoral fellow in Professor M. A. El-Sayed's group at U.C.L.A. and in Jan 1985, will join the faculty of the Department of Chemistry, University of California at San Diego.

"diffusion-controlled" regime.[1] Resulting in part from the limitations of various experimental techniques, there has developed, unfortunately, a common tendency to describe reaction dynamics in terms of diffusional properties, completely ignoring the question of coupling of molecular motions between reacting and solvent molecules. Since nanosecond flash photolysis is unable to resolve photochemical events faster than the rates associated with the diffusion of reactants in solution, this technique cannot be used to elucidate the molecular dynamics that occur once the reactive species have formed an "encounter pair". Picosecond techniques, however, offer the time resolution needed to study the

† Alfred P. Sloan Fellow and Camille and Henry Dreyfus Teacher-Scholar.
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