Surface-enhanced spectroscopy

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In 1978 it was discovered, largely through the work of Fleischmann, Van Duyne, Creighton, and their co-workers that molecules adsorbed on specially prepared silver surfaces produce a Raman spectrum that is at times a millionfold more intense than expected. This effect was dubbed surface-enhanced Raman scattering (SERS). Since then the effect has been demonstrated with many molecules and with a number of metals, including Cu, Ag, Au, Li, Na, K, In, Pt, and Rh. In addition, related phenomena such as surface-enhanced second-harmonic generation, four-wave mixing, absorption, and fluorescence have been observed. Although not all fine points of the enhancement mechanism have been clarified, the majority view is that the largest contributor to the intensity amplification results from the electric field enhancement that occurs in the vicinity of small, interacting metal particles that are illuminated with light resonant or near resonant with the localized surface-plasmon frequency of the metal structure. *Small* in this context is gauged in relation to the wavelength of light. The special preparations required to produce the effect, which include among other techniques electrochemical oxidation-reduction cycling, deposition of metal on very cold substrates, and the generation of metal-island films and colloids, is now understood to be necessary as a means of producing surfaces with appropriate electromagnetic resonances that may couple to electromagnetic fields either by generating rough films (as in the case of the former two examples) or by placing small metal particles in close proximity to one another (as in the case of the latter two). For molecules chemisorbed on SERS-active surface there exists a "chemical enhancement" in addition to the electromagnetic effect. Although difficult to measure accurately, the magnitude of this effect rarely exceeds a factor of 10 and is best thought to arise from the modification of the Raman polarizability tensor of the adsorbate resulting from the formation of a complex between the adsorbate and the metal. Rather than an enhancement mechanism, the chemical effect is more logically to be regarded as a change in the nature and identity of the adsorbate.

CONTENTS

I. INTRODUCTION

A. Background

From time to time a scientific discovery is reported that is both strikingly unexpected and the product of a relatively simple experiment. As a result of this unusual combination of attributes many groups enter the field almost in a frenzy, producing within weeks a hundred or more publications, many of which are "corroborative" rather than original. A new field is born, apparently in full adulthood, and complete with a name, its own symposia, and monographs, all within two or three years. Such was the case with the Mössbauer effect, and with polywater (Franks, 1981), and so, too, was the case with surface-enhanced Raman scattering (SERS). The first resulted in a Nobel prize, the second was shown to be spurious; SERS, I believe, has settled in the territory between.

Very briefly, SERS refers to the observation that for certain molecules adsorbed on specially prepared metal surfaces a Raman spectrum is observed whose intensity exceeds by a factor of 10^5—10^6 what one expects on the basis of simple calculations. The first such observations were made by Fleischmann *et al.* (1974) on the molecule pyridine adsorbed from aqueous solution onto a silver electrode roughened by means of successive oxidation-reduction cycles. Although those authors obtained Raman spectra equally as good in quality as subsequent workers, they apparently believed that the inordinate signal strength derived from a large increase in the electrode's surface area and therefore presumably also in the number of adsorbate molecules sampled. This is implied in their statement that in order to study molecules

adsorbed on electrode surfaces "it has been found necessary to prepare solid metal electrodes with high surface area" (Fleischmann et al., 1974, p. 163).

Van Duyne (Jeanmaire and Van Duyne, 1977) and independently Creighton (Albrecht and Creighton, 1977) were the first to recognize that the large intensity could not be accounted for by the increase in surface area alone, by showing that intense SERS signals could be obtained with electrode surfaces roughened too slightly for the increase in surface area to exceed a factor of 10.

Almost all early studies were performed with pyridine on roughened silver electrodes. Since then the effect has been reported for approximately a hundred molecules adsorbed on silver, gold, copper, lithium, sodium, potassium, indium, aluminum, platinum, and rhodium. Several reports on other metals have also appeared. Silver remains the most studied and the most efficient "SERS" metal, although the alkalis seem to produce SERS signals rivaling that of silver.

Besides producing enormous interest in Raman spectroscopy of surfaces, the discovery of SERS has stimulated and resurrected activity in classical electrostatic and electromagnetic theory, especially as applied to small particles; in the problem of radiating multipoles near metal surfaces, in optics of small particles and in the generation of surface plasmons. It has also brought the general area of surface-photon interactions to the foreground, prompting and encouraging experiments such as second-harmonic generation from molecules at surfaces. Largely as a result of interest in SERS the number of theoretical and experimental investigations of the optical properties of metallic gratings and molecules placed near them has greatly increased. The discovery of SERS has also renewed interest in the properties of aqueous metal sols, a well-established field of science that had fallen on hard times. This renaissance coincided to some extent with a growing interest in nonmetal colloids such as those of polymers. Additionally, the discovery of SERS helped pull together such observations as enhanced photoemission by gratings (Endriz, 1974), light emission from metal particles excited by inelastic electron tunneling (Lambe and McCarthy, 1976), anomalous absorptions in island films (Wood, 1919), and the excitation of surface plasmons into an obviously unified field of study, with experimenters now drawing from diverse areas of these cognate disciplines. Finally, the discovery of SERS has thrust physicists into such erstwhile unfamiliar a territory as electrochemistry, charge transfer, and the chemical aspects of adsorption. Hence while it is already clear that SERS has reached its zenith and has begun its Spenglerian decline, it is equally clear that it will live on a while through its various progeny, having served as a wonderful impulse that has changed somewhat the momentum of surface science.

B. The nature of the effect

SERS seems to be most intense when excited on metal surfaces containing many, usually coupled, microscopic metal domains. Such surfaces will be referred to as *SERS-active systems* for want of a better term. They include the following. (1) Electrode surfaces subjected to one or more oxidation-reduction cycles. During the oxidation half-cycle a metal salt, usually a halide, forms at the electrode surface. When reduced, the liberated metal does not redeposit itself uniformly over the electrode surface, but instead forms clusters of the metal. The average size of these small metal features has not been determined with certainty, but on the basis of scanning electron microscopy they cannot exceed 200 Å. (2) Island films consisting of small (50—200 Å diameter) metal particles usually resting on a glass or quartz substrate formed by vapor depositing a small quantity (50—150 Å mass-thickness) of metal on a warm substrate. The elevated substrate temperature increases metal atom mobility, causing nuclei to grow into islands. Samples employed consist of films with a metallic volume fraction of approximately 0.5. (3) Cold-deposited films. Metal vapor deposited on a cold substrate usually below 120 K, and often below 30 K, forms a rough film as a result of the greatly reduced mobility of the metal atoms on the cold substrate. In the limit of zero mobility one can show using Monte Carlo techniques (Moskovits, 1983) that a rough film is formed in which the rms height of the roughness features in the direction of deposition (which usually corresponds to the direction in which the thickness of the film is measured) is equal to $(dd_0)^{1/2}$, where d is the film thickness and d_0 is the diameter of a metal atom. For silver, $d_0 = 3$ Å; hence the rms height of the roughness features is approximately 77 Å for a 2000-Å film. The calculation also shows that the roughness consists of rather sharp, closely packed surface features separated by sharp pores that cannot realistically be modeled by means of isolated spheres or even prolate spheroids except at a very low order of approximation. The actual geometry suggests that the surface resonances would be delocalized over many surface features and the voids between them. (4) Lithographically produced metal spheroid assemblies (Liao et al., 1981). One of the most interesting SERS-active surfaces is produced by coating a silicon surface oxidized to a depth of 500 nm with 300 Å of chrome and 1000 Å of photoresist. A two-dimensional grating is produced by exposure to 325-nm radiation. After development the array of posts consisting of unexposed photoresist serves as a mask for argon-ion milling of the underlying chrome. The chrome pattern then in turn serves as a mask for reactive plasma etching of the SiO_2 in a CHF_3 plasma. The result is a two-dimensional array of rather conical SiO_2 posts roughly 500 nm high, 100 nm in diameter, and spaced about 300 nm apart. By evaporating silver at a glancing angle along a direction in which the ports shadow each other, one obtains isolated silver particles on top of each post, roughly ellipsoidal in shape (Liao et al., 1981). An electron micrograph of such an array produced in this way is shown in Fig. 1. (5) Lithography was previously used to produce metal gratings (Sanda et al., 1980), which also produced SERS. (6) Metal colloids. Metal sols are prepared by reducing a dissolved metal salt by means of
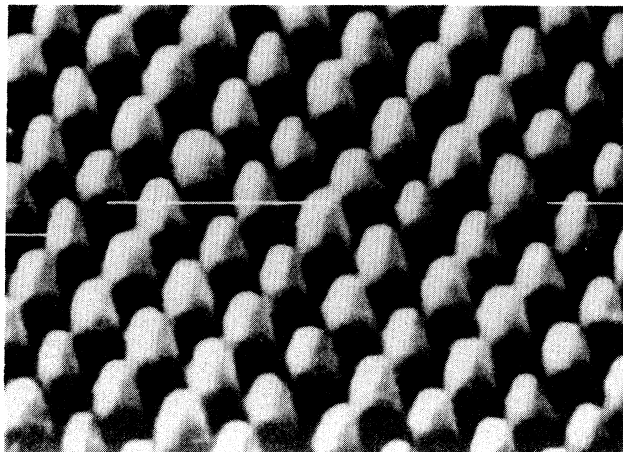
FIG. 1. Electron micrograph of silver particle array produced by evaporating silver onto SiO₂ posts produced by microlithography. The bar is 1.0 μm in length (Liao et al., 1981).

an appropriate reducing agent in either an aqueous or nonaqueous medium (Creighton, 1982). For example, silver nitrate solution reduced with sodium borohydride produces sols consisting of roughly spherical silver particles each about 200 Å in diameter and of rather narrow size distribution. The most intense SERS signals are obtained, however, from aggregated metal sols consisting of large assemblies of individual colloidal particles each more or less 200 Å in size (Fig. 2). Matrix-isolated silver and potassium colloids have also been used in SERS (Abe et al.,
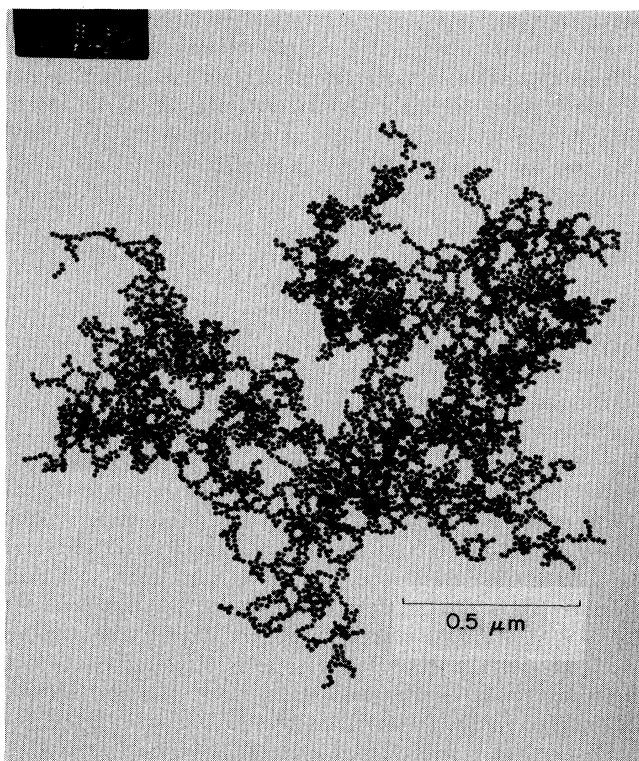
1981; Manzel et al., 1982). These are made by quenching the metal vapor in an argon atmosphere (Abe et al., 1980). The resulting particles, which can be made in size distribution whose center may be varied from about 10 Å to several hundred angstroms, are then co-condensed with adsorbate onto a low-temperature surface. (7) Other techniques. Rough silver was also produced by first depositing a CaF₂ film approximately 400 Å in mass thickness. CaF₂ is known to form a rough film (Murray et al., 1980; Murray, 1982). By depositing silver over this, one produces a rough silver film in which the silver protrusions correspond to the voids in the CaF₂.

Metals have also been roughened by means of ion bombardment in vacuo (Wood, Zwemer et al., 1981), mechanical "polishing" (Schultz et al., 1981), and acid etching—for example, silver metal slowly etched in nitric acid vapor. Rough silver is also produced when silver halide—for

FIG. 2. TEM image of gold colloid aggregate containing 4739 gold particles (Weitz and Oliveria, 1984).
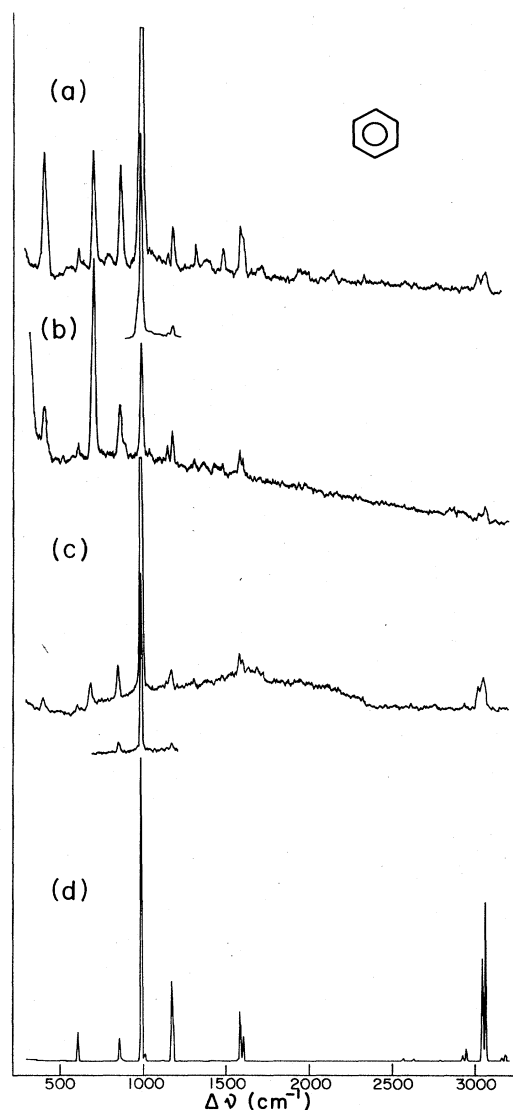

FIG. 3. SERS spectra of benzene adsorbed on cold-deposited silver (a), lithium (b), and indium (c) compared to the Raman spectrum of bulk polycrystalline benzene (d).
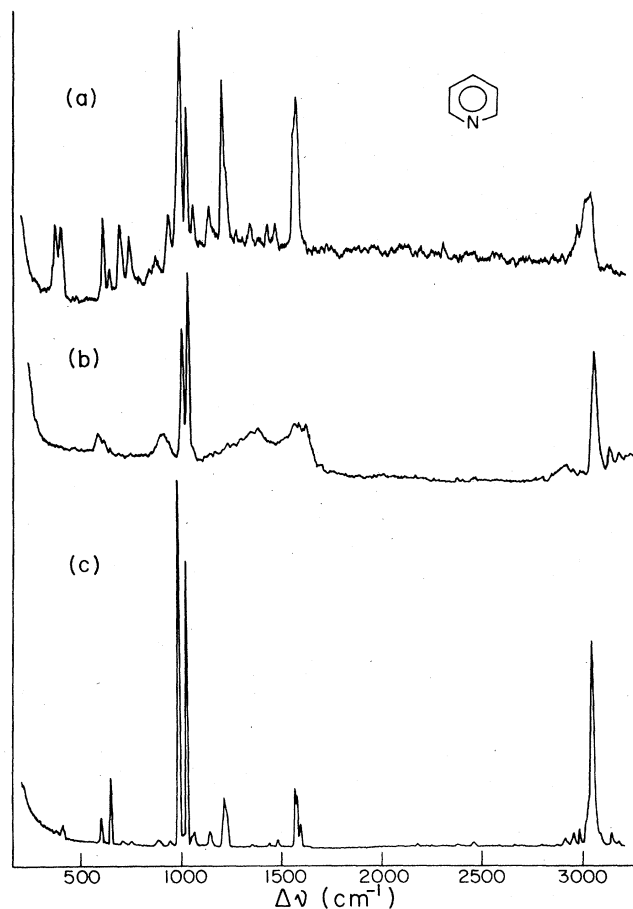
FIG. 4. Comparison of the SERS spectrum of pyridine adsorbed on a cold-deposited silver film (a) and aqueous silver colloid (b). (c) is the Raman spectrum of liquid pyridine.

example, silver bromide—films are exposed to uv radiation *in vacuo*, releasing the halogen vapor and leaving behind a rough metal surface (Rowe *et al.*, 1980). SERS has also been observed on silver powders (Dorain *et al.*, 1981; von Raben *et al.*, 1983), platinum particles supported on an oxide (Krasser and Renouprez, 1982), colloidal Pt (Benner *et al.*, 1983), rhodium particles (Parker *et al.*, 1984), and colloidal silver particles adhering to an oxide filter through which the aqueous sol was passed (McBreen and Moskovits, 1985).

Examples of SERS spectra obtained with cold-deposited films of silver, lithium, and indium are shown in Fig. 3, while a comparison of the SERS spectra of pyridine adsorbed on cold-deposited silver and aqueous silver colloid is shown in Fig. 4.

II. THE THEORIES

A. Electromagnetic theories of enhancement

1. Background

A flat surface of a good conductor has an electromagnetic resonance called the surface plasmon whose frequency and parallel momentum obey the dispersion relation

$k_{\parallel}^2 = (\omega/c)^2 \text{Re}[\varepsilon_0 \varepsilon (\varepsilon_0 + \varepsilon)^{-1}]$, where $\varepsilon(\omega)$ is the dielectric function of the conductor and ε_0 that of the ambient. For a plane wave incident from the ambient to excite the plasmon, both the frequency and parallel momentum must be conserved. This condition cannot normally be achieved with air or vacuum as the ambient (except at zero frequency); hence a surface plasmon does not radiate but is confined to the metal surface (its amplitude decaying exponentially with distance away from the surface), eventually dissipating its energy as heat.

The plasmon can be helped to radiate by ruling the surface with a grating. For a grating of wavelength Λ a new parallel momentum conservation rule obtains in which $k_{\parallel}$ for the photon must equal $k_{\parallel}$ for the plasmon plus integral multiples of $2\pi/\Lambda$. Making the surface randomly rough is tantamount to ruling a two-dimensional Fourier superposition of gratings on it, thereby again allowing a portion of the surface plasmon's energy to be radiated.

Small particles have electromagnetic resonances similar to the surface plasmon. When the particle is small compared to the wavelength of an incident plane wave, a plasmon can be excited that has the symmetry of a time-varying dipole. Once excited, this dipolar plasmon can, of course, radiate. For a sphere this resonance occurs at the frequency ω_R, for which the condition $\text{Re}[\varepsilon(\omega_R)] = -2\varepsilon_0$ is satisfied.

A sphere has other resonances whose frequencies may be obtained from the relation $\text{Re}[\varepsilon(\omega_N)] = -[(N+1)/N]\varepsilon_0$, where N is an integer. Except for the $N=1$ resonance, which is dipolar, the others have symmetries corresponding to higher multipoles and therefore cannot radiate.

An emitting molecular dipole placed near a metal sphere can excite resonances of any order, provided the sphere is large compared to the wavelength of the radiation in question and assuming a fair degree of resonance between the dipole's frequency and those of the electromagnetic resonances of the sphere. Since only the dipolar plasmon can radiate, the fraction of the dipole's energy transferred to the metal sphere that has excited resonances corresponding to $N > 1$ will be degraded to heat. Likewise, an emitting dipole placed near a flat surface can excite the surface plasmon, since there is no momentum conservation restriction limiting the coupling of a point emitter and the plasmon. The plasmon, once excited, cannot radiate, however.

Surface-enhanced Raman seems to be an effect observed strongly in systems that can couple plasmonlike electromagnetic resonances to electromagnetic plane waves, i.e., small metal features and gratings. Metiu and Das have expressed the following paradigm: "Large enhancements are produced when the structure absorbs the photon and localizes it. Gratings and flat surfaces (in the ATR configuration) absorb the photon and 'store' the electromagnetic energy into the surface plasmon; this is delocalized in the direction parallel to the surface but localized in the perpendicular one. This increases the electromagnetic energy density near the surface. A sphere localizes the photon, by plasmon excitation, in all directions

and the resulting concentration of electromagnetic energy is larger than that produced by a grating" (Metiu and Das, 1984).

Presumably, gaps between closely spaced metal features, as in aggregated colloids or cold-deposited films, concentrate the electromagnetic (em) energy even further, producing even higher enhancements.

2. Flat surfaces

In the early days of SERS several groups considered possible enhancement mechanisms that would result from electromagnetic interactions between a molecule and a flat surface. A popular model due to King, Van Duyne, and Schatz (1978) and independently to Efrima and Metiu (1979a,1979b,1979c) attributes the enormous enhancement to the large polarizability that one calculates for certain choices of parameters when the Raman emitting system is taken to be a composite of the molecule and its conjugate-charge image in the metal. This model is therefore known as the "image field model." I outline it according to the version of King et al. (1978) (the Efrima-Metiu form is discussed below in another context). For simplicity one assumes a diagonal Raman polarizability tensor and a field polarized along the normal of the flat surface (the z axis). The problem therefore becomes one dimensional.

The dipole moment induced in the molecule by the incident field and its image field is

$$\mu = \alpha(E + E_{im}) \ ,$$

where E and E_{im} are the incident and image fields, and α is the zz component of the molecular polarizability.

E_{im} is given by $E_{im} = [(\varepsilon - \varepsilon_0)/(\varepsilon + \varepsilon_0)]\mu/(4r^3)$ where r is the distance between the (point) dipole and the surface. Defining this distance for real molecules and surfaces (i.e., ones containing metal atoms) is a serious problem in this model and ultimately contributes to its downfall. Substituting and rearranging, one obtains

$$\mu = \alpha[1 - (\alpha/4r^3)(\varepsilon - \varepsilon_0)/(\varepsilon + \varepsilon_0)]^{-1}E \ .$$

This looks like a conventional expression for a dipole moment μ induced by a field E except that instead of the polarizability α one has an effective polarizability

$$\alpha_{eff} = \frac{\alpha}{1 - (\alpha/4r^3)(\varepsilon - \varepsilon_0)/(\varepsilon + \varepsilon_0)} \ .$$

This expression has a pole at the frequency at which $Re[\alpha(\varepsilon - \varepsilon_0)/(\varepsilon + \varepsilon_0)]/(4r^3) = 1$. Clearly this is related to surface-plasmon excitation in the metal surface at the frequency for which the condition $Re(\varepsilon) = -\varepsilon_0$ obtains; otherwise, the quantity $(\alpha/4r^3)(\varepsilon - \varepsilon_0)/(\varepsilon + \varepsilon_0)$ would not approach 1 except for unrealistically small values of r. As it is, the magnitude of α_{eff} depends dramatically on r, and it is only at very small distances that α_{eff}/α exceeds unity to any significant extent [this type of resonance was previously pointed out in the context of the infrared spectrum of adsorbed molecules (Dignam and Fedyk, 1977)].

Using reasonable parameters, King et al. (1978) show that on silver Raman enhancements in excess of 10^6 are possible at or below $r = 1.65$ Å, the enhancement dropping to around 10^2 for $r = 2$ Å.

Estimates of the possible image field enhancement are dramatically reduced in calculations in which the point dipole approximation or the assumption of a local dielectric function for the metal have been removed. Hilton and Oxtoby (1980) determined the static polarizability of a hydrogen atom near the surface of a perfect conductor (i.e., taking the image to be an antihydrogen atom). They conclude that the polarizability of the combined system varies little with hydrogen-antihydrogen separation until that quantity falls below an unrealistic 1 Å.

Weber and Ford (1980,1981) have refined the King—Van Duyne—Schatz (KVS) model by using the expression of Kliewer and Fuchs (1968) for the metal's dielectric response, thereby removing the local assumption, and a sphere for the adsorbed molecule thereby eliminating the point dipole restriction. By so doing they reduce the expected image-field enhancement by $\sim 10^3$ below the KVS model at corresponding values of r.

Feibelman (1980) finds essentially no image-field enhancement in a model that uses linear response theory to treat the response of the metal (jellium) electrons to the time-varying induced dipole due to the adsorbed molecule. A feature of this treatment is the choice of location for the image plane. Feibelman attributes the weak effect of the image field to screening. A similar calculation by Korzeniewski et al. (1980) finds a field enhancement of the order of 10^2.

Lee and Birman (1980a,1980b) have addressed the image-field problem as part of their general coupled-state quantum formalism for treating SERS. In that model surface excitations (mainly the plasmon but including, where pertinent, surface states and other excitations) are coupled to molecular excitations. The calculated enhancement depends on three parameters: the plasmon lifetime, the molecular dipole excitation oscillator strength, and the molecule-metal separation. Using a value of 0.08 eV for the plasmon bandwidth and silverlike parameters, Lee and Birman obtain an enhancement of approximately 10 at uv frequencies and essentially no enhancement in the visible.

It therefore appears that according to the majority opinion image-field enhancement is not an important contributor to SERS. An eloquent minority position, however, has been expressed by Schatz (1982).

A decidedly real surface-enhancement process, electromagnetic in origin, which occurs at flat metal surfaces is due to the fact that the molecule near the metal surface is illuminated by both a direct and a reflected field, coherently superimposed to give an intensity up to four times the incident intensity. Likewise, the Raman scattered field is composed of a direct and reflected field yielding up to fourfold an increase in its intensity for a total maximum enhancement of 16. This effect has been dubbed the "minor" enhancement by Efrima and Metiu (1979a,1979b,1979c). The factor of 16 is for perfect con-

ductors. Calculations with real metals show (Moskovits, 1982) that a factor of 5 or 6 is more realistic. To this one must add the possibility that the molecule is oriented on the surface; hence the component of Raman polarizability that is responsible for the observed surface Raman may be larger (or smaller) than the rotationally averaged quantity.

Other possible enhancement effects at flat or almost flat surfaces will be discussed later.

3. Simple models for roughness

A successful group of theories, which has been able to account for a large number of the features of SERS, is based on the response of small metal particles to electromagnetic fields. For simplicity I shall call this group of models the em model. Its essential features were first enunciated by Gersten (1980a,1980b) and Gersten and Nitzan (1980) and simultaneously by McCall et al. (1980). A most thorough exposition is due to Kerker et al. (1980), whose analysis will be used to introduce this topic [see also Wang et al. (1980)]. The broad assumptions of the em theory are that the various metal-surface treatments that produce SERS, be they electrochemical oxidation reduction or evaporation onto a cold substrate, produce a surface covered with submicroscopic surface roughness features whose response to electromagnetic waves may be modeled as regards most essential features by considering a small metal ellipsoid near which the adsorbed molecules are placed. This model is, naturally, most consonant with unaggregated colloidal particles. The dipole moment induced in an adsorbed molecule will be due both to the incident field and the field elastically scattered by the metal ellipsoid. For ellipsoids small compared to the wavelength of light, this scattered field becomes much larger than the incident field when the frequency becomes resonant with that of the dipolar surface plasmon. This may be regarded as a field concentration effect in a region of space just outside the ellipsoid. Hence the radiation by the molecular dipole at both elastic (Rayleigh) and inelastic (Raman) frequencies is increased. Moreover, the Raman-scattered field will, for small Raman shifts, itself be resonant or near resonant with the surface plasmon of the metallic particle causing the field scattered by the metal particle to be unusually large. That is, the power drawn from the oscillating molecule will be unusually large as a result of this resonance.

Following Kerker et al. (1980) and Wang et al. (1980), let us first consider the case of a spherical particle. A molecule, treated as a classical electric dipole, is placed at a position $\mathbf{r}'$, outside a spherical metallic particle. Upon irradiation with a plane wave of frequency ω_0, the molecular dipole will radiate at the Raman frequency ω with a dipole moment

$$\mathbf{p}(\mathbf{r}',\omega) = \alpha' \cdot \mathbf{E}_p(\mathbf{r}',\omega_0) , \qquad (1)$$

where α' is the Raman polarizability of the molecule and $\mathbf{E}_p$ is composed of two parts:

$$\mathbf{E}_p(\mathbf{r}',\omega_0) = \mathbf{E}_i(\mathbf{r}',\omega_0) + \mathbf{E}_{LM}(\mathbf{r}',\omega_0) , \qquad (2)$$

$\mathbf{E}_i$ being the incident field and $\mathbf{E}_{LM}$ the scattered field, which is calculable using Lorenz-Mie theory.

The electric field associated with the Raman radiation at an observation point $\mathbf{r}$ is given, in turn, by

$$\mathbf{E}_R(\mathbf{r},\omega) = \mathbf{E}_{dip}(\mathbf{r},\omega) + \mathbf{E}_{sc}(\mathbf{r},\omega) , \qquad (3)$$

in which $\mathbf{E}_{dip}$ is the field that would have to be present at $\mathbf{r}$ due to the oscillating dipole $\mathbf{p}$ had the sphere been absent and $\mathbf{E}_{sc}$ is the field scattered by the sphere that must be computed by solving the appropriate boundary-value problem at the frequency ω.

The reader is referred to Kerker et al. (1980) and Wang et al. (1980) for details. In a nutshell, all four fields are expressed as linear combinations of vector spherical harmonics. The values of the coefficients pertinent to the field $\mathbf{E}_p$ are obtained directly from the Lorenz-Mie theory (Van de Hulst, 1957). The values of the coefficients of the expansions of $\mathbf{E}_{dip}$ (two are required, one each for $r > r'$ and $r < r'$) are obtained by relating $\mathbf{E}_{dip}$ to $\mathbf{p}$ and the free-space Green's dyad $\mathbf{G}$, which is a known function of the vector spherical harmonics. By equating coefficients one then obtains the coefficients in the expansion of $\mathbf{E}_{dip}$ in terms of those of $\mathbf{E}_p$. $\mathbf{E}_{sc}$ is derived in a manner analogous to the Lorenz-Mie theory.

The Raman scattering intensity is the square of the far-field amplitude of E_R, i.e.,

$$I_R = \lim_{kr \to \infty} |\mathbf{E}_R(\mathbf{r},\omega)\exp(ikr)/r|^2 . \qquad (4)$$

The quantity $\exp(ikr)/r$ is, of course, the space-dependent part of a spherical wave.

An enhancement factor G is now defined as

$$G = I_R / I_R^0 , \qquad (5)$$

where I_R^0 is the Raman intensity in the absence of the metal sphere. In which case, $\mathbf{p}$ is obtained from $\alpha \cdot \mathbf{E}_i$ and $\mathbf{E}_R$ is identical with $\mathbf{E}_{dip}$.

Using the treatment of Kerker et al., one can determine the expected enhancement for a molecule placed arbitrarily above a sphere of any size and with any polarization of the incident and Raman-scattered fields. The calculation does not consider retarded fields which would be important when either the sphere radius or the molecule-sphere distance becomes large or when both of them do. Nor does the calculation consider the effect on vibrational modes of the molecule which are represented by a nondiagonal Raman polarizability tensor.

Figure 5 shows the calculated enhancement for silver spheres of various sizes assuming that even for the smallest sphere bulk optical properties may be used for the metal. Values in excess of 10^6 are predicted. This, of course, is an upper limit, since the effective conductivity of a particle will be dramatically decreased when the particle size becomes smaller than the electronic mean free path (~ 300 Å for silver). Metal clusters of such small dimensions may also have lattice parameters somewhat different from the bulk (Yokozeki and Stein, 1978). This may change the optical properties especially near the crucial plasma resonance frequency. Finally, the metal
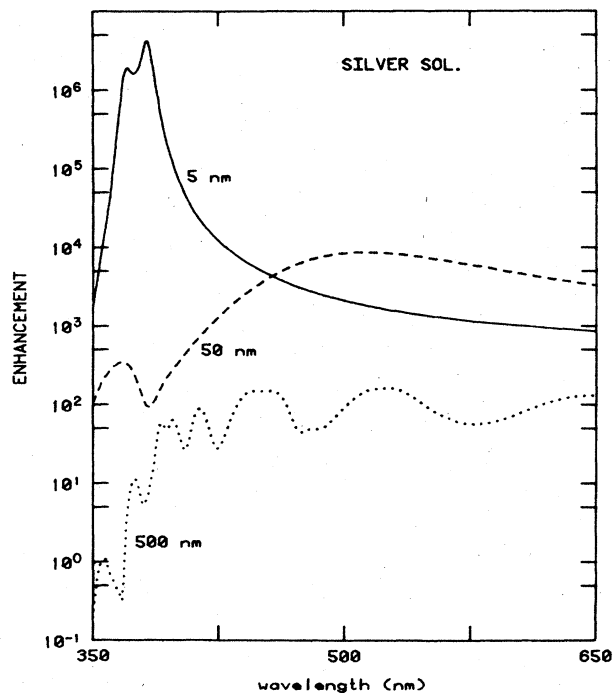
FIG. 5. Calculated enhancement for a 1010-cm^{-1} Raman band of a molecule adsorbed on silver spheres of radii 5, 50, and 500 nm (Kerker et al., 1980).

dielectric constant was assumed to be local. The effect of nonlocality, which will be touched upon later, is generally to decrease the sharpness of the resonances that are assumed to be responsible for the enhancement in the em theory. The effect of these refinements is to decrease the calculated enhancement for an isolated sphere by 2—3 orders of magnitude.

Particles approaching the wavelength of light in size show less dramatic enhancements. The dependence of the enhancement upon excitation frequency is also greatly affected by particle size, the smallest particles showing a rather sharp resonance due almost exclusively to the excitation of dipolar surface plasmons, while the larger particles show broader excitation spectra, resulting from the excitation of higher multipole plasmons.

The physics of the enhancement and its relation to the excitation of surface plasmons is most easily appreciated in the very small particle limit. In that limit the enhancement is given by

$$G = \left| \mathbf{i} + a^3 g_0 [3\mathbf{n}(\mathbf{n} \cdot \mathbf{i}) - \mathbf{i}]/r'^3 \right.$$
$$+ \frac{a^3}{r'^3} g [(a^3 g_0/r'^3 - 1)\mathbf{i}$$
$$\left. + (a^3 g_0/r'^3 + 1)3\mathbf{n}(\mathbf{n} \cdot \mathbf{i})] \right|^2, \qquad (6)$$

where $\mathbf{i}$ refers to the polarization of the incident field at $\mathbf{r}'$, i.e., $\mathbf{E}_i(\mathbf{r}', \omega_0) = E_0 \mathbf{i}$, $\mathbf{n} = \mathbf{r}'/r'$ and g and g_0 are the values of the function $(\varepsilon - 1)/(\varepsilon + 2)$ evaluated at ω and

ω_0, respectively, ε being the ratio of the complex dielectric function of the material comprising the colloidal particle to that of the ambient.

Equation (6) predicts a decrease in the degree of enhancement with distance H above the metal sphere that goes as $(a + H)^{-12}$ (the quantity $r' = a + H$).

In the most favorable configuration when the molecule is on the surface of the sphere $(r' = a)$ and the polarization of the incident and scattered wave is perpendicular to the scattering plane (all other polarization combinations are, in fact, zero for a single molecule near a sphere—the situation for a sphere fully enrobed in adsorbate will be considered shortly) the enhancement factor is given by (Kerker et al., 1980; Wang et al., 1980)

$$G = 5 \left| 1 + 2g_0 + 2g + 4gg_0 \right|^2. \qquad (7)$$

The quantity g (or g_0) becomes large when $\mathrm{Re}(\varepsilon)$ approaches -2. This is precisely the condition for the excitation of localized surface plasmons in the sphere. When that condition obtains, Eq. (7) is dominated by the gg_0 term and G becomes

$$G = 80 \left| gg_0 \right|^2. \qquad (8)$$

Hence according to this model, large SERS signals are expected when both the frequency of the incident and Raman-scattered beams approach the surface-plasmon (sp) resonance conditions, in which case (and assuming a small Raman shift) the quantity G becomes proportional to $[(\varepsilon' - 1)/\varepsilon'']^4$ (McCall et al., 1980), in which ε' and ε'' are, respectively, $\mathrm{Re}(\varepsilon)$ and $\mathrm{Im}(\varepsilon)$. Hence the metals which provide the greatest enhancement, according to this model, are those that have small ε'' values and large ε' values at the frequency at which $\mathrm{Re}(\varepsilon) = -2$. This condition immediately brands the alkali metals (group Ia) and the coinage metals (Ib) as good enhancers, producing G values in excess of 10^5. Moreover, the resonance condition for these metals lies in or near the visible region of the spectrum. All metals enhance, however, and spherical particles made of metals such as Pd and Pt are expected to yield G values of $10^2 - 10^3$ under the right excitation conditions (near uv). [Some indication of the enhancing ability of various metals may be obtained from Fig. 9 of DiLella et al. (1980), which plots a function roughly proportional to $\mathrm{Im}(g)$ versus exciting photon energy. The fourth power of the quantity plotted is approximately equal to G.]

The dependence of G upon $(a + H)^{-12}$ and $(\varepsilon' - 1)/\varepsilon''$ was first pointed out by McCall et al. (1980), Gersten (1980a,1980b), and Gersten and Nitzan (1980).

When a sphere is entirely covered with adsorbed molecules, one must extend this analysis by averaging the Raman-scattered light emanating from every molecule. Kerker et al. (1980) and Wang et al. (1980) have performed this average assuming each admolecule to be an oscillating dipole normal to the surface. This yields the result

$$G = \left| (1 + 2g)(1 + 2g_0) \right|^2 \qquad (9)$$

independent of the choice of polarization direction of the

incident or the scattered light.

Hence the em theory for SERS observed from molecules adsorbed on spherical metal particles predicts that a strong enhancement will be observed when the following conditions are met: (1) the particle size must be smaller than λ, (2) the frequency of excitation or scatter must be near the surface-plasmon resonance condition, and (3) the molecule cannot be too far removed from the surface.

B. Spheroidal particles

Although the physics of the em enhancement effect remains substantially the same when a molecule is adsorbed near a nonspherical metal particle, there are several important modifications that the new geometry brings about. Because the fields about a particle of arbitrary shape cannot be solved in closed form, the effect of particle geometry is usually presented by considering spheroids of revolution. On replacing a sphere by a spheroid, one finds the following. (1) The plasmon resonance shifts toward the red. (2) The SERS of molecules placed near the tip of prolate ellipsoids or near the waist of oblate ellipsoids is enhanced, while that of molecules placed near the sides of prolate and top of oblate ellipsoids is reduced as compared to the SERS of molecules placed near a sphere (the lightning rod effect). The former of these effects dominates, however, so that the average enhancement for a monolayer of adsorbate surrounding a spheroid increases by almost 2 orders of magnitude on increasing the aspect ratio (the ratio of the larger to the smaller axes) of the spheroid from 1 to 3 (Wang and Kerker, 1981). Since the enhancement is largest in the region of the highest curvature, the SERS spectrum will be dominated by molecules adsorbed near the tip of prolate and near the waist of oblate isolated ellipsoids. (3) The enhancement spectrum will have two peaks, one corresponding to the enhancement of the incident field, the other of the Raman-scattered field. The two peaks will be separated by an energy corresponding to the frequency of the vibration producing the Raman-shifted scattering. (4) When surrounded by an ambient medium of dielectric constant greater than unity, the plasmon resonance shifts further to the red. When the dielectric coating is finite, as in the case of a metal spheroid covered with a thin film of adsorbate, the enhancement spectrum may become more complicated. These effects will be discussed in detail in a later section. (5) Even metals that are not innately good plasmon enhancers are predicted to produce sizable SERS signals, provided one can produce colloidal particles or surface features of sufficiently large aspect ratio. (6) On considering the fields around a hemispherical or hemispheroidal bump attached to a metal plane as a model for SERS obtained from a rough surface, one encounters further new phenomena. When the underlying metal is taken to be a perfect conductor, for example, the enhancement is found to be 16-fold increased over the case of a free spheroid (Metiu, 1982). This is due to the image of the metal spheroidal dipole in the underlying

perfect mirror. Otherwise, the physics predicted for unattached metal spheroids is more or less left intact. On taking the underlying metal to be co-substantial with that of the bump, on the other hand, one obtains an enhancement spectrum considerably more structured than what was calculated for the colloidal ellipsoid.

A further modification is obtained when the rough surface is modeled by means of a large number of ellipsoids of differing size and aspect ratio packed close together on a surface. Simple dipolar coupling (which is a poor approximation when the distance between metal particles is small) predicts a red shift in the plasmon resonance frequency with increasing packing density and an overall increase in the intensity of the resonance. Not unexpectedly, when a sufficiently broad distribution of surface bump sizes and aspect ratio are considered, the calculated enhancement spectrum becomes rather broad and loses its resonance shape. When higher multipolar interactions are allowed, one finds [at least one extrapolates from a calculation on two interacting metal spheres (Aravind et al., 1981)] that the intensity of the resonance is reduced and the spectrum of the intensity of the electromagnetic radiation in the region between metal surface features will be broadened.

Now let us consider these points in a little more detail. McCall et al. (1980) predicted but did not work out in detail the effect of a nonspherical particle shape and a distribution of metal particle sizes on SERS. Coeval with that work Gersten (1980a,1980b) considered the Raman scattering by a molecule placed above a hemispheroidal cap atop a perfectly conducting metal plane, and even more detailed results are presented by Gersten and Nitzan (1980). By assuming the dimensions of the surface boss to be small compared to the wavelength of light, the fields about the metal bump become solutions of the Laplace equation, $\nabla^2 \mathbf{E} = 0$, rather than of the more complicated Helmholtz equation, $\nabla^2 \mathbf{E} + k^2 \mathbf{E} = 0$. The surface bump was taken to be half of an ellipsoid of revolution with semimajor and semiminor axes equal to a and b, respectively, and the "adsorbed" molecule was placed on the axis of cylindrical symmetry a distance H above the metal bump. Using spheroidal coordinates ξ and η and the geometrical parameter $f = (a^2 - b^2)^{1/2}$, Gersten and Nitzan calculate a Raman enhancement given by

$$G = \left| \frac{1 + (1-\varepsilon)\xi_0 Q_1'(\xi_1)/[\varepsilon Q_1(\xi_0) - \xi_0 Q_1'(\xi_0)]}{1-\Gamma} \right|^4 , \quad (10)$$

in which $\xi_0 = a/f$, $\xi_1 = (a+H)/f$, ε is the complex dielectric complex of the metal. Q_1 is Legendre function of the second kind and Γ is a complex-valued quantity (Gersten and Nitzan, 1980) that depends acutely on H. In the limit of $\varepsilon \to 1$, $\Gamma = 2\alpha/[2(a+H)]^3$ (α is the molecular polarizability). The term $1-\Gamma$ arises in the so-called image enhancement factor that was discussed above. This term approaches unity rapidly as H increases.

The quantity G as given by Eq. (10) can become large from three causes: (1) the quantity $|1-\Gamma|$ may become small, (2) the quantities ξ_0 and ξ_1 approach unity, i.e., the

ellipsoid becomes needlelike (the lightning rod effect), or (3) the quantity $|\varepsilon(\omega)Q_1(\xi_0)-\xi_0 Q_1'(\xi_0)|$ becomes small. This is the condition for surface-plasmon resonance, and it is clear that the precise frequency at which resonance occurs depends on ξ_0, i.e., on the aspect ratio of the surface boss. This is shown in Fig. 6. As discussed previously, the first effect is normally not very important. Calculations by Gersten (1980a,1980b), for example, indicate that the Γ is never larger than 0.1 (for $H = 1$ Å). The other two causes are, however, important contributors to SERS. The dependence upon H of the quantity G is also noteworthy. One finds that G drops off with H faster the larger the aspect ratio of the surface bump; hence for very sharp bumps only those molecules actually at the surface of the tip of the bump are expected to contribute to SERS.

Gersten and Nitzan (1980) consider also the effect of molecular orientation upon SERS. For simplicity they assume adsorption upon a spherical metal particle and allow the molecularly induced dipole to take on an arbitrary orientation with respect to the normal to the surface. Briefly, they find that the SERS signal for a molecular dipole directed along the surface normal is expected to be considerably stronger than for a tangential orientation.

Some of the elements contained in the Gersten-Nitzan calculation were also reported by Adrian (1981).

A somewhat more convenient statement of the lightning rod effect is due to Liao and Wokaun (1982), who proceed as follows.

For an ellipsoid small compared to λ, a uniform laser field E_L polarized so as to coincide with its major axis induces a polarization density

$$P = \frac{1}{4\pi}\frac{(\varepsilon-1)E_L}{1+(\varepsilon-1)A_\alpha} . \tag{11}$$

The field at the tip is

$$E_{\text{tip}} = \{1+(1-A_\alpha)(\varepsilon-1)/[1+(\varepsilon-1)A_\alpha]\}E_\alpha , \tag{12}$$

where $\varepsilon(\omega)$ is the dielectric function of the metal comprising the ellipsoid and A_α, the depolarization factor, is given by

$$A_\alpha = (ab^2/2)\int_0^\infty ds/[(s+\alpha^2)R] ,$$

in which α is either a or b and $R = (s+a^2)^{1/2}(s+b^2)$. For a sphere $A_\alpha = \frac{1}{3}$. The far field of the ellipsoid along its major axis is a dipole field given by $E_{\text{dip}} = 2\mu/a^3$, where $\mu = 4\pi ab^2 P/3$ (i.e., P times the volume of the ellipsoid) and the near field at the tip may be written as

$$E_{\text{tip}} = \gamma E_{\text{dip}} + E_L .$$

The quantity $\gamma = \frac{3}{2}(a/b)^2(1-A_\alpha)$ has the property that $\gamma = 1$ for a sphere; it therefore expresses the increase in the field at the tip due to nonsphericity. Since the SERS signal will depend on E_{tip} approximately as E^4, the quantity γ will likewise contribute to SERS as γ^4. For an aspect ratio of 3:1, for example, $\gamma = 12$ and $\gamma^4 = 2 \times 10^4$, a not insignificant enhancement that is entirely independent of the metal optical properties—hence the importance of the lightning rod effect.

Ruppin (1981) considered a hemispherical bump—i.e., the perfect conductor approximation was not made. He assumes the SERS intensity due to a molecule at position r to be more or less accurately given by $[E(r)/E_{\text{inc}}]^4$. A plot of this quantity as a function of frequency is shown in Fig. 7 for a surface bump made of silver. It is clear that the SERS enhancement spectrum is expected to be somewhat complex. This complexity will not be seen on actual rough surfaces containing surface irregularities of various shapes and sizes, since the precise position of the resonances in Fig. 7 will depend on the bump geometry;
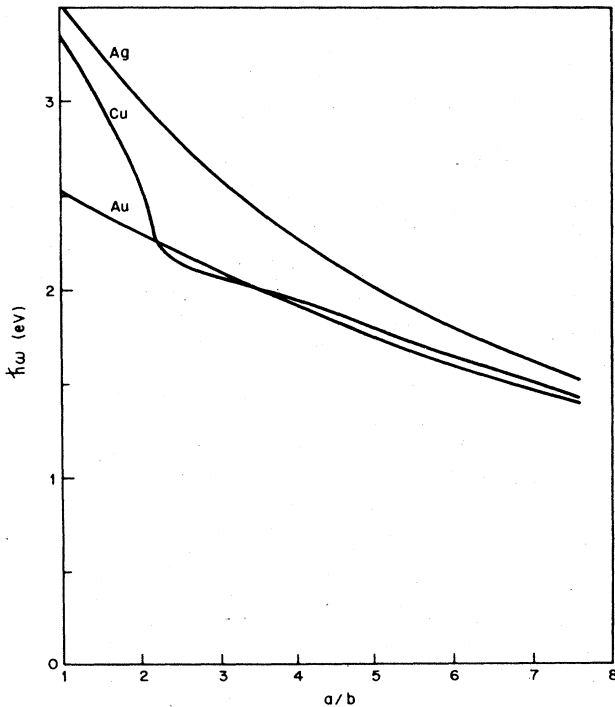
FIG. 6. The energy of surface plasmons for Ag, Cu, and Au as a function of the aspect ratio (Gersten and Nitzan, 1980).
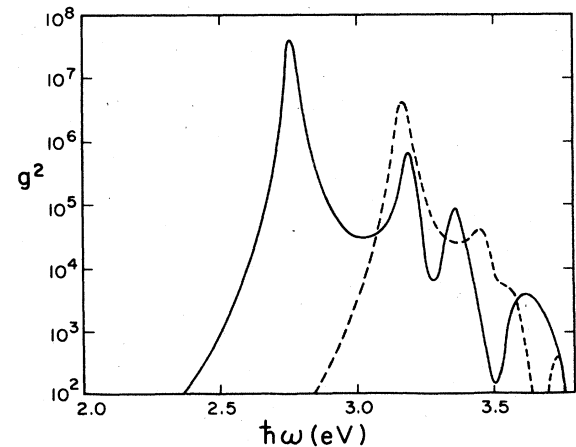
FIG. 7. Frequency dependence of the enhancement $|E/E_0|$ for a molecule located 0.05 sphere radii above a silver sphei surface and 87.5° from the vertical for a vertically polarized ir cident field. Solid curve—molecule in vacuum; dashed curve— in water (Ruppin, 1981).

hence the average enhancement spectrum will be less featured.

The same conclusion is arrived at by Laor and Schatz (1981), who consider the electrodynamics of distributions of hemispheroidal bumps on a perfectly conducting plane.

The authors assume dipolar coupling among spheroids and show that certain groupings of hemispheroid bumps result in multiple resonances with significant contribution in the red or near infrared even for only mildly aspheric bumps. This contrast with the predictions based on high-symmetry arrays or effective medium theories such as the Maxwell-Garnett (1904) theory. As a result of this, a "near continuum" of (plasmon) resonances will be observed for a surface covered with a random distribution of "spheroidal" caps. And the authors predict an electromagnetic contribution to SERS of the order of 10^2 rather than 10^6–10^8, as predicted for single bumps. This calculation is marred, however, by the exclusion by the authors of the em enhancement of the Raman-scattered field, arguing that simultaneous plasmon resonance cannot be achieved at both the incident and Raman-scattered frequencies. That this is not the case has been demonstrated most dramatically by the calculations of Wang and Kerker (1981), which will be discussed below. Laor and Schatz (1981) also ignore the effect of multipolar interactions, which they admit may make a significant difference to the result.

The sensitivity of the fields about an assembly of metal particles to the multipolar order of the interaction may be surmised from the work of Aravind et al. (1981), who considered the fields about two interacting metal spheres in the Rayleigh limit (size less than the wavelength). The parameter upon which their discussion rests, $\Lambda = R/(2R + D)$, where R is the sphere radius and D the separation between the outer periphery of the spheres measured along the line joining their centers, determines how strongly the two spheres interact. When Λ is smaller than 0.5, one requires as many as 60 terms in the multipolar expansion for the potential about the spheres to converge. Dipolar coupling is clearly not sufficient to describe the fields about closely spaced metal particles. Their results illustrate some of the changes to the fields that coupling brings about. The quantity whose properties were studied by Aravind et al. (1981) is the ratio $I = E^*E/E_0^*E_0$, i.e., the field intensity at a point relative to what would exist in the absence of the spheres. For two spheres separated by a large distance the quantity I shows a resonance at around 3.48 eV, clearly associated with surface-plasmon resonance (Fig. 8). As the two spheres are brought closer together, the single resonance splits into two, a low-frequency maximum that recedes to lower frequencies as the spheres are brought closer together and a high-frequency peak whose position remains more or less at 3.48 eV. The relative intensities of the two peaks depend markedly on the point of observation, so, for example, on the surface of one of the spheres at a point 45° with respect to the line joining their centers the intensity of the high-frequency peak exceeds that of the low-frequency one, while in the region between the
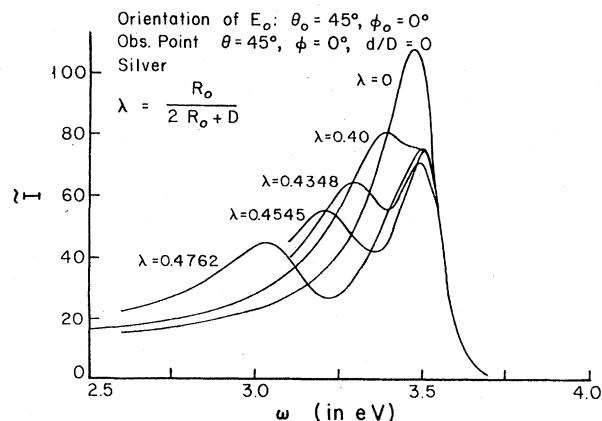

FIG. 8. Resonances of a two-sphere system for different values of the parameter λ (Aravind et al., 1981).

spheres the reverse is true.

The breakup of the spectrum of I into two peaks is reminiscent of the development of two resonances upon deforming a sphere into a prolate ellipsoid. However, in contrast with the ellipsoid that has high fields at the tips, the point of the high field is located between the two closely spaced particles. The interactions between the two spheres also tend to lower somewhat the strength of the resonance.

The most graphic calculation on spheroids is due to Wang and Kerker (1981), who extended the method described previously for spherical colloidal particles to ellipsoids. After calculating the Raman scattering intensity of a molecule, taken as a point dipole placed near an ellipsoid, Wang and Kerker average over all orientations of the ellipsoid, arguing that this is equivalent to averaging simultaneously over both the location of the molecules on the surface of the spheroid and its orientation in space. In this way they obtain a result that serves as a model for a colloid composed of randomly oriented spheroids covered by a monolayer of molecules. As before, Wang and Kerker predict that all polarization components of the scattered light will be equally enhanced.

The expected SERS excitation profiles for prolate silver spheroids are summarized in Fig. 9 as a function of aspect ratio, while the extinction cross section is shown in Fig. 10. Several features are worthy of note. The enhancement spectrum consists of two peaks, one due to resonance with the incident, the other with the Raman-shifted fields. The latter seems to be more intense than the former (note that the ordinate of Fig. 9 is logarithmic so that in an experimental excitation profile only the resonance in the Raman-shifted peak may be discerned). Second, the enhancement increases steadily with increasing aspect ratio, while the extinction coefficient seems to increase only slightly with increasing aspect ratio. Another interesting observation is that while the spectrum of the extinction cross section consists of two peaks for spheroids with aspect ratios different from unity, one whose frequency is calculated to be almost independent of the aspect ratio, while the other moves to longer wave-
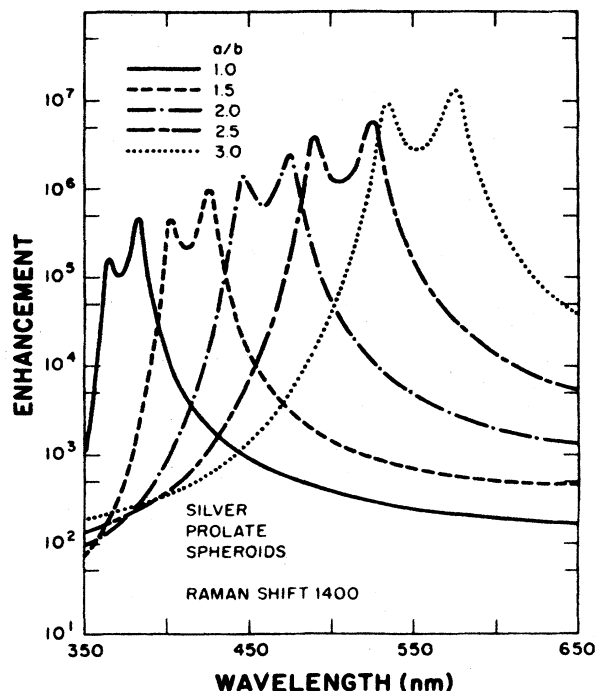
FIG. 9. Enhancement of a 1400-cm^{-1} Raman line vs excitation wavelength for a monolayer adsorbed on randomly oriented silver prolate spheroids in water for various aspect ratios (a/b) (Wang and Kerker, 1981).
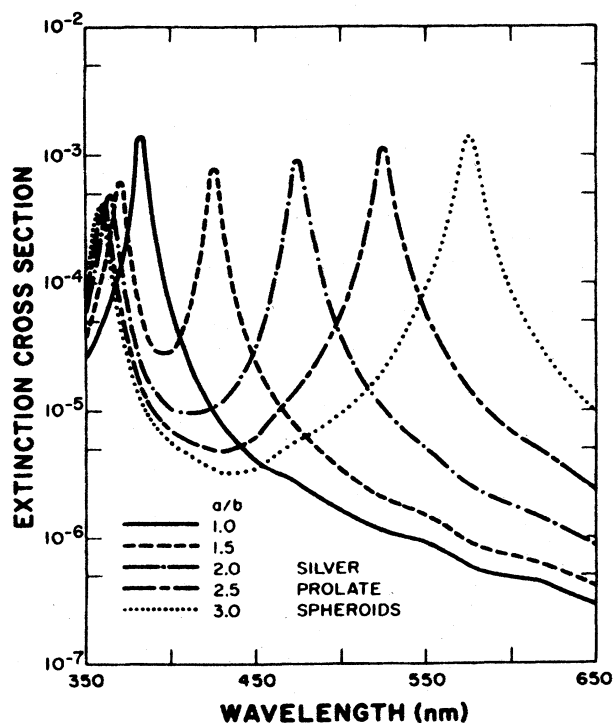

FIG. 10. Extinction cross section for small silver prolate spheroids in water for various aspect ratios (Wang and Kerker, 1981).

lengths with increasing aspect ratio, only the low-frequency peaks seem to be represented in the SERS enhancement spectrum. Hence in a system consisting of many spheres and a few ellipsoids the absorption spectrum is expected to be dominated by the high-frequency peak while the SERS excitation spectrum may consist almost exclusively of the lower-energy maximum (Kerker et al., 1984).

Wang and Kerker also report results for oblate spheroids of silver and for prolate spheroids of gold and copper. With oblate spheroids one expects more or less the same results as with prolate except that the resonance frequency does not decrease quite as rapidly with increasing aspect ratio. Nor does the enhancement increase quite as greatly. With both gold and copper the expected enhancement is 1—3 orders of magnitude lower than with silver, depending upon the aspect ratio (that is, the enhancement by spheres of gold and copper is expected to be, respectively, 2 and 3 orders of magnitude less than for spheres of silver and one must count more on the lightning rod effect to achieve the large enhancements for spheroids of those metals). The SERS enhancement spectra of Au and Cu are also broader and lie further in the red for silver.

Wang and Kerker end their discussion with two caveats. The first is a reminder that the calculation was for spheres small with respect to the vacuum wavelength of light, for which only dipolar surface-plasmon resonances are excited. With larger particles one would be dealing with the superposition of multipolar fields for which the calculated SERS enhancement is expected to be greatly attenuated. The second is a reminder that the absorption cross section and the Raman enhancement are not simply related. The former describes losses within the entire body of the particle, while the latter is the spatial average of the squared modulus of the field in the radiation zone (Wang and Kerker, 1981).

This warning notwithstanding, a very useful phenomenological relationship has been reported by Weitz, Garoff, and Gramila (1982a) connecting the Raman enhancement to the observed absorption spectrum (originally enunciated for island films). They express the fraction absorbed $A(\omega)$ by an island film of whose volume a fraction q is metallic by the equation

$$A(\omega) = q d \varepsilon_2(\omega/c) |\bar{E}_{in}|^2 / |E_0|^2 ,$$

where d is the film thickness, $|\bar{E}_{in}|$ and $|E_0|$ are, respectively, the moduli of the average electric field inside a metal island and the electric field incident upon it, and ε_2 is the imaginary part of the dielectric constant of the metal comprising the island. As in the em models the authors consider the SERS intensity to be the product of the local field-intensity enhancements at both the excitation and emission frequencies. Defining an "internal" field-intensity enhancement factor by $f^2(\omega) = |\bar{E}_{in}|^2 / |E_0|^2$, one obtains, using the conventional boundary conditions that the tangential-enhancement factor outside the island is just f^2, while the normal enhancement (assuming unity dielectric constant for the ambient medium surrounding
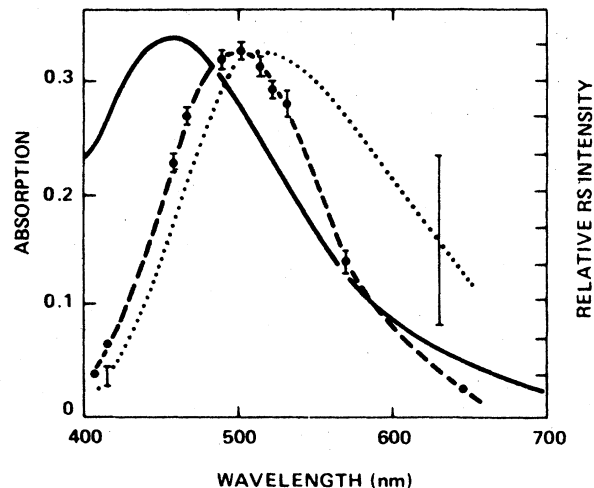
FIG. 11. Nitrobenzoate on silver-island film measured absorption (solid) and excitation (dashed) spectra. Calculated excitation spectra (dotted line) (Weitz, Garoff, and Gramila, 1982a).
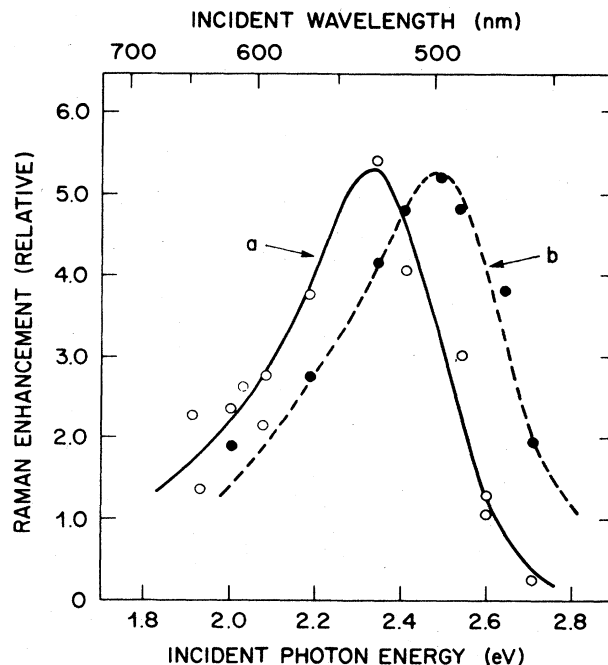

FIG. 12. Dependence of the Raman signal on the aspect ratio of silver ellipsoids. Points and lines are measured and calculated excitation spectra for the 2144-cm^{-1} SERS line of adsorbed CN on ellipsoids of 3/1 aspect ratio (a) and 2/1 (b) (Liao et al., 1981).

the islands) is $|\varepsilon|^2 f^2$, where ε is the dielectric constant of the metal. Arguing in a similar vein for the Raman-scattered field, one arrives at a relative SERS intensity expression

$$I_{SERS} = \frac{c^2}{q^2 d^2} \frac{|\varepsilon(\omega_L)|^2 A(\omega_L) |\varepsilon(\omega_S)|^2 A(\omega_S)}{\varepsilon_2(\omega_L)\omega_L \varepsilon_2(\omega_S)\omega_S},$$

in which ω_L and ω_S are the exciting and Raman-shifted frequencies and for which only the normal component of the electric field was considered, since, it was argued, $|\varepsilon(\omega_L)|^2 |\varepsilon(\omega_S)|^2 \sim 10^4$ for most metals. With this expression Weitz, Garoff, and Gramila were able to reconcile the differences between the absorption spectrum of their island film and the SERS excitation spectrum of nitrobenzoate adsorbed upon it (Fig. 11).

C. Comparison with experiment

The em model has been quite successful in explaining the major aspects of SERS and in predicting such new phenomena as nonlinear effects at rough surfaces. Quantitative agreement between observations and calculations based on the em model have been reported mainly for SERS-active surfaces whose geometries are rather well understood—for example, island films and microlithographically produced particles.

Liao et al. (1981), for example, find excellent agreement (Fig. 12) between the calculated and observed spectral dependence of the SERS enhancement of cyanide adsorbed on microlithographically produced silver ellipsoids of two different aspect ratios. Moreover, the shifts in the frequency of maximum enhancement as a function of the dielectric constant of the ambient was precisely what was expected on the basis of the em theory. Equally convincing results are obtained with island films (Weitz, Garoff, and Gramila, 1982). Nor is this agreement restricted to SERS molecules on silver or gold microstructures. Ra-

man scattering has been reported (Murphy and Brueck, 1983) from silicon phonon modes in 1000-Å silicon spheres, ellipsoidal posts, and gratings, which was more than one-hundred-fold more intense than with bulk silicon, and in good agreement with calculations based on the em model.

The predicted dependence of the SERS intensity upon the surface-molecule separation was also demonstrated in the now-classic experiments of Murray (1982), who showed that the SERS signal from p-nitrobenzoic acid persisted even at 100 Å from the rough silver surface, the separation being effected by an intervening polymer film of varying thickness. The distance dependence is also demonstrated by Liang et al. (1983), who report SERS from the longitudinal-optical mode of antimony films of varying thickness deposited on silver-island films.

With cold-deposited films, electrochemically roughened surfaces, and metal sols, quantitative agreement between calculations based on the em theory and what is observed has generally not been undertaken, mainly because the geometrical complexity of those surfaces makes precise calculations somewhat formidable. This is so even for aqueous colloids for which the SERS is dominated by signals originating from aggregates of colloidal particles that often contain hundreds of units. Nevertheless, good qualitative or semiquantitative agreement has been obtained on most issues. For example, SERS excitation spectra obtained with rough films are quite similar for different molecules adsorbed on films produced in more or less the
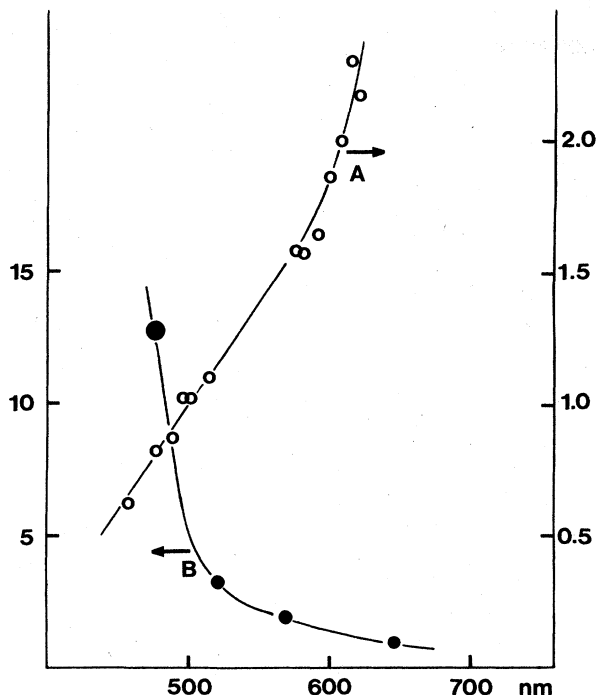
FIG. 13. SERS excitation spectra of the 2115-cm^{-1} vibration of CO adsorbed on cold-deposited silver (a) and matrix-isolated silver colloid (b).

FIG. 14. SERS excitation profile for the 1610-cm^{-1} line of ethylene adsorbed on cold-deposited indium.

same way but differ for a given molecule adsorbed on films produced under different conditions—for example, at different substrate temperatures or deposition rates, or after annealing the films. All this implies that SERS is connected with a resonance that depends markedly upon the surface geometry of the metal substrate, the most likely candidate being a localized surface plasmon. As an example Fig. 13 shows that the SERS excitation spectrum of the 2115-cm^{-1} vibration of CO adsorbed on cold-deposited silver peaks in the red, while on silver colloidal particles the peak is in the near uv. The SERS spectrum itself was identical for the two samples.

Moreover, the SERS excitation spectra follow the trend expected for surface-plasmon excitation albeit for one produced by coupled rather than isolated metal microstructures. So, for example, with cold-deposited films the SERS excitation spectrum peaks in the red with silver, and even further in the red with copper, gold, and lithium. With platinum (Krasser and Renouprez, 1982; Benner et al., 1983) and indium (Moskovits and DiLella, 1985) cold-deposited films, on the other hand, the SERS intensity peaks in the blue precisely as expected on the basis of the optical constants of those metals. The SERS excitation profile of ethylene adsorbed on cold-deposited indium is shown in Fig. 14.

The em model was also successful in accounting for the observation by Weitz et al. (1980) [see also Gersten et al. (1980)] that electrochemically roughened silver and copper surfaces exhibit a greatly enhanced low-frequency vibrational mode that was interpreted by the authors as inelastic Mie scattering from a "localized acoustic vibra-
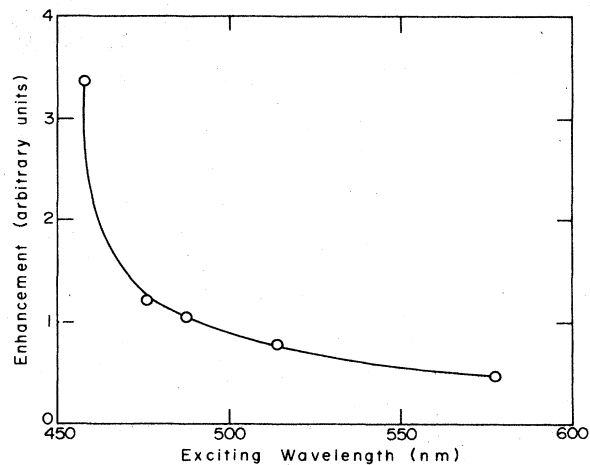
tion" of surface microstructures. A remarkable property of the spectrum was a large shift in the frequency of this vibration with the frequency of laser excitation. Gersten et al. (1980) were able to account for this by assuming the surface to consist of hemispheroidal caps of various sizes and aspect ratios. The acoustic vibration was interpreted to be much like the first overtone of a spheroidal bell in which the major axis expands while the minor contracts. The excitation frequency dependence of the frequency of the inelastic Mie peak was well reproduced by assuming that spheroids of different shape, each with its own characteristic "acoustic" frequency, resonate with a given laser excitation frequency. The observed data were consistent with a distribution of spheroids with a maximum at the following values of semiminor axes: 50 Å for silver and 40 Å for copper.

Despite the success of the electromagnetic class of theories it is clear that models based essentially on the electrostatics of isolated metallic spheroids will fail to account for several important features of cold-deposited films, electrochemically roughened surfaces, and aggregated colloids, systems characterized by highly coupled metal features. To begin, the "surface-plasmon absorption" maximum of these types of surfaces lies far to the red of the corresponding surface-plasmon absorption of an isolated sphere made of the same metal. If one assumes the red shift to be due entirely to the fact that the surface features are ellipsoids rather than spheres (all the while isolated), one would have to assume unrealistically elongated surface features. Applying effective medium models, such as the Maxwell-Garnett theory (Maxwell-Garnett, 1904) or modifications of it and taking the possible nonspherical shape of the particle into account explains the red shift in the absorption well, qualitatively. The Maxwell-Garnett theory assumes dipolar coupling among the surface features and is therefore expected to fail quantitatively for closely packed bumps. Even with dipolar coupling the surface plasmon is no longer isolated in individual bumps but becomes delocalized over many

features, acting thereby more like an ordinary transverse excitation. This fact has prompted Marton and Lemmon (1971) to dub that absorption "optical conduction resonance" in order to stress its difference from a surface plasmon localized on an isolated metal feature.

D. Rough surfaces as superpositions of gratings or as coupled metal features

A cursory survey of the body of experimental data dealing with SERS convinces one, in fact, that the effect is largely limited to assemblies of *coupled* small metal particles. Only rarely does a result suggest the possibility that the observed SERS spectrum might have originated from an isolated metal speck. This is so even with island films and lithographically fabricated ellipsoid assemblies, a fact indicated clearly by the frequency at which the plasmon absorption of those systems achieves a maximum. Although this fact has been recognized for some time, it is only recently that its central importance has been emphasized causing the em theory, in turn, to stress metal particle coupling in one of two ways: a renewed interest in the electromagnetic resonances of gratings in which periodicity is used to simplify the many-body coupling problem or the electromagnetic theory of *a few* coupled particles as a model for many coupled metal particles.

Coupling among metal particles also opens up the question of the precise locations at the surface at which the enhancement is expected to be largest. The isolated spheroid models implied these to be at the tips of prolate and waists of oblate spheroids. For coupled features, on the other hand, the spaces between metal features are the high-field locations. This is suggested by the calculations of Aravind et al. (1981), and a similar conclusion is arrived at by Wirgin and López-Ríos (1984) and Albano et al. (1983). The former treat the rough surface as a periodic grating consisting of deep narrow grooves that are meant to mimic the pores that exist on rough surfaces. With a silver grating of period $d = 1000$ Å and $\lambda = 514.5$ nm those authors find a resonance in the magnitude of the electric field strength within the groove that increases in intensity as the groove width decreases and whose resonant frequency shifts to the blue with decreasing pore height. The resonance may be construed to be like a waveguide resonance and the variation of the height of the surface bumps is akin to tuning a resonant circuit.

The authors use this result to account for two sets of observations. The first is due to Albano et al. (1983), who report on the basis of work function and photoemission measurements that xenon and pyridine adsorbed on cold-deposited films "disappear" on warming the substrate to around 130 K. Since thermal desorption (Seki and Chuang, 1983) indicates that these adsorbates are still present even at temperatures above 200 K, the "disappearance" is ascribed to the movement of the adsorbate into narrow surface pores. The second is the observation by several workers (Pockrand and Otto, 1981; Seki, 1981)

that the SERS intensity of molecules adsorbed on cold-deposited films formed and kept below 100 K increases at first with increasing substrate temperature reaching a maximum at about 190 K. Above that temperature the SERS signal drops rapidly to an undetectable level. Different workers report different values for the excursion in SERS intensity on warming the cold-deposited film from the lowest temperature to the temperature of maximum signal. Pockrand and Otto (1981) and my group find roughly a twofold increase in SERS intensity, while Seki (1982) reports a much larger increase. Wirgin and López-Ríos (1984) and Albano et al. (1983) suggest that the increase and subsequent decrease in the SERS signal results from the change in the channel depth of the "surface grating" with annealing passing over the resonant condition with the laser excitation used.

The single one-dimensional grating used by Wirgin and López-Ríos is, of course, a crude approximation of the actual surface of a cold-deposited film. The true surface may, naturally, be expressed exactly as a two-dimensional Fourier sum of many sinusoidal gratings and, at least approximately, as a two-dimensional superposition of the channel gratings used by Wirgin and López-Ríos (1984) by using many periodicities and channel heights. By so doing one expects the Wirgin–López-Ríos model to converge with the treatment of the surface as a collection of interacting metal bumps. Having many gratings weakens somewhat the concept of a "tuned circuit" resonance as a descriptive for the electromagnetic resonance occurring in the cold-deposited roughness layer. The emphasis that this model places on the field intensities *between* bumps as the locations of high enhancement and perhaps also the most likely adsorption sites is, however, a valuable insight, which would help clear up some of the problems inherent in the one-particle version of the em theory. The "coupled particle" point of view is, of course a direct extension of the single-particle em model, and, in fact, the surface-plasmon theories for SERS were born in the coupled form (Moskovits, 1978,1979).

An example of the use of coupled particles in attempting to treat SERS systems more realistically is the recent and elegant extension of the calculation of Aravind et al. due to Liver et al. (1984), who consider the field strengths at various points within and outside one-, two-, and four-metal sphere assemblies. They find that the fields at interstitial locations may exceed those near single spheres or near the exterior of assemblies by more than an order of magnitude, implying a 4-orders-of-magnitude further SERS enhancement for molecules residing at those locations. The frequency at which the enhancement peaks is shifted towards the red, moreover, as observed for aggregated colloids. Extrapolating their results to the case of highly aggregated colloidal assemblies where such interstitial locations abound, one concludes that a SERS spectrum would be dominated by emissions from molecules occupying such sites. In fact, even for two-sphere assemblies the average field strength is found to exceed substantially the average field strength about two isolated spheres, implying that for a colloid containing a small
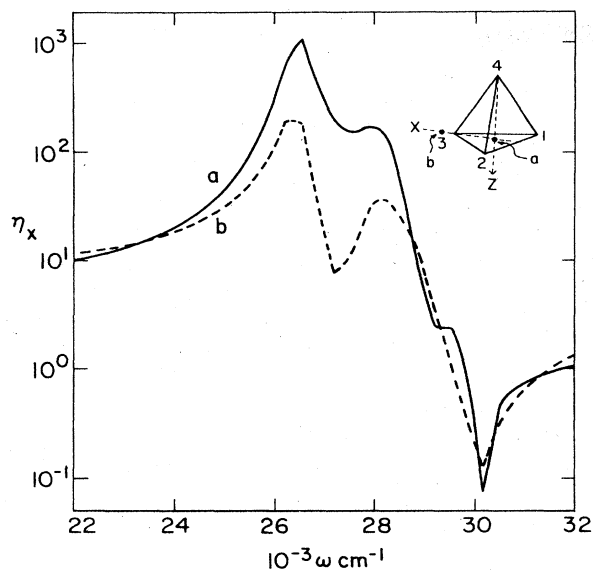
FIG. 15. The intensity enhancement (approximately equal to the square root of the Raman enhancement) as a function of exciting frequency at two locations near a cluster of four silver spheres (Liver et al., 1984).
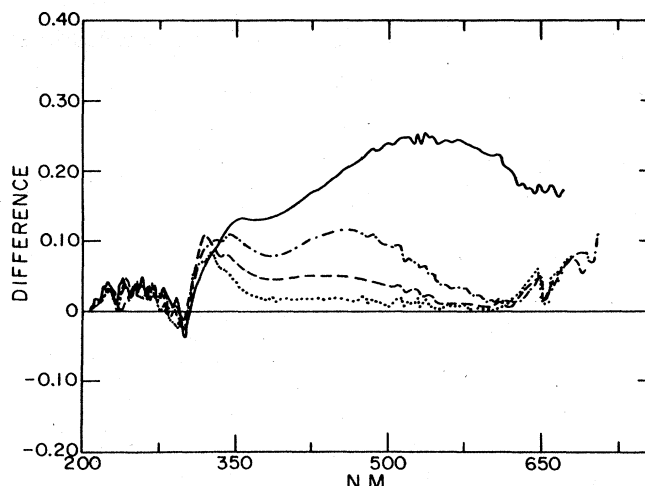

FIG. 16. Absorptions due to surface plasmons recorded ellipsometrically for cold-deposited silver films. The four spectra progressing from the solid line to the dotted line correspond to films annealed to progressively higher temperatures.

fraction of even slightly aggregated particles the SERS spectrum may be largely due to molecules adsorbed at interstices in aggregates rather than those adsorbed on isolated particles. Some of the results of the calculation of Liver et al. are shown in Fig. 15. Similar conclusions were also drawn by Inoue and Ohtaka (1983) based on calculations in which only dipolar coupling between metal particles was considered.

The observed increase in SERS intensity with annealing followed by an irreversible decrease is accounted for easily by all models that depend on electromagnetic excitation of surface microstructures of the cold-deposited films. Absorptions due to these resonances have, in fact, been reported by several workers (McBreen and Moskovits, 1983; Otto et al., 1982; López-Ríos et al., 1983). In Fig. 16, for example, one sees a series of spectra obtained by means of a polarization modulation technique (McBreen and Moskovits, 1983) that show the difference in the function $B = (\rho_p^2/\rho_s^2 - 1)/(2\rho_p \sin\Delta/\rho_s)$ for a film deposited under ultrahigh vacuum conditions onto a substrate cooled to 140 K and subsequently warmed to several temperatures, and the same film annealed at 300 K. In B the quantities ρ_p, ρ_s, and Δ are, respectively, the modulus of the p- and s-polarized reflection coefficients and the phase difference between them. The quantity B may crudely be assumed to be the reflection absorption of the surface layer of the film, since positive features in the former correspond to positive features in the latter. One sees in Fig. 16 that the absorption spectrum of a cold-deposited film has a large feature that moves towards the blue, narrows, and is attenuated with annealing. For surfaces deposited at even lower surface temperatures the large absorption features occur even further in the red. A similar observation has recently been reported (Kester,

1985) for silver electrodes whose potential was cycled in the non-Faradic region. It is at once obvious that an experimenter exciting SERS with the blue light (488 nm) of an argon laser while annealing the film will see the SERS signal first increase and then decrease as the resonance passes over the exciting line. The observed B spectra are well reproduced by modeling the cold-deposited film crudely by a layer of silver spheres atop a plane silver surface.

It should be pointed out in passing that the observation of anomalous absorptions due to surface roughness is not new. Wood observed them in granular films of sodium and potassium metal in 1902 and alludes (Wood, 1919) to an explanation due to Rayleigh for the brilliant colors based on the "cavities between the metallic crystals [which] act as selective absorbing resonators for the light-waves" (Wood, 1919). Others have reported (Dignam and Moskovits, 1973) anomalous changes in film transmittance and reflectance brought about by adsorbing molecules on rough film. These changes were successfully explained in terms of the frequency shifts of the conduction resonance (surface plasma resonance) in the coupled surface bumps brought about by the change in the Lorentz local field, resulting from the adsorbate's filling or partly filling the interstices between the bumps.

The application of the electromagnetic resonances of gratings in describing the em contribution to SERS enhancement predates the work just discussed. The earliest and most thorough discussion is due to Jah et al. (1980), who model the rough surface by means of a superposition of sinusoidal gratings of different periodicities each of an amplitude much smaller than λ. The authors consider one Fourier component at a time, the final expression for enhancement being a sum over the contribution from individual components. Solving Maxwell's equations with the appropriate boundary conditions on E and B and assuming the first order in $\omega\xi/c$ (where ξ mea-

sures the amplitude of the roughness), one finds that there are secondary transmitted and reflected waves with wave vectors $\mathbf{k}_t + \mathbf{g} = \mathbf{K}_g$ induced by the surface roughness in addition to the usual specular and refracted waves. ($\mathbf{k}_t$ and $\mathbf{g}$ are, respectively, the transverse wave vector of the incident field and the reciprocal net vector of the gth spatial Fourier component.) Solutions for bound, transverse to surface-plasmon waves are sought corresponding to the condition $K_g > \omega/c$, and the coefficient of the z component of the p-polarized surface-plasmon field amplitude E_{gz}^p is determined. The resonance condition is found from the expression $(\omega^2/c^2)\varepsilon_1(\omega) - K_g^2[\varepsilon_1(\omega) + 1] = 0$, where ε_1 is the real part of the metal's (local) dielectric function and the coefficient of the amplitude of the gth field component at resonance becomes equal to $2\varepsilon^2/i\varepsilon_2$, where ε_2 is the imaginary part of $\varepsilon(\omega)$. The SERS intensity would be roughly proportional to the fourth power of the modulus of this value, since, as before, the SERS enhancement is thought to involve both modulation of the molecular polarizability by the enhanced field as well as "conversion of the near-zero Stokes field into the scattered radiation field by the metal surface" (Jah *et al.*, 1980) (the authors suggest yet another mechanism that will be discussed later).

More recently Weber and Mills (1983) have solved for the field amplitudes at various points upon a sawtooth grating whose characteristic dimensions were not assumed small compared with λ. They obtain three reflectance dips associated with the excitation of surface-plasmon polaritons, and preempting the suggestions of Wirgin and López-Ríos, they show that the greatest field enhancement does not occur at the tips of the grating features but rather at points within the grooves.

E. Other forms of the em model

Two somewhat different approaches to the influence of roughness on the intensity of Raman emission by molecules at surfaces have been taken by Aravind and Metiu (1980) and by Weber and Ford (1980,1981).

The first set of authors assume that the incident field induces a dipole moment

$$\mu(t) = \mu_0(t) + \mu_1(t) ,$$

where $\mu_1(t) = (\partial\mu_0/\partial Q)Q(t) \equiv \mu_1(\omega)e^{-i\omega t}$ and $\mathbf{j}(t) = \partial\mu_1/\partial t$ is the current that radiates light at the Stokes-shifted frequency ω. The effect of roughness is taken into account by assuming that the height of the surface at a point (x,y) is given by $z = \xi(x,y)$. This function is assumed to be unknown, however, and only the probability, $P(z; x,y)$, that at the point (x,y) z has a given value, is known. A quantity $\Delta\varepsilon(x,y,z,\omega)$ is defined that measures the local difference in the dielectric function from its average value. This quantity is assumed to be a perturbation, and Maxwell's equations are solved using the Born approximation, resulting in

$$I = I_0 + D\langle\Delta\varepsilon\Delta\varepsilon^*\rangle[j,j^*] , \tag{13}$$

where D is a product of dyadic Green's functions and

their asymptotic forms, and the next two factors are the dielectric fluctuation correlation function and the current-current correlation function. The latter is proportional to the number of scatterers, assumed to be incoherent, and to $|\mu_1(\omega)|^2$. The $\langle\Delta\varepsilon\Delta\varepsilon\rangle$ correlation function plays a similar role to that of density fluctuations in light scattering from liquids. Equation (13) is shown to be a sensitive function of the mean-square amplitude of roughness and its correlation length. Maximum enhancement is obtained for short correlation lengths and at the condition for plasma resonance. Even so, maximum enhancements of only about 70 are obtained with a correlation length of 20 Å (and a mean amplitude of 30 Å).

Weber and Ford (1980,1981) consider an applied field normal to the metal surface (in the case of a rough surface, normal to the plane obtained by requiring the average surface height with respect to it to be zero).

The induced dipole is assumed to be given by $\mu(\omega) = \alpha(E_0 + E_r)\hat{z}$, where E_0 is the amplitude of the incident field and E_r is the portion of the field radiated by the dipole reflected back to the dipole by the metal.

The authors express the reflected field as a function of ω and the distance d of the dipole above the metal and derive an expression for the total power dissipated in the system that the authors separate into three contributions: $P_{tot} = P_{photon} + P_{sp} + P_{DSM}$. The first is the radiated power; the second is the power dissipated into surface plasmons corresponding to the pole at $p = [\varepsilon_0\varepsilon/(\varepsilon_0 + \varepsilon)]^{1/2}\omega/c$ in the Fresnel coefficient, which occurs in the expression for the total power as a result of the "reflected" field, p being the magnitude of the wave vector of light; and finally, P_{DSM}, the third, is the power emitted into the continuum of driven surface modes corresponding to the range $\varepsilon_0^{1/2}\omega/c \ll p < d^{-1}$. For a smooth surface only P_{photon} is observed. The authors used the Kliewer-Fuchs (1968) nonlocal expression for the dielectric constant ε in calculating the Fresnel coefficient. The calculated power dissipation shows that the driven surface modes dominate close to the surface. This is primarily due to electron-hole (e-h) excitations that are neglected in the local description. The e-h excitations are effective at coupling power out of the near field of the radiating dipole (and its image) but the power remains in the metal. Surface roughness provides the coupling mechanism for converting the power in the near field into radiation. The authors introduce roughness into the problem by assuming the surface region to be described by a polarizability per unit area $h(\rho)$ which is a function of (x,y), ρ being position in the xy plane. A Gaussian correlation is assumed for h with mean-square amplitude $\langle h^2\rangle$ and correlation length $a \ll \lambda$. Not unlike Metiu's treatment, the current density induced by the dipolar field is expressed as a function of $h(\rho)$, which in turn is taken to be equal to $[(\varepsilon - \varepsilon_0)/(\varepsilon + 2\varepsilon_0)]\xi(\rho)$, where $\langle\xi^2\rangle = a^2$. That is, the surface bumps are treated as little spheres on the surface. Although the roughness coupling is found to produce a sizable increase in the observed radiation, it is inefficient; only one in approximately a thousand electron-hole pairs

produces radiation.

The Weber and Ford treatment is interesting on several accounts, not least of which is their use of a nonlocal dielectric response to describe the metal.

Eesley (1981), however, discounts this treatment and that of Aravind and Metiu (1980) as a mechanism for SERS. In an elegant experiment Eesley introduces a silver surface electrochemically roughened into a vacuum system where the surface is cleaned by means of a light Ar^+ bombardment. When 1-KeV electrons were fired at the surface at 80° incident surface-plasmon fluorescence was observed. Areas of various degrees of roughness were excited and the roughness-coupled surface-plasmon radiation was found to scale as the square root of the SERS background emission. This in turn was shown, both by that author and by Chen and Burstein (1980) to be proportional to the SERS signal from adsorbed molecules. [That the SERS signal should scale quadratically with the surface-plasmon light absorption was explicitly proposed by Chen and Burstein (1980).] In the above study Eesley also showed that SERS results from an interaction with a continuum of excitations in the visible rather than with the peak surface-plasmon excitation, undoubtedly a result of the heterogeneity of the surface microstructures.

Eesley then argues that the models of Aravind and Metiu (1980) and Weber and Ford (1980,1981) find the SERS intensity to depend linearly upon the Fourier transform of the roughness autocorrelation. But the roughness-coupled surface-plasmon emission is known to scale as the first power of that quantity; hence, according to the result of Eesley's experiment, the SERS intensity should increase quadratically with the Fourier transform of the roughness autocorrelation. This conclusion by Eesley is not totally justified, however, since neither Weber and Ford (1980,1981) nor Aravind and Metiu (1980) consider explicitly the effect of the surface roughness on the incident field. In fact, the latter pair of authors states outright that surface roughness will enhance the incident field as well as the field in the emissive channel of the molecule. If both channels are then taken into account, the requisite quadratic relationship is recovered.

F. General criticisms of the electromagnetic theory

Several general criticisms of the em theory or at least of the most popular forms of this theory in terms of electrostatistics of metallic ellipsoids have been voiced. In addition, several controversies exist regarding the best way to interpret certain experimental observations, whether in terms of the em theory or one of its rivals. The latter group will be discussed in a later section, the former in this section.

Otto (1983a) has pointed out that an assumption made in most em calculations that the total enhancement contains the contribution from the excitation channel and the emission channel as a product of two similar factors differing only by the need to evaluate them at the appropriate frequency is not in general correct if retardation is included in the calculation.

The effect of retardation, has in fact been included in the calculation of Kerker et al. (1980) [see also Wang et al. (1980)] for a spherical particle. Nevertheless, the practice used by several authors of calculating the enhancement in one channel and simply squaring it to obtain the total SERS enhancement will certainly lead to error. In view of the fact that calculations on small spheroids are usually presented as models for much more complicated surface structures, the effect of neglecting retardation will generally be a minor assumption compared to the other assumptions made.

A more worrisome assumption is that the dielectric function is local, that is, independent of the wave vector of the electromagnetic wave. Metiu (1984) presents two examples: that of the scattering of fast electrons in a solid film and that of screening the Coulomb potential in a polarizable medium as instances where the neglect of spatial dispersion causes considerable error. In the latter case, for example, the potential at $\mathbf{r}$ is given by $\phi(\mathbf{r}) = e/(\varepsilon_0 r)$ when ε is taken to be local and equal to ε_0, while upon assuming a dielectric function of the form $\varepsilon(\mathbf{k}) = \varepsilon_0(\pi k_s^2/k^2)$, one obtains the Thomas-Fermi potential

$$\phi(\mathbf{r}) = [e/(\varepsilon_0 r)]\exp(-k_s r) ,$$

which reduces to the Coulomb potential only at small values of r.

The importance of spatial dispersion in the spectroscopy of molecules near conducting surfaces may be surmised from the work of three groups (Weber and Ford, 1980,1981; Fuchs and Barrera, 1981; Maniv and Metiu, 1980a,1980b). Metiu (1984) presents a lucid rationale of its role by pointing out that near a metal surface the field decreases rapidly (eventually to zero deep inside the metal). Hence, even when a single plane wave (in the far field) is used to illuminate the surface, the field near the surface must be expressed as a Fourier superposition of many plane waves, each with its own value of $\mathbf{k}$. Since the nonlocal solid responds to each plane wave with a different dielectric constant $\varepsilon(\mathbf{k},\omega)$, the local model, which in essence assumes a value of ε at $\mathbf{k}=0$, may be in error. Moreover, one expects the greatest errors to be encountered when the molecule is close to the surface, precisely in the region of interest of most experiments.

Weber and Ford (1980,1981) consider the effect of the inclusion of nonlocal response in the metal on SERS by placing a dipole above an initially smooth surface to which roughness is subsequently added in the manner discussed above. As previously stated, the authors find that the largest fraction of the power dissipation is into electron-hole excitations that are totally neglected in a local description. For a flat surface these excitations are nonemissive. (The presence of surface roughness provides a mechanism for coupling the near fields associated with these excitations into radiation.)

Another graphical study of the dynamical response of a dipole near the surface of a nonlocal metal is due to Fuchs and Barrera (1981). As in the previous study, the

authors determined a "renormalized" polarizability α which contains the effect of the molecules' innate polarizability α_0 and the field induced at the dipole location by the dipolar radiation "reflected" by the metal. Using a Lorentzian form for $\alpha_0(\omega)$, the authors calculated the imaginary part of α as a function of ω for several values of ω_0, the intrinsic resonance frequency of the dipole, assuming alternately a hydrodynamic nonlocal ε and a local ε. The resulting "spectrum" was found to depend markedly on the type of dielectric function chosen both as regards position of peaks and spectral breadth. In particular, the "nonlocal" spectrum possessed a broad continuum of emissions undoubtedly associated with excitations in the metal in addition to the sharp dipolar emission peak. The continuum was absent in the spectrum calculated with a local ε.

An even more fundamental criticism of the em models rests in the uneasiness one feels in employing classical electromagnetic theory whose application assumes continuous media to problems near a metal surface where the particulate nature of the species involved can hardly be ignored. At the very least, one should attempt to dispense with a sharp boundary between metal and ambient, replacing it with a transition region of dielectric properties intermediate between those of the two bulk phases.

Finally, one may criticize the perspective employed to date in dealing with SERS-active surfaces. While one cannot argue with the use of a simple system such as metal sphere in the first stages of modeling SERS-active surfaces, it is now apparent that such models are not adequate to simulate some of the most successful SERS systems, such as aggregated colloids, electrochemically roughened electrodes, and cold-deposited films. It is apparent from the foregoing discussion that at least some progress is being made to rectify this last shortcoming in em theory.

III. ENHANCED ABSORPTION, EMISSION PHOTOCHEMISTRY, AND NONLINEAR PROCESSES

The success of the em model in accounting for a large number of the aspects of SERS prompted several authors to seek other manifestations of the enhanced electromagnetic fields near metal surface bumps or colloidal particles. These include enhanced absorption, fluorescence, and photochemistry in molecules near rough surfaces, as well as enhanced second-harmonic generation, hyper-Raman scattering, and other nonlinear processes.

Nonlinear processes are expected to be greatly enhanced near surface protuberances as a result of field enhancement. In fact, second-harmonic generation (Heritage and Glass, 1984) is probably the most direct probe of the magnitude of the field at the surface. Likewise, enhanced molecular absorption might be seen for molecules placed near rough surfaces or colloidal particles, provided that the molecular absorption bands are close to the dipolar surface-plasmon frequency of the metal particle. When the absorption band is very close to or coincident with the surface-plasmon frequency, the resulting absorption spectrum is not simply a superposition of the molecular and plasmon absorptions. Rather, the spectrum consists of several discernible peaks that are not coincident, in general, with either the molecular absorption or the surface plasmon.

Fluorescence, phosphorescence, and resonance Raman emissions from the adsorbed molecule may benefit from the enhanced absorption processes as well as the amplification of the field of the emitted light (analogous to SERS), in cases where the Stokes shift is not so large as to bring it out of resonance with the surface plasmon; however, in competition with this, one has nonradiative damping processes that reduce the lifetime of the excited molecule by exciting surface-plasmon resonances (of various multipole order) and electron-hole excitations, often so efficiently that the overall effect is a *reduction* in fluorescence quantum yield, or at most a ten- to one-hundred-fold increase rather than the 10^6-fold increase common in SERS.

Enhanced photochemistry of two varieties is also predicted. In the first the chemical process subsequent to absorption is very fast; hence the enhanced photochemistry parallels the enhanced absorption. In addition to the enhancement, one has in this case the additional interesting feature that when the molecular absorption band and metal-particle plasmon band do not overlap but are not too far apart, one can have very facile energy transfer from the metal to the molecule. Hence one can pump the metal-particle plasmon absorption and bring about surface photochemistry. In the second case the chemical reaction requires a longer time to take place, as in infrared multiphoton dissociation or photochemical reactions whose products derive from molecular intermediates. In this case there is the aforementioned competition between enhanced absorption and quenching by the metal. The interesting feature here is that the best place to see enhanced photochemistry of this sort (or of enhanced fluorescence, for that matter) is not directly on the surface but a short distance above it where the best compromise is struck between field enhancement and nonradiative damping.

The earliest report of enhanced absorption and luminescence by dyes adsorbed onto SERS-active surfaces are by Glass *et al.* (1980), who investigated the properties of rhodamine B and Nile blue dye on an island film elegantly fabricated so that its mass thickness and hence the maximum in the position of the plasmon resonance varied continuously across its length. In this way the degree of overlap of the two absorptions (that of the dye and that of the surface plasmon) was controlled. Glass *et al.* found that when these two absorptions were well separated the spectrum resulting from overlaying the dye upon the silver island film was more or less a superposition of the two spectra except that the plasmon peak was attenuated while that of the dye was enhanced. For less—well-separated absorptions the spectra of the overlayed silver films were no longer simple superpositions but showed a complex splitting of peaks.

Laying a 30-Å film of a transparent plastic (PMMA) spacer on the silver island film before depositing the dye layer yielded absorption spectra that still gave clear indication of Ag-dye interactions. Dye-silver contiguity is, apparently, not necessary to see these effects. The development of the observed spectral splittings were qualitatively well reproduced by Craighead and Glass (1981) by using the Maxwell-Garnett model (Maxwell-Garnett, 1904) to describe the effective dielectric constant ε of an island film consisting of metal spheres with and without an overlayer. Using the expression

$$\varepsilon = \varepsilon_H(3 + 2F\alpha)/(3 - F\alpha) \; ,$$

in which ε_H is the dielectric constant of the ambient, F the volume fraction of the film occupied by the spheres, and α is a closed form expression (Craighead and Glass, 1981) proportional to the sphere's polarizability, which is a function of the dielectric constants of the sphere material and dye and the ratio of the total sphere volume to the core volume, and simplifying the problem further by using a simple Drude expression for the dielectric function of the metal with parameters (ω_p and τ) more or less consistent with those of silver, and a Lorentz oscillator expression for the dielectric function of the dye, Craighead and Glass were able to reproduce the observed splitting of the plasma resonance that they recognized to be due to the resonant coupling of the dye electronic modes and the metal's conduction electron resonance.

Similar results and interpretation are presented by Garoff et al. (1981) for rhodamine 6G adsorbed on a series of silver-island films of differing mass thickness and of fixed mass thickness but with different thicknesses of dye overcoat. Rather than using an effective medium theory like the Maxwell-Garrett theory, Garoff et al. (1981) prefer to concentrate on a single spheroid and its interaction with the dye. Using Mie theory for an oblate spheroid and assuming the particle to be small, Garoff et al. calculate the extinction efficiency Q (ratio of absorption cross section to geometric cross section of the spheroid) from the expression $Q = 8\pi B\alpha''/\lambda$ in which B is the semiminor axis of the spheroid and α'', the imaginary part of the polarizability of the spheroid, is obtained by solving Laplace's equation in the three regions of space: the metal, the dye overcoat, and the ambient medium, applying the usual boundary conditions at the interfaces.

Their calculations predict that for thin overcoats the spectrum is indistinguishable from that of the bare island. For thicker films the results are shown in Fig. 17, which shows the effect upon the observed absorption spectrum of matching and mismatching the dye resonance to the surface plasmon.

Garoff et al. (1981) also performed an interesting analysis of the power dissipation in the dye-coated metal particle, finding that more power is deposited in the dye layer when it is coating a silver island than when it is laid upon a nonresonant dielectric structure of similar geometry. Less power is dissipated in the silver core of a coated spheroid than in the bare spheroid. More power is dissipated by the dye than by the silver of a coated island
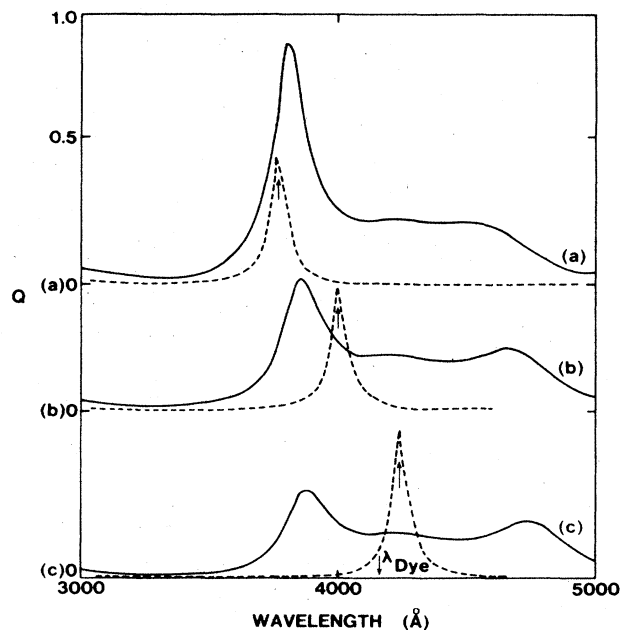

FIG. 17. Calculated absorption of bare (dashed) and coated (solid) silver spheroids with varying aspect ratio, showing the effect of matching and mismatching the dye-absorption frequency (λ_{dye}) with that of the plasmon (λ_{Ag}) (Garoff et al., 1981).

even when the coating represents only 4% of the mean-spheroid diameter. This prompts one to conclude that near the frequency of the plasmon resonance the silver particle acts as an antenna that draws radiation from an area larger than its geometric size and concentrates it in itself and, when coated, in the dye.

Three rather detailed calculations concerned with the problem of the absorption by a single or an assembly of dye-coated spheres have been carried out by Egan (1981), Wang and Kerker (1982), and Kotler and Nitzan (1982). Egan considers a hexagonal net of ellipsoidal silver particles with a confocal ellipsoidal dye layer. Using the known expression for the polarizability of an overcoated spheroid (Kerker, 1979; Van de Hulst, 1957), Egan calculated the local electric field at a spheroid by summing up the (static) dipole field originating from all other spheroids. The presence of the substrate is taken into account by including the contribution of the image dipole of each spheroid in the substrate. The spheroid layer is then assumed to be an optically homogeneous (but anisotropic) region of a thickness equal to the height of the coated spheroid and dielectric function obtained from the dipole moment per unit volume computed as described above and assuming the conventional boundary continuity properties upon the electric field and displacement. The anisotropy results from using a different value for the normal and tangential components of the spheroid polarizability.

The normal incidence absorption spectrum of a hexagonal net of (uncoated) silver spheroids was calculated and shown to possess a single absorption peak associated with the surface plasmon. The frequency of the peak shifts to

lower energies when the aspect ratio of the spheroids differs from unity. Hence one cannot determine from the normal-incidence absorption spectrum alone the aspect ratio of the spheroid. There will always be both a prolate and an oblate spheroid for which the plasmon will peak at the same frequency. Egan shows, however, that this uncertainty can be removed by measuring simultaneously the p-polarized oblique-angle transmission spectrum that will contain two peaks whose relative positions to the single peak in the normal-incidence spectrum will yield the desired information.

In considering the properties of dye-coated islands Egan used literature values for the complex dielectric constant of the metal core (ε_1), while for the dielectric constant of the dye layer (ε_2) he employed a modified Lorentzian expression

$$\varepsilon_2 = 1.69 + (4\pi e^2/m)nf/(\omega_0^2 - \omega^2 - i\Gamma\omega) ,$$

with parameters approximating those of rhodamine 6G ($\Gamma = 0.215$ eV, $\omega_0 = 2.34$ eV, and $f = 1.72$).

The resonances of an isolated coated sphere were obtained from the complex poles of its polarizability. For a very small metal core the singularities in the polarizability are determined by the zeros of $(\varepsilon_2 + 2)(\varepsilon_1 + 2\varepsilon_2)$. The condition for the excitation of plasma resonances in the metal sphere with dye as ambient corresponds to the second term's vanishing while a zero first term determines the dipolar Mie resonances of a dye sphere surrounded by vacuum. This condition is satisfied for at least two values of the (complex) frequency.

Thus a sphere of dye with ε_2 given by a modified Lorentzian will have two absorption peaks, even though a Lorentzian with a single resonance is used to describe its dielectric function. This result depends sensitively on the form of the expression used for ε_2. Kotler and Nitzan (1982) obtained a single peak for a sphere and a double peak for a spherical shell upon using a Clausius-Mossotti function [$\varepsilon_2 = (1 + 8\pi N\alpha/3)/(1 - 4\pi N\alpha/3)$] for ε_2, and a Lorentzian for α, the polarizability.

For an Ag spheroid of aspect ratio 2 coated with a thin confocal dye layer of approximately 5 Å thickness and a value of 0.895 for the ratio of the core volume (this corresponds approximately to a mean-core diameter of 30 Å, Egan calculates 2.33, 2.84, and 3.29 eV as the real parts of the complex zeros of the polarizability reciprocal of the coated spheroid. The last is shown to be associated with plasma oscillations in the metal core, while the other two are normal modes of the dye layer (note that ω_0 was set at 2.33 eV). A calculation of the RMS fields within the Ag core and the dye indicates that within the former the fields are very large only at 3.29 eV, while in the latter intense fields (and intense power absorptions) occur at both 2.84 and 3.29 eV. Thus there are power absorptions in the dye sympathetic with the Ag plasma resonances. One may construe this to be a form of energy transfer from the metal to the dye.

When one makes an island film—that is, when one allows the spheroids in the hexagonal net to interact with each other in the aforementioned fashion—the three com-
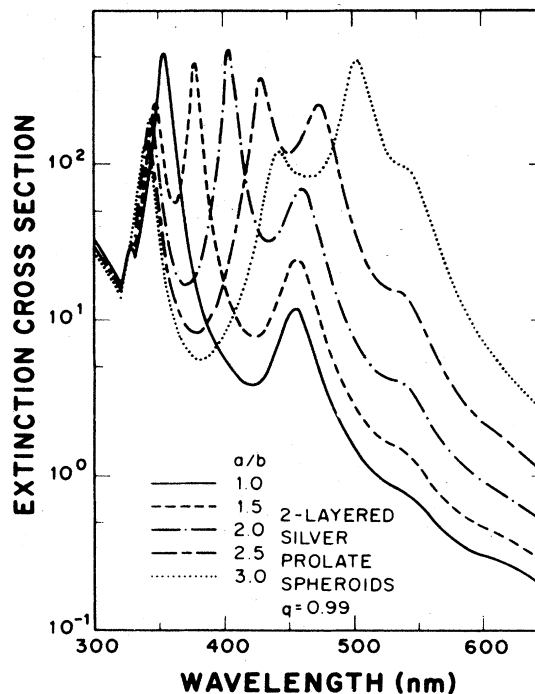

FIG. 18. Extinction cross section vs wavelength for silver spheroids coated with confocal spherical shells of dye. The ratio of inner to outer axes is 0.99. The various aspect ratios is given by a/b (Wang and Kerker, 1982).

plex poles of the dielectric function describing the film are shifted from those of the polarizability of an individual spheroid. Moreover, new absorption maxima appear that are associated with the overlap of the intrinsic loss of the silver with the maxima of the local field.

Wang and Kerker's (1982) calculation is in spirit related to those above, except that they calculate the rotationally averaged value of the excitation cross section, bringing to mind dye-coated colloidal particles rather than island films. For coated spheres the findings of Wang and Kerker parallel those mentioned above. Figure 18 shows the calculated extinction cross section as a function of wavelength for a series of coated prolate spheroids of varying aspect ratio of which the dye layer's dielectric function is represented by a simple Lorentzian.

A. Luminescence from "SERS-active" systems

Glass et al. (1981) and Ritchie and Burstein (1981) found that for several dyes adsorbed onto silver-island films the maximum luminescence yield is obtained when the dye absorption maximum coincides, more or less, with the metal-conduction resonance absorption maximum, which could be shifted by varying the island film "mass thickness." This certainly is prima facie evidence that the luminescence enhancement is electromagnetic in origin. The observed luminescence enhancement was but a weak cousin of the SERS effect. Rhodamine 6G on a 40-Å Ag-island film luminescence was roughly sixfold more in-

tense than an equivalent layer of R6G on glass (Ritchie and Burstein, 1981). The observation that fluorescence is far less enhanced than Raman has been put to good use (Lippitsch, 1981) in registering the SERS spectra of various biological molecules whose ordinary Raman spectrum was bedeviled by fluorescence. Ritchie and Burstein (1981) also reported appreciable light emission close to the exciting laser line. This they attributed to hot luminescence (i.e., fluorescence from vibrationally excited levels of R6G prior to thermalization). They accounted for this by noting that in the absence of metal the rate of thermalization is rapid compared to the radiative rate. On placing the molecule on the metal, one sees that the nonradiative damping rate becomes faster than the thermalization rate; hence fluorescence from hot states is placed on more equal footing with that from the relaxed state; and of course, both benefit from the enhanced absorption, which more than offsets the increased nonradiative damping.

Although their absorption spectrum of dye-coated island films consisted of two major peaks, Glass et al. (1980,1981) found that fluorescence excitation spectrum did not replicate the absorption spectrum but consisted of only one broad fluorescence that overlapped the absorption spectrum of the dye in the absence of metal. Their conclusion that energy transfer from the silver particles to the dye occurs only for excitation in the spectral region where there is considerable overlap between the particle and the dye absorptions is only one possible explanation, the other being that the damping rate is greater at the plasma-resonance frequency.

It is clear, therefore, that in contrast to Raman, which is a process in which the molecule may be construed to be a driven oscillator, and in which energy losses into the metal may hence be ignored, in fluorescence the molecule is a free-running oscillator; hence its enhancement by SERS-active surfaces will depend on three things: enhanced absorption, which has already been discussed, enhancement by the em mechanism of the field associated with the emitted light, which is in almost every way similar to what was discussed in the context of SERS, and, finally, nonradiative processes which transfer the excitation from the excited molecule to the metal through several decay channels. This final contributor will now be discussed.

B. Emission by dipoles near metals

The effect of a conducting plane on an oscillating dipole is a problem (and a solution) of long standing. It was considered and solved by Sommerfeld for a radio antenna emitting near the surface of the earth (Sommerfeld, 1949). A thorough and lucid account of the fate of the luminescence lifetime and the apparent quantum yield of an electric dipole placed near a plane surface was given by Chance, Prock, and Silbey (1978) (CPS), who obtained expressions based entirely on classical em theory for the decay rates of emitting dipoles of varying orientation in terms of integral equations containing as parameters the dielectric functions of the metal and the thin film upon it

containing the emitting dipole, the distance of the emitter from the metal surface, and its fluorescence quantum yield. CPS consider also various experimental configurations of this problem. Their results, in broad terms, indicate that the decay rate and quantum yield decrease by several orders of magnitude as the molecule approaches the surfaces. In the region of space close to the surface, approximately 200 Å and less under most circumstances, the decay rate is predicted to depend on the distance d of the dipole from the surface as d^{-3}. Beyond that, the change of the decay rate with distance is less severe, and beyond $d = \lambda$ one may see oscillations in the decay rate, with distance resulting from coherence effects.

These predictions have been strenuously tested experimentally, mainly on the surfaces of noble metals and for values of $d > 20$ Å, and found to be in excellent accord with the calculations. The earliest experiments utilized fatty acid layers of varying thickness to separate a chromophore (usually a europium ion) from the surface [Chance et al. (1978) and references therein]. Later experiments used either argon matrices of various thickness containing pyrazine uniformly distributed within it (Adams et al., 1980) or as in the elegant experiments of Rossetti and Brus (1982) and Whitmore et al. (1982), solid argon layers whose thicknesses were measured ellipsometrically to obtain the rather small separations between the metal [in the last case Ag(111)] and the emitter $^3B_{3u}$ pyrazine, needed to check the d^3 dependence of the luminescence lifetime. In both cases excellent agreement was achieved between experiment and the CPS calculation as may be gauged from Fig. 19. [A dissenting result does exist, however. Based on an electron energy-loss bandwidth measurement, Avouris et al. (1983) report a tenfold faster decay of excited N_2 adsorbed on Al(111) than predicted by CPS. Avouris et al. are able to account for this by considering surface electron-hole pair generation
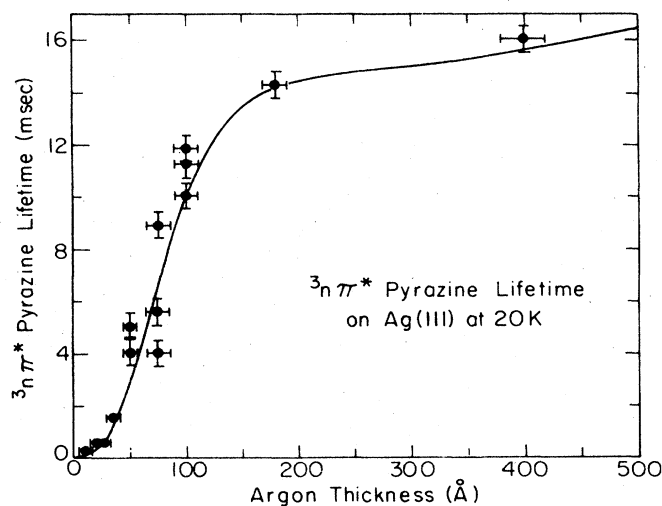

FIG. 19. Phosphorescence lifetime of $^3n\pi^*$ pyrazine at 20 K as a function of distance to a Ag(111) surface. The experimental points are compared with the line calculated according to CPS theory (Chance et al., 1978); fig. from Whitmore et al. (1982).

as well as bulk processes and a nonlocal dielectric response function for the metal. They point out that in noble metals, however, the deviation from CPS is expected to be considerably less.]

The exact nature of the decay channels responsible for the increased decay rate of the dipolar emitter near the metal surface has been considered by a number of workers [Morawitz and Philpott (1974), Philpott (1975), Weber and Eagan (1979)]. A most lucid discussion is due to Weber and Eagan (1979), who show that when emitting in a region stretching from approximately 20 to 160 Å above a silver surface at least 80% of the energy lost by the dipole to the metal results in surface-plasmon (sp) excitation. For distances closer in to the surface the sp fraction decreases monotonically to zero at the surface, with electron-hole excitation gaining as a result. The sp fraction was elegantly verified by Weber and Eagan (1979) using emissions from sp-coupled fluorescence from rhodamine 6G.

Inspired largely by SERS, several authors have considered the effect of surface geometry upon the decay rate of a molecule. Ruppin (1982) and Gersten and Nitzan (1981), and in the context of enhanced photochemistry Nitzan and Brus (1981a,1981b) have considered the decay rate of an excited molecule near a small metal sphere. Ruppin (1982) and Gersten and Nitzan (1981) view the energy dissipation process in the same way. When a molecule radiates near a metal sphere or spheroid, it excites surface-plasmon modes of many orders, provided that the wavelength region is correct, and provided that it is close enough. If the metal particle is small compared to the wavelength of light, only its dipolar surface plasmon can radiate, the higher-order modes resulting in Joule heating, i.e., in nonradiative losses.

Gersten and Nitzan (1981) compute the radiative rate from the power radiated divided by $h\omega$, while the nonradiative rate is obtained from the (joule power)/$h\omega$, i.e.,

$$\Gamma_{nr} = (\tfrac{1}{2}h\omega) \int \sigma \, |E|^2 d\mathbf{r} ,$$

and

$$\Gamma_r = (\omega^3/3hc^3) \left| \int [(\varepsilon-1)/4\pi]E \, d\mathbf{r} \right|^2 ,$$

where $\sigma = (\omega/4\pi)\mathrm{Im}(\varepsilon)$, the conductivity of the metal at frequency ω. Gersten and Nitzan calculate explicit expressions for both $\Gamma_{nr}(\perp)$ and $\Gamma_{nr}(||)$ (emitting dipole along the line joining the spheroid center to the dipole and at right angles to it, which in the limit of infinite radius of curvature become, respectively, dipoles normal and parallel to the metal surface), in terms of the emitter's dipole moment, spheroidal geometry, and a sum of terms involving the metal's dielectric function, each term resulting from a surface-plasmon mode of order higher than dipolar.

The results of the calculation indicate that when the molecule is several spheroid diameters removed from the spheroid the nonradiative rate approaches that of the free molecule. Figure 20 shows that for a sphere of 100 Å radius the lifetime (inverse of decay rate) of an emitting
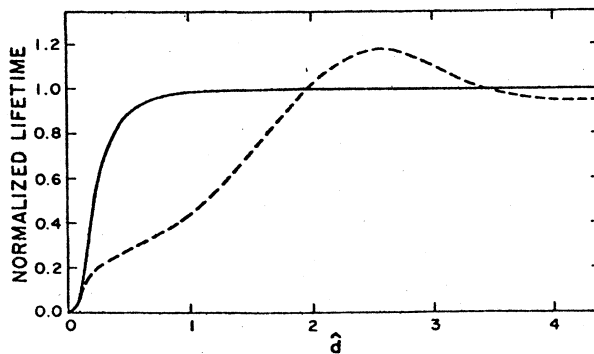

FIG. 20. Normalized lifetime vs distance from a 100-Å-radius silver sphere (solid line) compared with that of a molecule near a flat silver surface (Ruppin, 1982).

molecule placed approximately 3000 Å from the surface is almost that of the free molecule, while under similar circumstances but above a *plane* metal surface, the lifetime would be only 0.3 that of a free molecule. Gersten and Nitzan (1981), on the other hand, find that the nonradiative rate of molecules near a spheroid could sometimes exceed that near a plane surface (Fig. 21). Close enough to the metal spheroid the decay rate again follows the d^{-3} distance dependence—that is, the molecule sees the spheroid as essentially a flat surface when close enough to it. Ruppin points out that another important difference between the plane surface and that of a spheroid is the dependence of the rate of energy dissipation upon the frequency of the emitting dipole. As the sphere radius increases, the prominence of dipolar over higher multipolar surface plasmons also increases in the "spectrum" of decay rate versus frequency of emission.

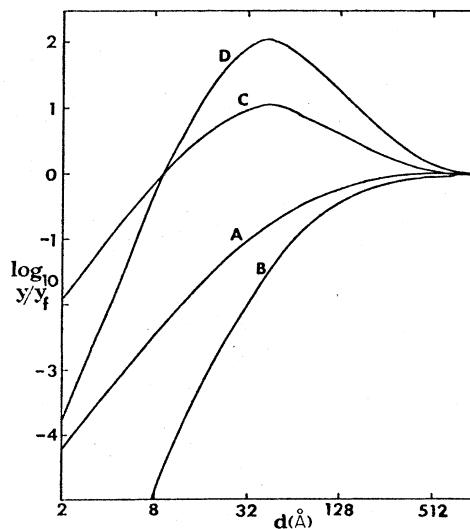Arias *et al.* (1982) adopt another approach in calculat-

FIG. 21. Log of the yield ratio (sphere to flat surface) as a function of distance above a 200-Å-radius silver sphere (Gersten and Nitzan, 1981).

ing the lifetime of a molecule emitting near a rough surface. They describe the time dependence of the molecular dipole using the Drude-Lorentz equation, in which the driving term is both the primary field and an image field. The roughness is introduced by assuming the metal height y to be a Gaussian random function in which any two points are correlated as follows:

$$\langle y(\mathbf{r})y(\mathbf{r'})\rangle = \delta^2 \exp(\,|\,\mathbf{r}-\mathbf{r'}\,|^2/a^2)\ .$$

The two parameters δ^2 and a are the mean-square height and correlation length. With a rough silver surface and $\delta = 150$ Å Arias et al. find that below 3.65 eV the decay rate may be as much as twenty times larger than for a flat surface. At 3.65 eV there is a sudden decrease in decay rate. Moreover, the d^{-3} dependence of the decay rate is found to break down near a rough surface, with the decay rate increasing even more rapidly than d^{-3}.

One of the consequences of all of these calculations is that the optimum fluorescence yield may not come from a molecule directly in contact with either a metal spheroid or a rough metal surface but at some (usually small) distance above it (Nitzan and Brus, 1981a,1981b; Wokaun et al., 1983). This fact may be most easily seen by considering a small sphere. The enhanced electric field decreases with distance d as measured from the surface of the sphere as $(R+d)^{-3}$, R being the sphere radius, while the decay rate decreases as d^{-3}. Hence, when $d < R$, the field decreases slowly as one leaves the surface of the metal sphere, while the nonradiative damping rate decreases rapidly. This fact was wonderfully confirmed by Wokaun et al. (1983), who followed the fluorescence yield of basic fuchsin, a dye with low intrinsic quantum yield (purposely chosen so as to obtain stronger luminescence enhancement) as a function of distance above a silver-island film.

Nonstoichiometric SiO, which can be controllably deposited to within 5 Å thickness, was used as a spacer. The apparent yield, Y_{app}, obtained as a function of d_{SiO} is shown in Fig. 22. The experimental result was satisfac-
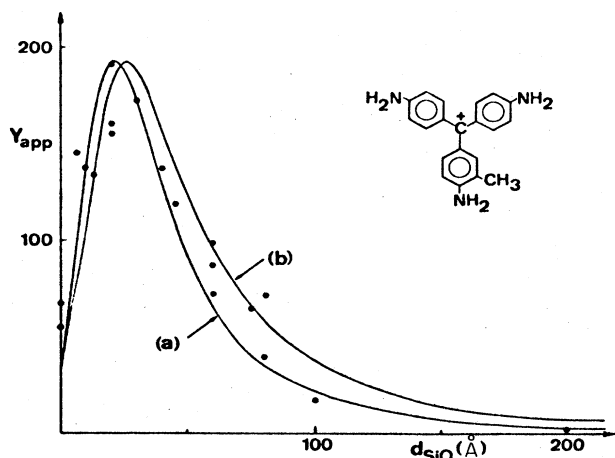

FIG. 22. Apparent yield vs thickness of SiO_x spacer layer from 0.1 monolayers of basic fuschin on a 40-Å Ag island film. Experimental points are compared with calculated curves based on Gersten-Nitzan Eqs. (34) assuming spheroids with dimensions (a) 300 Å × 140 Å and (b) 400 Å × 225 Å (Wokaun et al., 1983).

torily fitted using the expression

$$Y_{app} = |\,g(\omega_{ex})\,|^2\,|\,g(\omega_{fl})\,|^2(\Gamma^f/\Gamma)^2\ ,$$

where

$$g(\omega) = 1 + \frac{[1-\varepsilon(\omega)]\xi_0 Q_1'(\xi_1)}{[\varepsilon(\omega)+\varepsilon_1]Q_1(\xi_1)}\ ,$$

in which the first term is the enhanced absorption rate at the exciting frequency ω_{ex}, the second is the enhanced emission rate of fluorescence at frequency ω_{fl}, and the third is the ratio of the decay rate Γ^f of the free molecule to the decay rate Γ of the adsorbed molecule. The last quantity was calculated with the expression of Gersten and Nitzan (1980). Satisfactory agreement was obtained by assuming oblate spheroids of approximate aspect ratio 2, as detailed in Fig. 22.

The direct measurement of the fluorescence lifetime of a molecule adsorbed on a silver-island film is reported by Weitz, Garoff et al. (1982), who found that upon adsorption the fluorescence intensity of europium thenoyltrifluoracetonate (ETA) increased approximately fivefold, while its lifetime decreased some 3 orders of magnitude from 280 μsec, the lifetime in a solid sample of ETA. The observed nonexponential time dependence of the fluorescence of the adsorbed molecule was successfully explained by assuming that the average fluorescence signal may be approximately obtained by considering a single metal spheroid at the center of a disc of molecules and calculating the signal $s(t)$ from

$$s(t) = N \int d^2r\,\sigma(r)Y(r)\Gamma(r)\exp[-t\Gamma(r)]\ ,$$

in which N, δ, Y, and Γ are the number of molecules per unit area, the absorption cross section, the quantum yield, and the total decay rate, respectively. The last was once again obtained from the work of Gersten and Nitzan (1980).

C. Resonance Raman and photochemistry

A clear discussion of the various factors that affect the relative enhancements of Raman (R), resonance Raman (RR), and fluorescence (F) from molecules adsorbed on rough silver surfaces or small silver particles is due to Weitz et al. (1983). The discussion considers only the electromagnetic contributions. Using a four-level system, Weitz et al. report equations for the surface-enhancement factors associated with the three processes, which, though developed "heuristically" are justified using density matrix formalism (Mukamel and Nitzan, 1977). The enhancement factors obtained are

$$G_R = |\,g(\omega_L)\,|^2\,|\,g(\omega')\,|^2\ ,$$

$$G_{RR} = |\,g(\omega_L)\,|^2\,|\,g(\omega')\,|^2\frac{\gamma_1}{\gamma_1+\Gamma_1^S}\frac{\Gamma_1+T_{01}}{\Gamma_1+T_{01}+\Gamma_1^S}\ ,$$

and

$$G_F = |\,g(\omega_L)\,|^2\,|\,g(\omega')\,|^2\frac{\gamma_1}{\gamma_1+\Gamma_1^S}\frac{\Gamma_1+T_{01}}{\Gamma_1+T_{01}+\Gamma_1^S}\frac{\Gamma_0}{\Gamma_0+\Gamma_0^S}\ ,$$

in which the g terms refer, as before, to the em-enhancement terms of the incident and scattered fields and γ_1 is the total decay rate from the state initially excited (including dephasing and thermalization contributions), Γ_i the sum of radiative and nonradiative decay rates from state i for the free molecule, Γ_i^S the same for the molecule on the surface, and T_{01} the thermalization rate from state $|1\rangle$ to $|0\rangle$, the former being the state excited, the latter the state (of the electronically excited molecule) from which relaxed fluorescence originates.

The three decay factors in the expression for G_F refer, from left to right, to the effect of a possible broadening of the absorbing state resulting from placing the molecule on the surface (this effect is clearly not effective in Raman, a nonresonant process), nonradiative decay from state $|1\rangle$ including thermalization and relaxation to decay channels in the silver, and decay from state $|0\rangle$ to the metal. The major difference between resonance Raman (RR) and relaxed fluorescence as regards surface enhancement is that in the latter the molecule has two chances to damp its excitation, once in state $|1\rangle$, and the other after relaxing to state $|0\rangle$. Hence RR could have larger enhancement than fluorescence.

Estimates of the three G values, based on an observed G_R value of 10^5, yield typical values of 10^3 for G_{RR} and a range of 10^{-1} to 10 for G_F; the lower and upper limits are obtained with molecules that have high and low intrinsic quantum efficiency, respectively.

Weitz et al. (1983) confirmed these conclusions experimentally by investigating the SERS spectrum of p-nitrobenzoate, and surface-enhanced resonance-Raman scattering and fluorescence from rhodamine 6G and basic fuchsin, all adsorbed on similar silver-island films. The consistency of their results was interpreted by the authors as a vindication of the postulate that the em mechanism is the major surface-enhancement factor in the three phenomena.

A phenomenon closely allied to enhanced luminescence is enhanced photochemistry. The seminal paper on the subject was written by Nitzan and Brus (1981a,1981b), who consider two extreme classes of photochemistry near surfaces. In the first the chemical process following absorption is fast, as, for example, in direct photodissociation. In this case enhanced photochemistry and enhanced absorption are equivalent. In the second the chemical reaction requires the accumulation of a certain threshold energy as in infrared multiphoton dissociation.

In considering these two cases the authors begin with the equations of motion for the molecule and the metal sphere dipole, assuming the Drude approximation for the latter and the harmonic model for the former. An expression is obtained for the absorption cross section.

The equations were applied to several model systems—for example, I_2 decomposition. Figure 23 shows the absorption cross section for I_2 near a silver sphere (500 Å) (with the molecule perpendicular to the surface). It is clear that excitation into either the I_2 absorption or the silver-plasmon absorption could bring about photodecomposition; moreover, the I_2 absorption cross section is
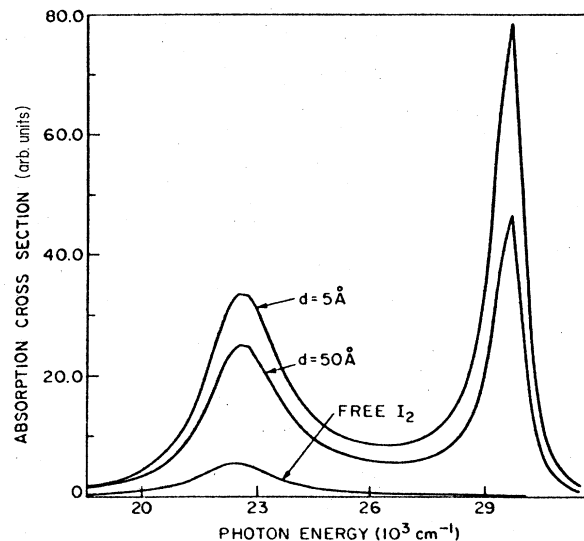

FIG. 23. Visible absorption cross section of a model I_2 molecule near a silver sphere (500 Å radius). The molecular axis is perpendicular to the surface (Nitzan and Brus, 1981a,1981b).

enhanced as a result of its proximity to the silver.

The authors point out that these effects are not limited to noble metals in the plasmon-absorption region of the spectrum. Colloidal particles of a doped semiconductor such as n-type InSb may be used to enhance ir multiphoton absorption by SF_6. Likewise, insulator particles such as those of MgO or SiC could be used to excite photochemistry when excited with light of frequency corresponding to their reststrahlung absorption.

As with enhanced fluorescence, Nitzan and Brus recognize that the optimal location for the photodecomposing molecule may not be directly on the surface but a short distance above the surface.

Such effects have been seen. A monolayer of s-triazine adsorbed on rough silver could not be decomposed (Moskovits and Wolkow, 1984) with either 337-nm N_2 laser radiation, which is almost in resonance with the $^3A_1''$ ($n\pi^*$) state reported to be 345.5 nm above the ground state (Hochstrasser and Zewail, 1971), nor with visible light, although in the latter case a surface reorientation of the molecule was observed due presumably to surface heating. With multilayers, on the other hand, s-triazine decomposed rapidly (Moskovits and Wolkow, 1984) with visible light to form a carbonaceous deposit. The initial rate of decomposition was found to be quadratic in laser power. Goncher and Harris (1982), by contrast, report decomposition of pyridine and pyrazine adsorbed on rough silver with uv (350 nm) laser photons to form HCN, the expected gas-phase product with no decomposition occurring after irradiation with visible light. The field of surface photochemistry is clearly still in its infancy.

D. Nonlinear effects

The final examples of effects due to the electromagnetic-field intensification near metal features of high curvature are two-photon effects. Chen, de Castro, and Shen (1981) were the first to report enhanced second-harmonic generation (SHG) by electrochemically roughened silver. Using the 1.06-μm output of a Q-switched Nd:YAG laser, they obtained approximately a thousandfold greater intensity at 530 nm with the roughened sample as compared with what is observed with smooth silver. Second-harmonic generation by island films has also been reported. Using the wedge technique reported previously, Wokaun et al. (1981) show that maximum SHG is obtained from 40-Å mass-thickness silver-island films in good agreement with the mass thickness that produces the optimum enhanced Raman. Once again, a thousandfold enhancement in SHG signal is found on the island film.

One of the most intriguing sources of enhanced SHG has been the regular array of ellipsoidal silver particles discussed earlier in the context of SERS. Liao (1982) has observed collimated SHG emitted at the angles predicted by a suitably modified grating equation. The fundamental is predicted and observed to be emitted at angles different from that of the SH beam, making beam separation easy.

SHG and other two-photon processes have also been observed from ions and molecules adsorbed on SERS-active surfaces. Although it was concluded, based on early studies of bulk SHG, that nonlinear emissions from the surface would be swamped by that of the bulk, the concentration of the electric field outside the SERS-active surface over that within makes such observations possible. Chen, de Castro, and Shen (1981) and Chen et al. (1981) observe a fiftyfold increase in the SH intensity on electrochemically cycling a silver electrode in a solution containing $0.05 M$ pyridine as opposed to what was observed in the absence of pyridine. Pyridine is known to adsorb to no greater an extent than one monolayer under the circumstances used. Even more interesting is the observation of enhanced SHG from pyrazine adsorbed on electrochemically roughened silver (Heinz et al., 1981). Pyrazine possesses a center of inversion and therefore also a zero second-order nonlinear polarizability. Heinz et al. (1981) suggest that a small amount of metal-molecule charge transfer may result in the loss of the center of inversion in the adsorbed molecule. An alternative explanation (Moskovits and DiLella, 1982a) attributes the observation of SHG from centrosymmetric molecules adsorbed on metals to the rapid decrease of the electric field near the surface of the metal, increasing the importance near a conducting surface of terms such as $\chi^0_{2a} E \nabla E$, which also contribute to SGH (Heritage and Glass, 1984). Another noteworthy result is the observation of four-wave mixing (FWM) by a regular array of uniformly shaped and sized silver ellipsoidal particles (Chemla et al., 1983). The measured conversion efficiency indicates an enhancement in the silver particles' third-order polarizability of the or-

der of 900 over bulk silver in satisfactory agreement with the SERS enhancement observed on similar particle arrays. The well-collimated FWM signal observed decayed by a factor of 8 during the first 20 sec. This was successfully ascribed to laser heating of the silver ellipsoids' causing them to become rounder, reducing thereby their FWM efficiency.

Hyper-Raman scattering, yet another nonlinear effect, has also been reported (Murphy et al., 1982), as has enhanced fluorescence spectroscopy following two-photon absorption (Glass et al., 1980). Submonolayer quantities of Rh B absorbed on silver-island films produced about 150-fold enhancement in fluorescence intensity at 590 nm after excitation with 1.06-μm Nd:YAG laser. Enhanced single-photon fluorescence following 530-nm (doubled YAG) excitation was also observed. The relative one- and two-photon fluorescence output agreed well as a function of the mass thickness of the island film with what was calculated on the basis of the em theory. Specifically, the one-photon output peaked at approximately 40-Å mass thickness, while the two-photon yield was maximum at about 80-Å mass thickness. For diphenyl anthracene and Nile blue dye, whose absorbing states lie above the silver-particle resonance, no enhancement is observed even when the fluorescence falls within the conduction resonance bandwidth. This observation is wholly in keeping with the conclusions of Weitz et al. (1983), who state that, for molecules with high quantum efficiency, the enhancement of fluorescence arises only from the increased excitation rate, with essentially no contribution being made in the emission portion of the fluorescence, as a result of the domination of nonradiative decay processes in that leg of the process.

IV. NONELECTROMAGNETIC CONTRIBUTIONS TO SERS

As successful as the em theory has been, there exists a number of observations that do not seem to be easily explicable in terms of it, which include, for example, the following.

(1) The molecules CO and N_2, whose Raman cross sections are almost identical, produce SERS spectra of rather different intensities (Moskovits and DiLella, 1982b). When coadsorbed in equal numbers onto cold-condensed silver films, CO produces a broad Raman peak shifted by some 28 cm^{-1} from that of unbonded CO, while N_2 produces a narrow Raman peak, shifted by only 2 cm^{-1}, whose intensity is about fifty times lower than that of CO. Suggestions that CO perhaps displaces N_2 from the surface were countered with experiments in which N_2 and CO were adsorbed independently with results similar to those in the coadsorption experiments. Likewise, postulating different surface bonding orientations for CO and N_2, the former being "end-on" bonded, while the latter is sidewise bonded, cannot account for the full fiftyfold discrepancy. On the basis of the Raman depolarization ratios of the two molecules, at most a factor of 10 may be obtained for the ratio of the Raman intensities resulting

from the adoption of the two orientations.

Molecules such as methane and ethane produce SERS spectra some one-hundred-fold less intense than do ethylene or benzene, even though the ordinary Raman spectra of all of these molecules contain bands of equivalent strength.

(2) In its simplest forms the em theory predicted that the SERS spectrum of a molecule should be a uniformly enhanced version of the ordinary Raman spectrum (McCall et al., 1980). Observations show this not to be true. This discrepancy is dramatically shown in the SERS spectrum of C_6F_6 (Fig. 24), which shows the C-F symmetric "breathing" vibration to be the dominant feature, while the same vibration is among the weakest in the ordinary Raman spectrum of the same molecule. Moreover, the SERS spectrum of many molecules (Erdheim et al., 1980; Dornhaus et al., 1980; Moskovits and DiLella, 1980,1982a,1982b) displays normally forbidden features, often with intensities comparable to the most intense of the allowed transitions.

(3) In SERS studies involving roughened electrodes immersed in aqueous electrolytes or aqueous metal colloids one does not observe a strong SERS spectrum of water, which presumably surrounds the SERS-active features in abundance.

(4) It has also been observed that the SERS excitation spectrum obtained from aqueous colloidal silver does not correspond well with the absorption spectrum of the same colloid (Creighton et al., 1979; Mabuchi et al., 1982; Siiman et al., 1983). The latter usually consists of a strong peak at about 390 nm with weaker features to the red of this. The 390-nm peak is associated with spherical colloidal particles, while the red peak or peaks are commonly believed to come about from aggregated colloid whose op-

tical properties were discussed either in terms of ellipsoidal particles or by considering coupling between two or among several spheres. Although it is clear from the work of Aravind et al. (1981) that dipolar coupling is insufficient to account for the electrostatic fields about spheres spaced so closely together, dipolar coupling, often couched in the language of effective medium theories such as the Maxwell-Garnett theory does produce a redshift plasmon peak whose exact position depends on the density of (hence average distance between) the colloidal spheres.

The apparent problem is that one often sees only the 390-nm peak in the absorption spectrum of a colloid/adsorbate system, yet the SERS excitation profile achieves a maximum at a frequency in the red that sometimes does not appear to correspond to any discernable absorption peak, the implication being that the excitation profile maximum corresponds to an absorption (perhaps an adsorbate-metal charge transfer absorption) whose absorption strength is too low to be detected.

The experience with aqueous colloids contrasts with what is seen for matrix-isolated colloidal silver (Abe et al., 1981), island film systems, and a few studies with aqueous colloids in which aggregation was carefully avoided (Wetzel and Gerischer, 1980). In these last-mentioned systems there is more or less good correspondence between the absorption spectrum and the SERS excitation profile, if one keeps in mind the expected shifts in peak positions discussed in Sec. II.A.

(5) Another challenge to the em theory comes from the observation that the excitation profile measured for several Raman modes of pyridine adsorbed on roughened silver electrode seem to be functions of the Raman-shifted frequency only (Pockrand et al., 1983), rather than showing the two features (one associated with the incident resonance, the other with the scattered beam resonance) which the em theory predicts.

(6) Finally, there are several effects observed with silver electrodes that are in apparent conflict with the em model. These are the observed poisoning of a SERS-active electrode by a relatively small fraction of a monolayer of thallium, lead, and several other ions (Pettinger and Moerl, 1983), causing the SERS signal of pyridine to be lost irretrievably.

From a somewhat related experiment Owen et al. (1983) claim to see an irreversible loss in SERS enhancement from adsorbed halide ions and pyridine on cyclically ramping the potential of a silver electrode in the non-Faradic region where one expects reversible adsorption-desorption behavior and little electrochemical behavior to occur. The implication is that both the roughness features which are the necessary agents of the em theory and the overall concentration of adsorbate are unaltered by the voltage cycling; hence the decrease in SERS intensity signals the destruction of another crucial ingredient to the SERS effect, such as surface adatoms.

An interesting observation has been reported that the SERS intensities of the various Raman lines of pyridine adsorbate on a silver electrode exhibit a maximum as a
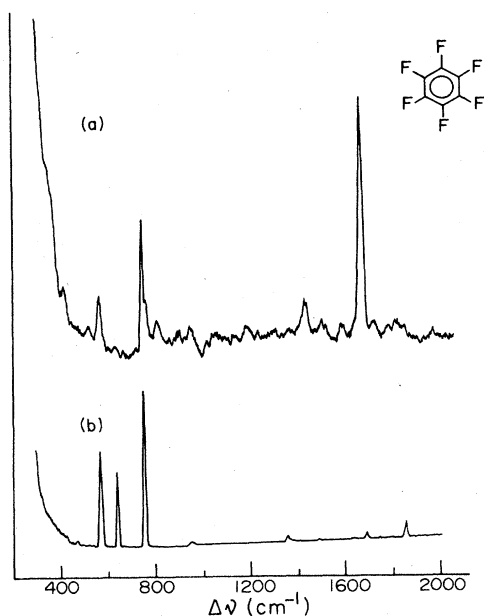

FIG. 24. (a) SERS spectrum of C_6F_6 adsorbed on cold-deposited film; (b) ordinary Raman spectrum of a solid polycrystalline layer of the molecules.

function of the electrode potential. The value of the electrode potential at which the maximum occurs, however, depends markedly on the frequency of laser excitation used (Billman and Otto, 1982; Furtak and Macomber, 1983). So, for example (Otto, 1982), the SERS intensity of the 1006-cm^{-1} line of pyridine peaks at about -0.60 V [measured against a saturated calomel electrode (SCE)] when 457.9-nm argon laser excitation is used, while 647.1-nm Kr$^+$ laser excitation produces maximum SERS intensity at -0.76 V (SCE). Otto (1982) and others (Billman and Otto, 1983; Furtak and Macomber, 1983) suggest that the em theory cannot easily account for such an observation; hence here again one must invoke another major contributor to SERS.

(7) Finally, there is controversy regarding the extent of the enhancement from the surface. The previously cited results of Murray et al. (1980) [see also Murray and Allara (1982)] suggest that the enhancement continues outward from the surface more or less in agreement with the em model. Others (Sanda et al., 1980; Smardzewski et al., 1979) suggest that the SERS effect saturates at about the monolayer stage with subsequent monolayers enjoying little or no enhancement.

In attempting to deal with these observations, investigators have proposed a number of models, some competitive with the em theory, others supplementary to it.

A. The adatom—charge-transfer complex model

Otto proposed that "a strong Raman enhancement for an adsorbate on a silver surface is only possible when the adsorbate is bound to an atomic scale roughness, e.g., an adatom" (Otto et al., 1980; Billmann et al., 1980).

Although he does not insist that atomic-scale roughness is restricted to single atoms, Otto distinguishes strictly between small-scale roughness and the size of roughness operative in the em model. What the minimum-size feature for producing the em effect is, is of course difficult to say; one guesses, however, that bumps smaller than about 20 Å in mean diameter would no longer be very effective in the em model (these nevertheless contain hundreds of silver atoms); moreover, surface features larger than 1000 Å would again be progressively less effective as multipolar resonances higher than dipolar become excited. Atomic-scale roughness (ASR), on the other hand, is seen to be associated with the adsorption site; hence clusters no bigger than five or six atoms are likely to qualify. Nevertheless, the emphasis in the ASR literature has been largely on actual adatoms.

In its original form the adatom model was thought to enhance surface Raman scattering by increasing the magnitude of the three matrix elements in the expression for the Raman cross section of an adsorbed molecule:

$$\sigma(\omega_v) \propto \sum_{ij} \frac{\langle 0 | H_{e\text{-}p} | j \rangle \langle 1,j | H_{ev} | 0,i \rangle \langle i | H_{e\text{-}p} | 0 \rangle^2}{(\omega_L - \omega_v - \omega_j)(\omega_L - \omega_i)} .$$

(14)

Here H_{ev} expresses the interaction between the metal electrons and the vibration of frequency ω_v of the admolecule, while $H_{e\text{-}p}$ is the electron-photon interaction term $e(\mathbf{p} \mathbf{A} + \mathbf{A} \mathbf{p})/2mc$. The authors argue that $H_{e\text{-}p}$ is greatly increased due to the additional momentum available for scattering of electron-hole pairs at atomic-scale roughness.

Likewise, the H_{ev} term is purported to be increased due to the "relaxation of momentum conservation by the presence of the adatom to which the adsorbate is bound" (Billmann et al., 1980; see also Otto et al., 1980). Hence atomic-scale roughness helps create many more electron-hole pairs and also helps to couple the excited electrons to adsorbate vibrations. A similar argument is used to explain the presence of the luminescent continuum that is observed when SERS-active surfaces are laser excited. By replacing the H_{ev} matrix element by a $H_{e\text{-}e}$ (electron-electron interaction) factor in the equation, one can obtain the cross section for electronic resonance Raman and again invoke the relaxation of the momentum conservation rule by ASR to explain its increased magnitude with SERS-active surfaces.

Despite the fact that no attempts are made to calculate the expected increase in the magnitudes of the matrix elements involved resulting from ASR, Billmann et al. (1980) and Otto et al. (1980) conjecture that "the resonance effect, introduced by the atomic scale roughness of the surface, is the most important enhancement mechanism." The discussion surrounding the equation bears many similarities to prior proposals made by Burstein and co-workers (Burstein et al., 1979,1982; Chen et al., 1979), who also attribute at least part of the enhancement of both the Raman scattering and the luminescent continuum to inelastic light scattering by charge-carrier excitations in the metal through $(\mathbf{p} \cdot \mathbf{A})^2$-type processes that are made possible by the breakdown of momentum conservation caused by submicroscopic roughness. These authors, however, do not limit the range of roughness to ASR, and suggest, moreover, that the continuum may also be due to electron-hole pair recombination radiation in addition to electronic Raman processes.

Burstein et al. (1979,1982) enumerate three mechanisms for Raman scattering by electron-hole (e-h) pair excitation. These are the A^2, the $(\mathbf{p} \cdot \mathbf{A})^2$, and the $(\nabla \cdot \mathbf{A})^2$ mechanisms. The first is a one-step process, while the next two involve a virtual electron-hole excitation or recombination process. The virtual state may be either intraband or interband.

The precise manner in which the admolecule is involved in these processes is left somewhat speculative. The most straightforward is that there is Coulombic coupling between the admolecule and the em fields associated with e-h excitation and recombination. One effect of this is to modulate the metal's reflectivity in synchronism with the molecular vibration. This process was discussed by Maniv and Metiu (1981). A more interesting proposal is that the virtual state resides upon the molecule. A part of the excitation is therefore a metal-to-molecule charge transfer process. The trapping of the electron in the emp-

ty virtual molecular orbital may be accompanied by a relaxation along the normal coordinates of the molecule so that when the electron leaves the virtual orbital the molecule is left in a vibrationally excited state. The polarization selection rules for all three mechanisms are that $e_i \cdot e_s = 0$ where $e_{i,s}$ are the polarization unit vectors for the incident, or scattered radiation. For s-polarized radiation for which $\nabla \cdot A = 0$ only the $(p \cdot A)^2$ and A^2 mechanism are expected to contribute. Moreover, the $(p \cdot A)^2$ and A^2 processes are expected to be weak for free-electron metals in the Drude region. For p-polarized light Burstein *et al.* (1979,1982) suggest that the $(\nabla \cdot A)^2$ mechanism makes the dominant contribution. No systematic attempt seems to have been made to test these predictions. To be sure, such analyses would have to disentangle somehow the fraction of the SERS that one attributes to the electron-hole pair production mechanism from the em enhancement, which all but few authors believe makes a significant contribution.

Although, as originally stated, the salient physics in the adatom model (Otto *et al.*, 1980; Billmann *et al.*, 1980) was the possible increase in electron-hole pair production due mainly to the proposed more efficient coupling between the incoming photons and bulk excitations due primarily to a relaxation of momentum conservation constraints, the model converged with several others in which the SERS effect was largely ascribed to the formation of a colored surface complex, be it with the adsorbate (Pettinger *et al.*, 1979) or with the radical anion of the adsorbate (Regis and Corset, 1980). According to this view, SERS was merely a resonance Raman effect—the bonding of the erstwhile transparent adsorbate with the surface produced new states in resonance with the incoming photon.

In the absence of numerical calculations to determine the expected order of magnitude of the matrix elements in Eq. (14) it is difficult to ascertain to what extent ASR, and what scale of roughness is the most efficacious in producing a sizable contribution to SERS entirely through effects such as those summarized by Eq. (14).

One should say parenthetically that the excitation of surface plasmons is itself a manifestation of the relaxation of the momentum conservation rule due to the roughness or as a result of surface curvature. Hence a complete quantum-mechanical theory addressing the question of electron-photon coupling in a rough metal would automatically include surface-plasmon excitation. It is clear, however, that very—small-scale surface features, such as those containing one to a dozen atoms, cannot be expected to participate greatly in surface-plasmon excitation, since one would hardly expect conduction electrons to be a strong concept in such small features.

The major event that fixed the attention of some upon atomic-scale rather than larger-scale roughness in promoting the nonelectromagnetic contribution to SERS as well as the aforementioned convergence with the surface complex model was the discovery by Avouris and Demuth (1981) [see also Schmeisser *et al.* (1982)] of a weak absorption (Fig. 25) in the electron energy-loss spec-
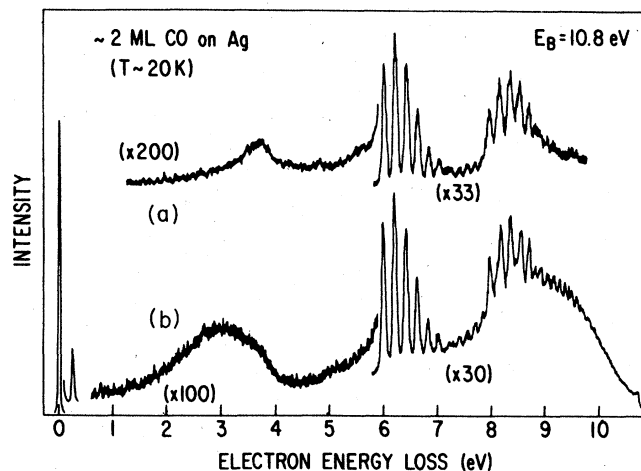

FIG. 25. Electron energy-loss spectra of approximately two monolayers of CO adsorbed at 20 K on Ag films prepared by evaporation at room temperature (a) and at 20 K (b) (Schmeisser *et al.*, 1982).

trum of several molecules adsorbed on silver close to the surface-plasmon absorption but not coincident with it. The strength of this absorption was more or less consistent with the relative SERS enhancement in the spectra of the same molecules. So, for example, for N_2 adsorbed on silver the band was almost unobservable. With adsorbed CO, on the other hand, it was strong. This absorption was interpreted as a charge transfer band (originally it was not specified whether it was a metal-to-adsorbate or adsorbate-to-metal charge transfer) and immediately changed the emphasis on the role of adatoms from the first postulated "electron-hole" mechanisms to one involving sites capable of forming charge transfer complexes. Since formation of a complex is mandatory in this aspect of the theory of SERS, it is called the "chemical" contribution to SERS.

Two other pieces of evidence also seemed to confirm a chemical contribution to SERS. These are the reported observation of SERS from molecules adsorbed on liquid mercury (Naaman *et al.*, 1980; Sanchez *et al.*, 1981) and the demonstration (Lombardi *et al.*, 1981) that for a series of adsorbates whose SERS spectrum contained a band ascribable to the metal-molecule vibration, the frequency of this vibration seemed to be (with considerable scatter) more proportional to $\mu^{-1/2}$, where μ is the reduced mass obtained from the mass of the molecule and that of a single silver atom, than it was to $m^{-1/2}$, where m is the mass of the adsorbate molecule atom alone, the implication being that the vibrating adsorbed molecule behaved more like a pseudodiatomic molecule in which one member was a silver adatom rather than one bonded directly to an infinite mass. These two sets of observations did not prove as durable as the previously mentioned EELS results. One of the reports of SERS from liquid mercury (Sanchez *et al.*, 1981) proved spurious, and while

no obvious fault can be found with the other (Naaman *et al.*, 1980) attempts by several groups to observe intense Raman emissions from molecules adsorbed on liquid mercury under like conditions failed. Likewise, the reduced mass versus adsorbate mass arguments proposed by Lombardi *et al.* (1981) were shown to be entirely inconclusive (Moskovits, 1983). Indeed, it was argued that the concept of an adsorbate vibrating against an infinite mass was inaccurate in treating low-frequency vibrations where there is near resonance with phonon modes of the underlying metal.

The involvement of a charge transfer process in SERS seems to explain some of the list of observations that seemed inexplicable in terms of the electromagnetic effect. For example, the weakness of the SERS effect with adsorbates such as N_2, CH_4, and C_2H_6 is simply a manifestation of the absence of both a chemical bond and a charge transfer band. Likewise, the difference between the relative intensities of the many lines in a SERS spectrum of a molecule and its spontaneous Raman spectrum again rests on the fact that in the former case one is actually measuring the resonance Raman spectrum of a complex whose spectrum could differ from the spontaneous Raman spectrum of its ligands. This is not a strong argument against the em theory, since one might say that the bonding to the surface may alter the frequencies and intensities of the Raman spectrum and adsorbate without necessarily contributing to the enhancement mechanism. The em mechanism would then enhance the Raman spectrum of the surface-bound adsorbate.

Likewise, the shift in value of the electrode potential at which the SERS intensity is maximum with the frequency of the exciting light is also attributed to the involvement of a charge transfer process in SERS; the change in electrode potential changes the relative energy between the metal's Fermi energy and the adsorbate energy levels, thereby changing slightly the resonance condition between the charge transfer condition and the incoming photon. Both changes implying metal-to-molecule and molecule-to-metal (Furtak and Roy, 1983) charge transfer have been reported.

The discovery of the low-frequency loss band by Avouris, Demuth, and co-workers prompted a number of authors to consider the possible contribution of a charge transfer (CT) absorption to SERS in some detail. Most discuss the process in terms of a metal-to-molecule transfer.

Avouris and Demuth (1981) present an order-of-magnitude calculation to estimate the CT contribution to the Raman polarizability of a metal-molecule system, writing $(\partial\alpha/\partial Q_A)_{CT}$ as equal to

$$(\partial q_A/\partial R)(\partial R/\partial Q_A)(\partial\alpha_A/\partial q_A - \partial\alpha_D/\partial q_D),$$

where q_A and q_D are the charges on the donor (metal) and acceptor (molecule). Likewise, α_A and α_D are their polarizabilities and R the donor-acceptor separation. Based on a free-electron model, the quantity $\partial\alpha_D/\partial q_D$, i.e., the change in the metal's susceptibility resulting from the removal of a charge δq_D, is estimated to be $\sim 2\times 10^{-23}$

cm^3/e. This is assumed to be the major contribution which, together with estimates for the other quantities, produces a value of $(\partial\alpha/\partial Q_A)_{CT}$, which is about tenfold larger than for the isolated molecule. Avouris and Demuth (1981) are careful to distinguish between this CT mechanism and the one based on electron-hole pair excitation discussed above. The process of *e-h* production followed by the hopping of the electron into an empty molecular virtual level and back is equivalent to an "inelastic scattering of the electron via a negative ion resonance of the adsorbed molecule" (Avouris and Demuth, 1981). Such processes have been observed in the gas phase (Schulz, 1973), giving rise to many intense vibrational overtones in addition to the fundamental. The failure to observe intense overtones with SERS convinces Avouris *et al.* that the *e-h* mechanism is not a dominant one in SERS.

Almost all recent theoretical papers dealing with the CT mechanism have as a common theme the development of an accessible surface absorption due to the broadening and shifting in energy of the free molecular states upon adsorption due both to the formation of a surface energy band (i.e., molecule-molecule interaction) and to interactions with metal energy states. This is shown in Fig. 26. Hence while the HOMO-LUMO transition in the free molecule may be too energetic to excite with a convenient laser, once the molecule is adsorbed, one finds resonance or near resonance between the laser photon and the surface absorption.

Such a process was foreshadowed by King and Schatz (1979) and by Efrima and Metiu (1979a,1979b,1979c). The first group considers the problem to be one of resonance Raman scattering and calculate the matrix elements involved in the conventional expression for the Raman scattering tensor assuming a simple diatomic as the adsorbate. Instead of broadening and shifting the adsorbate levels through the adsorption process, King and Schatz vary the local, static electric field at the surface, modeling
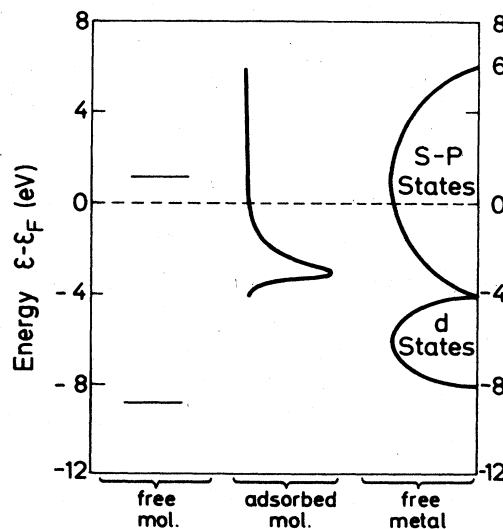

FIG. 26. Energy-level scheme comparing free molecule with adsorbed molecule (Araya and Zeyher, 1981).

thereby the case of SERS obtained from electrodes where the electrochemically induced fields may exceed 10^6 V/cm. This has the effect of shifting the charge transfer states into resonance, a process described by the authors as "intensity borrowing." Depending on electric field strength, enhancements of up to 10^8 are predicted. While this model calls to mind the aforementioned observations involving the dependence of SERS intensity excited by photons of different frequency as a function of electrode potential, it is rather unrealistic. Not least of its faults is the omission of the broadening in the charge transfer states produced to a large measure by the nonradiative processes discussed above. This would reduce greatly the calculated enhancement.

Efrima and Metiu (1979b) use a classical electromagnetic model to calculate the Raman scattering by a molecule whose polarizability is given by the expression

$$\alpha_0(\omega) = (e^2/m)f/(\omega_e^2 - \omega^2 - i\omega\Gamma_0) .$$

When the molecule is placed near a metal surface, its effective polarizability becomes

$$\alpha(\omega) = (e^2/m)f/\{\omega_e^2 - \omega^2 - \Delta(\omega) - i\omega[\Gamma_0 + \Gamma(\omega)]\} .$$

Expressions for Δ and Γ are given by Efrima and Metiu (1979b). The modified expression comes about as a result of the interaction at the location of the molecule of the em field directly incident upon it and the radiation of the dipole induced in the molecule, which is reflected back to the molecule by the surface. The effect is to lower the resonant frequency of the system and to broaden the resonance. Here again one can induce resonance by virtue of the adsorption process. The difference between this model and those that follow rests upon the fact that in the present case the shifts are brought about by purely physical processes without the assumption of chemical bond formation. In fact, the shift and width of the polarizability are exactly those calculated by Chance, Prock, and Silbey (1978) for fluorescence emission by a dipole near a flat surface.

A prototype of what is now the canonical CT model is given by Persson (1981), who describes the scattering process by a Hamiltonian of the form

$$H = [\varepsilon_a(Q) - edE_z]\hat{n}_a + \sum_k \varepsilon_k a_k^\dagger a_k$$
$$+ \sum_k V_{ak} a_k^\dagger a_k + \hbar\Omega b^\dagger b + H_{EM} ,$$

in which Q is a displacement along a normal coordinate of the molecule, $\varepsilon_a(Q)$ are molecular energy levels, ε_k is a set of energy levels for the metallic electrons, and V_{ak} describes the transfer of an electron between the metal and the molecule.

The coupling between the molecule and the field is effected by $-edE_z\hat{n}_a$, where d is the distance between the "center of charge" of orbital $|a\rangle$ and the image plane. With $E_z = 0$ and with $Q = 0$, this Hamiltonian becomes the well-known Newns-Anderson Hamiltonian (Newns, 1969).

The transition rate for the Raman process is calculated

by assuming that ε_a may be expanded to first order in Q. The Hamiltonian is written as $H = H_0 + V$ with

$$V = [Q\partial\varepsilon_a/\partial Q \mid_0 - edE_z] \sum_{\alpha\beta} \langle \beta \mid a \rangle \langle a \mid \alpha \rangle c_\beta^\dagger c_\alpha .$$

Noting that $|\alpha\rangle = c_\alpha^\dagger |$ vacuum$\rangle$ are eigenfunctions of the Hamiltonian H_0, and using perturbation theory, the transition rate can be shown to have the form of the golden rule, with the perturbation H' of the form

$$H' = QE_z^2(ed)^2\partial\varepsilon_a/\partial Q \mid_0 G(\omega,\omega') .$$

The form of $G(\omega,\omega')$ is given by Persson (1981). It is a function of the density of states $\rho_a(\varepsilon)$ for the adsorbed molecule. For simplicity $\rho_a(\varepsilon)$ is taken to be a simple Lorentzian with peak at ε_a and width Γ, while for the gas-phase molecule $H' = -\alpha(0)E^2/2 - \alpha'(0)QE^2/2$, where $\alpha(Q)$ is the polarizability of the molecule, taken as a simple scalar.

The "chemical" enhancement is therefore

$$\eta_{\text{chem}} = \mid [(ed)^2\partial\varepsilon_a/\partial Q G(\omega,\omega')]/[\alpha'(0)/2] \mid^2 .$$

Estimates for η_{chem} were obtained by using parameters for ε_0 and Γ inspired by the work of Avouris and Demuth (1981). With $2\Gamma = 0.6$ eV and assuming $\partial\varepsilon_a/\partial Q = 10$ eV Å, one obtains

$$\eta_{\text{chem}} \simeq 30 \mid d^2/\alpha'(0) \mid^2 ,$$

which yields enhancements in the range 10—100 for typical ratios of $d^2/\alpha'(0)$.

Interestingly this model predicts a greater enhancement for large molecules standing up on the surface (i.e., d large), so long as the bonding that facilitates charge transfer is not disrupted, than for small molecules "lying down" on the surface. Moreover, Raman modes with small values of α'_{zz} should be more enhanced than those with large values of the Raman polarizability. Neither of these predictions is systematically observed.

Ueba (1980) takes a similar approach in a paper that predates that of Persson by about a year. I have chosen to follow the latter's development for the sake of ease of presentation.

A somewhat different approach is taken by Adrian (1982), who uses the semiempirical Wolfsberg-Helmholz method to relate the charge transfer states created during the chemisorption process to the overlap integrals between the conduction-band orbitals and an acceptor or donor orbital of the admolecule. The method is applied to ethylene adsorbed on silver. With charge-transfer excitations of an electron from the metal to the π^*-ethylene orbital, peak enhancements of around 600 are calculated assuming the unrealistically narrow width of 0.02 eV for the band. With the use of 0.2-eV width the peak enhancement reduced to around 70.

An elegant calculation by Araya and Zeyher (1981), based on the Newns-Anderson model for chemisorption, produces an expression for the enhancement that is broken down by the authors into three contributions, two resulting from a flat metal surface and a third due to a superimposed sinusoidal grating that is taken by the authors

to represent one of the spatial Fourier components representing roughness on the surface. The three contributions are the local field effect, i.e., the image effect, chemisorption, i.e., charge transfer, and the grating. For silver the first two produce a broad, almost constant, enhancement of about 50 to 100, respectively, in magnitude. The third was sharply peaked at the surface-plasmon frequency, where its contribution was about 2000.

The extent to which chemical effects contribute to SERS is still controversial and has resulted in two schools of thought. The one greatly overestimates both the size of its contribution to the enhancement and the extent to which experimental evidence corroborates its participation. The second minimizes the role of chemical effects. Often results which are presented by the first school as totally inexplicable in terms of the em model may be reconciled with it using a slight modification of the pertinent equations or reinterpretation of the results. So while most em calculations have considered a physisorbed molecule, it is implicit in the theory that should a strong metal-molecule surface bond be formed, the polarizability to be included in the pertinent equations must be that of the metal-molecule complex rather than that of the molecule alone. This is the tack taken by Murray and Bodoff (1984a,1984b), who performed what are probably the most careful measurements and calculations aimed at disentangling the em from the chemical effect. Using ^{14}C-labeled KCN to establish the CN coverage, the authors measure the SERS intensity of CN adsorbed on a 50-Å mass-thickness island film as a function of CN coverage and find an amonotonic coverage dependence, as has already been reported for pyridine (Pockrand and Otto, 1980) and ethylene (Pockrand, 1983). The experimentally observed behavior is reproduced well by a model which considers the effect of the local field, due to the polarization of neighboring admolecules, upon a given admolecule. The effective Raman polarizability of the adsorbate is obtained from the fit and found to be about 2.4 times larger than that of HCN, i.e., of the same order of magnitude as the Raman polarizability of the complex $Ag(CN)_2^-$ expressed per CN unit. Thus the "chemical" enhancement amounts to about a factor of 6 as compared to the em enhancement of 10^4 measured and also calculated by those authors on the basis of an assembly of ellipsoids. The analysis removes to some extent the central role played by a specific charge transfer state, placing the emphasis instead on the fact that when chemisorption occurs the identity of the adsorbate changes from a CN ligand to an AgCN complex. To be sure, in terms of the expression for the Raman polarizability derived from second-order perturbation theory, an increase in Raman polarizability suggests a summation either over more states or lower-energy states or both to which a low-lying charge transfer state would certainly make an important contribution. Adatoms as such are not required, however, in such a scheme. Indeed, the CT model does not require adatoms but merely chemisorption sites. With some metals and for some adsorbates such sites may be adequately

provided by single-crystal surfaces, while in other cases one needs kinks, steps, edges, or indeed adatoms for an appreciable surface bond to form.

Of all the aspects of the chemical enhancement the required participation of adatoms is among the least well supported by experiment. Some experimental results often cited as defense for the importance of adatoms appears, in fact, to argue against their importance—for example, the aforementioned observation that the SERS intensity of molecules adsorbed on cold-deposited films first *increases* with increasing substrate temperature and then *decreases*. It is clear from the mechanism of formation of these films that the abundance of adatoms must be greatest immediately upon deposition and that on warming the quantity of adatoms must decrease due to diffusion into surface receiving sites. Hence the initial increase in SERS intensity is more easily understood in terms of the tuning of the surface structures in order to achieve good em enhancing properties as discussed earlier than to one involving adatoms. The diffusing species during these experiments, of course, are adatoms. Their diffusion, however, brings about not only diminution of their own number but that of larger surface bumps and cavities as well.

Many, many papers for and against adatoms have appeared, most of which suffer from inconclusiveness. Wood (1981,1983) has deposited carefully monitored thicknesses of fresh silver upon an annealed silver substrate held at a low temperature. When the substrate was overlaid with pyridine, he noted that a SERS signal was not obtained until a silver deposit of approximately 150 Å thickness was achieved. Arguing that the concentration of adatoms was more or less independent of deposit thickness beyond, say, 10 Å, Wood concluded that the larger thickness was required to build larger roughness features such as might effectively participate in the em mechanism. Otto (1983b) countered this by suggesting that the concentration of adatoms increases with the size of large-scale roughness features, introducing at the same time a new definition of ASR as a surface site (on an fcc metal) with metal coordination number less than 6. In turn, Ertürk et al. (1983) report two sets of Raman lines obtained from pyridine adsorbed on cold-deposited silver. One group is attributed to adsorbate residing on atomically smooth parts of the surface, while the second, more intense group originates from pyridine at ASR sites. While 2 orders of magnitude of extra enhancement were estimated for the second group, the uncertainty in the relative concentration of the two types of species placed large error limits on that estimate.

Attempts to determine the non-em contribution to SERS were made by using annealed (and hence presumably flat) deposited metal surfaces (Yamada et al., 1982). Enhancements of the order of 10^2 were deduced therefrom. Here the em effect cannot be excluded out of hand. Even annealed films have a certain degree of roughness. Surface-plasmon absorptions and adsorbate-induced shifts in absorption have been reported for Cu and Ag films deposited at room temperature (Moskovits

and McBreen, 1978; Dignam and Moskovits, 1973). Moreover, Avouris and Demuth's EELS results (Avouris and Demuth, 1981; Schmeisser et al., 1982) show a surface-plasmon absorption even for silver films deposited on a room-temperature substrate, albeit weaker than that observed for the cold-deposited film.

Likewise, SERS results obtained from adsorbate on metals other than Cu, Ag, and Au have been cited as indicators of non-em contributions (Yamada and Yamamoto, 1982; Yamada et al., 1982). For example, Krasser and Renouprez (1982) report surface-enhanced Raman spectra from benzene adsorbed on small silica-supported platinum clusters. An enhancement in the range $10^3 - 10^4$ is claimed with a SERS excitation profile's increasing towards the blue. An enhancement maximum in the near ultraviolet is, however, the expected behavior for platinum based on the em model. Moreover, em calculations indicate that platinum, while not at all as good as silver, could nonetheless provide a thousandfold enhancement and even more for nonspherical particles.

Enhanced Raman spectra obtained on NiO and TiO_2 (Yamada and Yamamoto, 1982; Yamada et al., 1982) have also been referred to as SERS and used to support the CT model. With cases such as these it becomes difficult to draw the line between SERS and resonance Raman. TiO_2 behaves like an insulator in the visible range; hence the electronic bands of any colored surface complexes formed would not be broadened as a result of the aforementioned nonradiative decay mechanism that operates with metals. Thus while the TiO_2 results are very interesting as surface spectroscopy and may announce the possibility of investigating adsorbate-semiconductor interactions using resonance Raman spectroscopy, they are not as pertinent to the clarification of the chemical contribution to SERS as the authors imply.

High-quality Raman spectra of molecules adsorbed on single-crystal silver surfaces have been reported by Campion and co-workers (Campion and Mullins, 1983), who find that very little if any enhancement is observed in those systems. While the ability to make that statement with precision rests upon an accurate knowledge of the α_{zz} Raman polarizability component of the adsorbed molecule, the estimates seem to be sufficiently accurate to say that if any enhancement exists it is less than a factor of 10. While this does not bear directly on the charge transfer model, since in all but one study the molecules physisorbed rather than chemisorbed on the crystalline faces used, the results do indicate that the "physical" enhancement mechanisms which should operate at flat surfaces, such as those based on images, do not seem to contribute significantly.

The disparate manner in which results of Campion and his group have been interpreted by the SERS community demonstrates wonderfully the polarization into ASR and em supporters. In an interesting series of experiments Campion and Mullins (1983) have shown that pyridine adsorbed on various faces of single-crystal silver, among them Ag (100), (110), and (111), produce Raman spectra characteristic of the physisorbed molecule; this means that the frequencies of the ring modes of the molecule are not unlike those in liquid pyridine, while those observed in SERS are shifted up in frequency by $10-20$ cm^{-1} and on that basis are designated as chemisorbed. At the same time, the spectra recorded on the aforementioned silver single-crystal faces were convincingly shown to be either unenhanced or very little enhanced except as regards the "minor" enhancement resulting from the presence of the reflecting metal surface and the orientational effect of the molecule on the surface.

Advocates of the ASR model point to this observation and state that there was no enhancement because there is no chemisorption; the chemical model demands the presence of a bond. Supporters of the em model, on the other hand, point to the lack of roughness as the important missing ingredient in the absence of enhancement. Clearly what is necessary is a case in which roughness is definitely lacking while enhancement is observed or contrariwise a case where chemisorption is clearly present while enhancement is absent. The former situation is difficult to prepare, since even the flattest of surfaces may have faults too small to detect by readily available means. The latter experiment, however seems to have been performed recently (Mullins and Campion, 1985), tilting the game in favor of the em model. Pyridine adsorbed on Ag(540), which abounds in kink sites, produces a Raman spectrum characteristic of chemisorbed rather than physisorbed pyridine with frequencies in the ring breathing region not unlike those observed in the SERS spectra of that molecule, the crucial point being that to the best of their estimates the authors calculate the surface Raman spectrum to be without enhancement. Here, therefore, is a case where chemisorption is seen without enhancement.

Most of the other observations listed earlier as challenges to the em model may be interpreted in terms concordant with the em model. Before outlining how one goes about doing this, I should stress that the importance of "active sites" in chemisorption is conceded by all. Hence in many SERS experiments carried out at room temperature—in electrochemical cells, colloids, or on catalyst particles—active sites are crucial in fixing the molecule to the surface so as to allow whatever enhancement mechanism exists to operate upon it. Even the em model with its long-range effect would produce only a very weak SERS signal if it had only the relatively few molecules that are normally found within the 100-Å layer of solution next to the electrode to operate on. It, too, benefits from the increased concentration of molecules near the bumpy electrode surface that chemisorption produces. (This, of course, is not the case in the low-temperature experiments or when highly involatile molecules such as polymers are deposited on the SERS active surface.) With many metals active sites for chemisorption are found even on single-crystal surfaces. Silver single-crystal surfaces, on the other hand, are inert to many of the molecules commonly used in SERS experiments; hence the rough surfaces are called upon to provide both the em active features and the active chemisorption sites.

Let us now reconcile some of the aforementioned chal-

lenges to the em model with it.

(1) The weakness of the SERS spectrum of water in experiments using colloids was recently convincingly shown (Blatchford, Kerker, and Wang, 1983) to be due to the inherent weakness of the Raman effect in water coupled with its high-vibrational frequency, which makes the simultaneous resonance between the surface-plasmon frequency and the incident and Raman-scattered beam hard to achieve.

(2) The apparent saturation of the SERS effect at the monolayer level in some cases is also understandable. The long-range effect is best observed with surface features of low curvature. The roughness produced by cold evaporation contains features of rather small radius of curvature for which the effect becomes considerably shorter ranged. Alternatively, it is the pores that provide the largest em enhancement locations, and these saturate quickly with adsorbate.

(3) The electromagnetic contribution to the electrode effects have by no means been exhaustively investigated. The experiments of Owen et al. (1983) may in fact demonstrate the destruction of em-active surface features just as easily as adatoms. And, in fact, a recent reflectance study (Kester, 1985) suggests strongly that this is the case. With prolonged cycling the investigators found that the plasmon absorption produced on the electrode shifts to the blue and is attenuated in much the same manner as was observed upon annealing cold-deposited films. Likewise, the dependence of the maximum in the SERS intensity as a function of electrode potential with the frequency of excitation may be due to the change in carrier concentration within the SERS-active bumps, hence its plasma frequency brought about by varying the electrode potential coupled with potential-induced desorption at negative potentials. Otto (1982) has argued that such an extrapolation would produce an effect opposite to that observed. That statement is based on the assumption that the surface-plasmon frequency shifts towards the red with decreasing carrier concentration. If, on the other hand, one assumes that the effect of changing electrode potentials is better described by the formation of an electron-rich or electron-poor layer of metal on the surface bump, then the situation becomes more complicated. Blatchford, Siiman, and Kerker (1983), for example, have considered this problem for a sphere. They show that changing the surface potential of the sphere results in a complicated SERS excitation spectrum, with maxima both red- and blue-shifted from the maximum in the zero-potential case. It seems, nevertheless, that this effect is best described in terms of some sort of modulation of the electronic levels of the electrode-adsorbate system. It almost never produces more than a threefold effect upon the SERS intensity and seems once again to be an example of the change in the surface-complex's Raman polarizability, as the metal-adsorbate bond is modified as a result of the change in electrode potential. This is not to denigrate the very interesting chemistry contained in this observation. It does not seem, however, to be as seminal as has been made out in accounting for 5 or 6 orders of

magnitude of enhancement.

(4) The nonobservation of two peaks (one corresponding to enhancement of the incident field, the other of the Raman-shifted field) in the SERS excitation spectra of molecules may also be summarily dealt with. Most calculations predict that the peak corresponding to enhancement of the Raman-shifted field dominates by a factor of 5 or so. (This fact is often missed due to the fact that a log scale is used to report these data.) That, coupled with experimental noise, makes the second maximum difficult to observe.

(5) The domination by low-frequency features of the SERS excitation profile obtained from aqueous sols together with the weakness of the SERS signal when the sample is excited with laser frequencies corresponding to the high-frequency absorption maximum is an intruiging problem for which one cannot as yet give a good quantitative account. It is nonetheless qualitatively understood in terms of the em model. To begin with, it is clear that the low-frequency absorptions are associated with surface plasmons rather than with CT absorptions. This is because one can cause this spectral feature to shift in frequency dramatically in response to increasing the degree of aggregation of the sol. This behavior is characteristic of surface-plasmon absorptions that are sensitive to the geometry and packing of the metallic particles and decidedly uncharacteristic of local effects such as CT transitions. It is also quite clear from the work of Aravind et al. (1981) and Liver et al. (1984) that molecules adsorbed in the region between metal spheres are subject to fields considerably higher than the simple sum of the fields due to the same number of isolated spheres. Electron microscopic studies show (Weitz and Oliveria, 1984) that when aggregation of aqueous sols takes place the spherical particles that form the unaggregated colloid and that may be remarkably uniform in size seem to form a random assembly of spheres which do not in general coalesce to form larger spheres or ellipsoids (Fig. 2). Hence discussing the electromagnetic behavior of such aggregates in terms of ellipsoids does not seem to be a wise approach (Kerker et al., 1984). The current calculations (Aravind et al., 1981; Liver et al., 1984; Inoue and Ohtaka, 1983) indicate, however, that the description of the fields about such closely packed spheres poses a formidable problem if it is to be taken substantially beyond the dipolar level. Nevertheless, the results suggest that the fields surrounding the metal spheres within an aggregate of colloidal particles are so much larger than those about a single sphere, that SERS from aggregates dominate the spectra far in excess of their concentration.

(6) The most robust observations arguing for an effect on top of the em effect are the experiments with CO/N_2, ethylene/ethane, and the like. These force the inescapable conclusion that there is either an enhancement mechanism some fiftyfold more powerful than the em effect acting in parallel with it (i.e., an additive effect) or that there is, at most, a fiftyfold enhancement on top of the em effect, i.e., a multiplicative effect. The second possibility is considered the more likely. The fiftyfold

enhancement may be reduced if in the case of the chemisorbed molecule (e.g., CO) the molecule is oriented on the surface with its largest polarizability components along the surface normal, while its physisorbed counterpart (e.g., N_2) is either lying down or randomly oriented. Hence a figure of around 10 is a good average non-em contribution to SERS associated with chemisorbed molecules, which of necessity may occupy only the first monolayer.

(7) Last, the observation that most SERS spectra are not simply enhanced duplicates of the ordinary Raman spectrum of the adsorbate brings up the question of the surface selection rules pertinent to SERS. This question is sufficiently important and sufficiently ignored in the literature to warrant the following section. Needless to say, the conclusion will be that one can understand the modifications in the relative intensities of different Raman bands upon adsorption in terms of the em model. It will also suggest that Raman modes belonging to different irreducible representations may have different SERS excitation profiles.

B. Surface selection rules

It is well known that the relative intensities of different modes in the infrared spectrum of a molecule will be

dramatically changed when it is placed near a metal surface. The intensity of some modes may even be almost totally suppressed. This phenomenon is usually referred to as a "surface selection rule." Similar surface selection rules are expected to operate for surface Raman spectroscopy and have been the subject of at least four papers (Greenler and Slager, 1973; Hexter and Albrecht, 1979; Richardson and Sass, 1979; Nichols and Hexter, 1981; Moskovits, 1982). Although it is popular to express the origin of these rules in terms of image charges (Pearce and Sheppard, 1976), one is less prone to error and calculating quantitative aspects of the surface intensities is easier if one adopts a different approach (Moskovits, 1982). Let us first consider the situation at a flat surface.

A molecule adsorbed near a flat metal surface and illuminated at an angle of incidence φ may be thought to be illuminated by two beams, a direct beam and one reflected at the surface. The beams superimpose coherently. Likewise, the Raman-shifted beam scattered in a direction φ' is a coherent superposition of a directly scattered beam and one first scattered towards the metal and reflected into the required direction.

Four "logical" intensity components may be defined for a Raman experiment according to the state of polarization of the incident and Raman scattered beams. These are given as follows:

$$SS \propto |\alpha_{xx}(1+r_s)(1+r_s')|^2 ,$$

$$PS \propto |\alpha_{xy}(-1+r_p)(1+r_s')\cos\varphi + \alpha_{xz}(1+r_p)(1+r_s')\sin\varphi|^2 ,$$

$$SP \propto |\alpha_{yx}(1+r_s)(1-r_p')\cos\varphi' + \alpha_{zx}(1+r_s)(1+r_p')\sin\varphi|^2 ,$$

$$PP |[\alpha_{yy}(1-r_p)\cos\varphi + \alpha_{yz}(1+r_p)\sin\varphi](1-r_p')\cos\varphi' + [\alpha_{zy}(-1+r_p)\cos\varphi + \alpha_{zz}(1+r_p)\sin\varphi](1+r_p')\sin\varphi'|^2 .$$

(15)

The quantity PS, for example, is proportional to the intensity of s-polarized Raman-scattered light excited by a p-polarized incident beam. The other three components are defined by analogy. Moreover, the Raman polarizability components in Eq. (15) are defined with z along the metal surface normal, and the primes on $r_{s,p}$ indicate that those quantities are to be evaluated at the frequency and angle (φ') of the scattered beam, while the unprimed quantities refer to the incident beam.

Different vibrational modes of a molecule belong to different irreducible representations of the point group to which it belongs. Raman-active modes are those that possess nonzero components of the Raman polarizability tensor α. Normal modes belonging to different representations will, in general, have different components of α nonvanishing. So, for example, a molecule belonging to C_{2v} poised on the surface so that its C_2 axis coincides with surface normal can in general have four types of modes:

A_1	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$
A_2	α_{xy}
B_1	α_{xz}
B_2	α_{yz}

It is clear that a given mode will be strong, weak, or ab-

sent according to one's choice of polarization, angle of incidence, and wavelength, with all three parameters determining the magnitude of the Fresnel coefficients that enter into Eq. (15). It is also clear that A_1-type modes are restricted by symmetry to contribute to the SS and PP intensity components. A_2 modes, on the other hand, contribute to the PS and SP intensity components. B_1 and B_2 modes cannot contribute to the SS component. More crucially, a given Raman intensity component will be weak or strong according to the magnitude of terms such as $r_s \pm 1$ and $r_p \pm 1$ that occur in Eq. (15). The behavior of such terms is easily surmised from the expressions for the Fresnel coefficients for light incident upon a metal surface from vacuum as a function of ε, the dielectric function of the metal:

$$r_s = \frac{\cos\varphi - (\varepsilon - \sin^2\varphi)^{1/2}}{\cos\varphi + (\varepsilon - \sin^2\varphi)^{1/2}} ,$$

$$r_p = \frac{\varepsilon\cos\varphi - (\varepsilon - \sin^2\varphi)^{1/2}}{\varepsilon\cos\varphi + (\varepsilon - \sin^2\varphi)^{1/2}} .$$

It is clear that in the limit of $|\varepsilon|$ very large $r_s \rightarrow -1$ and $r_p \rightarrow +1$. This limit is progressively attained as one goes towards the red region of the spectrum. Hence at long enough wavelengths the tangential component of the sur-

face field is nearly zero due to the superposition of the incident field with an out-of-phase reflected field, while the normal component of the incident field is reinforced by the reflected field. In that limit only the term in PP proportional to α_{zz}^2 will survive; hence A_2, B_1, and B_2 modes will no longer be observed, and only those A_1 modes will be observed that have a non-negligible α_{zz} component. It is clear, moreover, that the relative intensities of A_1 modes in a surface Raman spectrum can be significantly different from those of an ordinary Raman spectrum, since only α_{zz} contribute to the former, while all three components—α_{xx}, α_{yy}, and α_{zz}—contribute to the latter.

It is not always easy to find individual values of α_{xx}, α_{yy}, and α_{zz}. While they can be determined from the Raman of crystals, an exhaustive literature of such values does not exist. For certain molecular symmetries $\alpha_{xx} = \alpha_{yy}$ and ratios of α_{zz}/α_{xx} may then be determined from the gas-phase depolarization ratio. (Condensed-phase depolarization ratios are often very different from the gas-phase values due to local-field effects.) Even then there exists some ambiguity due to the fact that the equation relating α_{zz}/α_{xx} to the depolarization ratio is a quadratic producing two roots.

The presence of a strong electric field normal to the surface has become a familiar paradigm in surface spectroscopy, yet under the right circumstances the tangential field component may be the stronger one. This is best seen when r_s and r_p are rewritten as follows:

$$r_s = \frac{\cos\varphi/\sqrt{\varepsilon} - (1 - \sin^2\varphi/\varepsilon)^{1/2}}{\cos\varphi/\sqrt{\varepsilon} + (1 - \sin^2\varphi/\varepsilon)^{1/2}},$$

$$r_p = \frac{\cos\varphi - (1/\varepsilon - \sin^2\varphi/\varepsilon^2)^{1/2}}{\cos\varphi + (1/\varepsilon - \sin^2\varphi/\varepsilon)^{1/2}}.$$

When $1/|\varepsilon|$ becomes large, $r_s \rightarrow +1$, while $r_p \rightarrow -1$. Now the s component of the field is reinforced, while the p-component is greatly attenuated; consequently, the tangential component of the field becomes the stronger one. Maxima in $1/\varepsilon$ define the condition for bulk-plasma resonance. Hence near the plasma frequency one expects to see strong Raman scattering from Raman modes that possess nonvanishing values of α_{xx}, α_{yy}, and α_{xy}. For most metals the bulk-plasmon frequency lies in the ultraviolet. Copper, gold, and silver, on the other hand, possess bulk-plasmon frequencies in more accessible regions of the spectrum where one expects to see strong SS, SP, and PS Raman emissions. Calculations demonstrating these effects have been reported (Moskovits, 1982). They show that the surface Raman spectra of molecules, even those physisorbed on a smooth metal surface, will contain three classes of bands: those involving α_{zz} (among other components), those involving one or all of α_{xx}, α_{yy}, and α_{xy}, and those involving one or both of α_{xz} and α_{yz}. Each of the three types of bands will have its unique type of excitation spectrum; and the Raman intensity of each will deviate from the ν^4 rule, often markedly. Moreover, with sufficiently red excitation frequencies the intensities of α_{zz}-type modes could be enhanced by as much as a factor of 16 in the spectrum of the adsorbed molecule over that of the free molecule, even for a flat surface and even in the absence of chemical interactions between adsorbate and metal surface. For real systems the factor of 16 is not easily attainable, while a factor of 6–10 is. The surface selection rules which should operate in SERS if SERS were primarily an em effect may be roughly understood by considering molecules adsorbed on a colloidal metal sphere. The treatment follows in the footsteps of several references (Greenler et al., 1982; Creighton, 1983; Moskovits and Suh, 1984).

For a sphere small with respect to λ we may treat the problem as one of electrostatics. The potential about a sphere of dielectric function ε immersed in an ambient of dielectric constant ε_0 and exposed to radiation whose incident field strength (far from the sphere) is E_0, polarized in the z direction, is given by

$$V(r,\theta) = E_0(r - gR^3/r^2)\cos\theta,$$

where $g = (\varepsilon - \varepsilon_0)/(\varepsilon + 2\varepsilon_0)$ and R is the sphere radius. The radial and tangential field components are calculated in the customary fashion and the squares of the moduli of the two field components are calculated and averaged over all solid angles yielding at $r = R$ (i.e., on the surface)

$$\overline{E_t^2} \propto 2 \, | \, 1 - g \, |^2 \, ,$$

$$\overline{E_n^2} \propto \, | \, 1 + 2g \, |^2 \, .$$

One can claim simple-mindedly that the average SERS intensity will depend on the average intensities associated with the incoming and scattered fields. Since α_{zz}-type modes require a radial field to be excited and produce an induced dipole with only a radial component, then the average square radial field alone will contribute to its intensity. It will contribute twice, however: once in excitation and once again in emission. Similar arguments may be made for $\alpha_{xx}, \alpha_{yy}, \alpha_{xy}$- and α_{xz}, α_{yz}-type modes. This assumes that the molecule is adsorbed on the sphere surface in such a way that the z axis of the molecule-fixed coordinate frame lies along the metal surface normal.

The three categories of vibrational modes will therefore have SERS excitation spectra as follows:

α_{zz}-type:

$$\overline{E_n^2} \, \overline{E_n'^2} \propto \, | \, 1 + 2g \, |^2 \, | \, 1 + 2g' \, |^2 \, ,$$

α_{xz}, α_{yz}-type:

$$\tfrac{1}{2}(\overline{E_n^2} \, \overline{E_t'^2} + \overline{E_t^2} \, \overline{E_n'^2})$$

$$\propto [\, | \, 1 + 2g \, |^2 \, | \, 1 - g' \, |^2 + | \, 1 - g \, |^2 \, | \, 1 + 2g' \, |^2] \, ,$$

$\alpha_{xx}, \alpha_{yz}, \alpha_{xy}$-type:

$$\overline{E_t^2} \, \overline{E_t'^2} \propto 4 \, | \, 1 - g \, |^2 \, | \, 1 - g' \, |^2 \, ,$$

where the prime, as before, indicates properties to be calculated at the Raman-shifted frequency.

The frequency dependences of the above three functions are shown in Fig. 27 calculated for a fictitious free-
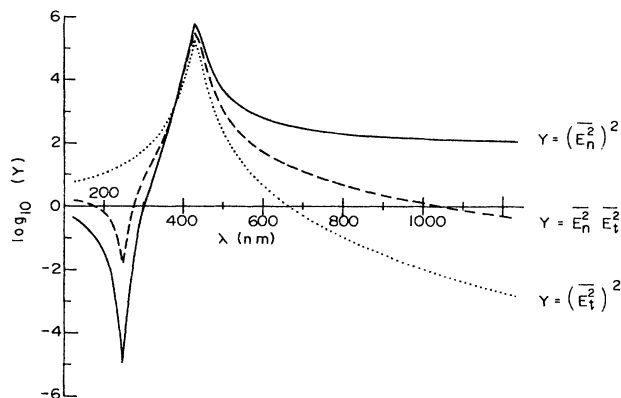
FIG. 27. Calculated excitation spectra for silverlike free-electron metal comparing the expected behavior of the three classes of Raman modes.

electron metal with the further simplification of $\varepsilon_0 = 1$ and $g = g'$. All three peak at a frequency satisfying the surface-plasmon resonance condition, $\mathrm{Re}(\varepsilon) = -2\varepsilon_0$. At and to the red of that frequency α_{zz}-type modes dominate the spectrum, because E_n^2 exceeds E_t^2. Immediately to the blue of the maximum all three types of modes are expected to be about equally enhanced, since in that region $E_n^2 \simeq E_t^2$. Since SERS experiments have been carried out precisely in the region of the spectrum just to the blue of the surface-plasma resonance maximum, it is consequently not surprising that SERS spectra have been so rich in modes that appeared to violate the surface selection rule.

As in the case of the flat surface there are excitation frequencies (Fig. 26) that will produce Raman spectra in which $\alpha_{xx}, \alpha_{yy}, \alpha_{xy}$-type modes will dominate. This is achieved when E_t^2/E_n^2 is a maximum. For a sphere E_t^2/E_n^2 can be shown to equal $2 \,|\, \varepsilon_0/\varepsilon \,|^2$, which has a maximum at the bulk-plasma frequency, precisely as in the case of the flat surface.

For ellipsoidal particles or aggregated colloids the situation is somewhat more complicated, with the location of the surface plasmon shifted towards the red. The basic physics remains the same, however. With rough metal films made either electrochemically or by cold deposition the averaging process used above becomes even more complex. One has, moreover, the presence of the bulk metal below the roughness layer to contend with; nevertheless, this model seems an adequate one to explain at least qualitatively the presence of such intense non-A-type modes in the spectrum of SERS.

One should point out emphatically that the above discussion does not address the common observation of vibrational modes in the SERS spectrum that are normally not Raman allowed (Erdheim et al., 1980; Dornhaus et al., 1980; Moskovits and DiLella, 1980). The occurrence of Raman forbidden modes has been attributed either to the lowering of the symmetry of the adsorbate

due to bonding to the surface or to the presence of a steep field gradient near the surface of the metal. The origin of the field gradient close to the metal surface depends on the microscopic details of the electron density near the surface and cannot be treated simply with electrostatics.

Although not extensively studied, the dependence of the intensities of SERS modes belonging to different representations on wavelength has indeed been found to behave in the manner outlined above, at least for adsorbate-covered colloidal metal particles (Moskovits and Suh, 1984). A detailed analysis of this permits the determination in most cases of the orientation of the molecular adsorbate with respect to the "average" surface normal, with the more symmetric molecules being more prone to such an analysis.

The excitation wavelength behavior described in this section is found even with rough films, as Lund et al. (1984) point out—although they present a different interpretation for their observation. The surface geometry of a molecule may often be surmised from a single SERS spectrum, provided that it is dominated by α_{zz} modes and provided that the relative values of α_{xx}, α_{yy}, and α_{zz} may be gauged either from depolarization ratios or intuitively. C_6F_6, for example, must clearly "lie down" on the surface in order to produce a SERS spectrum such as the one shown in Fig. 23. This is because one expects the value of the polarizability component "normal" to the ring to be larger for the C-F breathing, a_{1g} vibration (1490 cm^{-1}), than for the C-C breathing, a_{1g} mode (560 cm^{-1}). In solution the inverse is true (i.e., the trace of the Raman tensor is larger for the C-C mode than for the C-F mode). Were the molecule lying on its edge, the inverse intensity pattern would have been expected.

The unusually large depolarization ratios measured for a_1 modes in SERS spectra may also be rationalized in terms of the foregoing discussion. Using equations reported by Creighton (1983) and Moskovits and Suh (1984), one obtains the following expression for the depolarization ratio of a molecule oriented with its z axis normal to the surface and for molecular symmetries for which $\alpha_{xx} = \alpha_{yy}$:

$$\rho = (\alpha_{xx} - \eta\eta'\alpha_{zz})^2/(8\alpha_{xx}^2 + 4\eta\eta'\alpha_{xx}\alpha_{zz} + 3\eta^2\eta'^2\alpha_{zz}^2) \,,$$

where $\eta = |\,(1+2g)/(1-g)\,|$.

With this expression for ρ, the depolarization ratio varies from its gas-phase value when $\eta\eta'$ is approximately unity to 0.33 when E_n^2/E_t^2 is large. Hence depolarization ratio values that in the gas phase may be almost zero could be increased substantially for the molecule when it is adsorbed on a metal particle.

One should say in passing that the em theory is not unique in predicting depolarization ratios close to 1/3. A resonance Raman explanation for SERS, based possibly on a charge transfer band, could also produce such a value under the right circumstances (Rousseau et al., 1979).

C. The appearance of forbidden bands

Conventional wisdom suggests that normally forbidden bands arise in the spectrum of an adsorbed molecule as a result of the reduction in the symmetry of the molecule (Brundle and Morawitz, 1983). So, for example, benzene with its D_{6h} symmetry could have its effective symmetry reduced to C_{3v} if it were to adsorb on a surface site composed of three close-packed silver atoms (a threefold site). Such reduction of symmetry normally accompanies strong bond formation, which also causes significant shifts in the vibrational frequencies of the adsorbate. The absence of significant frequency shifts simultaneous with very intense, normally forbidden transitions in the SERS spectrum of benzene adsorbed on silver impelled Sass et al. (1981) to suggest that the presence of forbidden lines is due to the steep electric field gradient that exists near an illuminated metal surface. Classically, the em field accompanying light would drop to zero at the vacuum/metal interface. Feibelman (1975) has shown that the drop is more gradual at jellium surfaces, the field dropping over some 4 or 5 Å.

The dipole moment μ induced in a molecule by a field **E** is given in part by the following expression:

$$\mu = \alpha \cdot \mathbf{E} + \tfrac{1}{3} \mathbf{A} \cdot \nabla \mathbf{E} + \cdots .$$

The ratio of the second term to the first can be shown to be roughly a_M/λ in vacuum, a_M being a molecular dimension. This is a quantity of the order of 10^{-3}. Near a metal surface this ratio may be approximately a_M/a', where a' is the width of the region near the metal surface over which most of the em field is dropped. Hence the Raman selection rules of molecules adsorbed at metals (even flat metal surfaces) should be modified to allow not only vibrations belonging to irreducible representations spanning components of α but also those of **A**. These are easily determined, since **A** is isomorphous with the second-order (hyper-Raman) polarizability tensor (Cyvin et al., 1965). The result, in brief, is that all the "extra" lines in the SERS spectrum of benzene and of forty or so other, highly symmetric, molecules are predicted to be active through the **A** tensor, and no line that is forbidden through both the α and **A** tensors has been seen.

The unenhanced Raman spectrum of benzene on single-crystal (111) silver also shows this effect (Campion et al., 1983). The most intense lines in the spectrum are those belonging to representations spanning α_{zz} and A_{zzz}, the last normally Raman forbidden.

The steep electric field gradient near illuminated metal surfaces should manifest itself in other spectroscopies as well. So, for example, in absorption spectroscopy quadrupole-allowed but dipole-forbidden transitions should become intense. This is because the absorption coefficient associated with these is proportional to $|\theta : \nabla \mathbf{E}|^2$, where θ is the transition quadrupole moment. This has indeed been observed. By following the fluorescence excitation from the excited ^1A_g state of diphenyloctatetraene and diphenylhexatriene, intense spectral features due to the dipole-forbidden $^1A_g \leftarrow X^1A_g$ absorption were observed (Moskovits, 1982).

V. OTHER MODELS PROPOSED TO EXPLAIN SERS

In addition to the models mentioned in the preceding sections, several other proposals have been made to explain SERS. Most of these have not enjoyed the popularity of those already discussed. They will nevertheless be presented in brief, partly because they may suggest interesting surface experiments quite separate from SERS, and partly because some aspects of some of them may contribute to SERS.

A. Modulated reflectivity model

In discussing this and the next model, it is prudent to distinguish among three related but separate phenomena, all referred to as charge transfer. The first is the static charge redistribution that takes place when a molecule forms a chemical bond with a surface. This may involve donation of metal electrons to the molecule or vice versa. This effect will be referred to as charge redistribution. The second is the charge transfer transition that was discussed in the previous section. It is an electronic effect involving an electronically excited state of the system. The third is the movement of charge that accompanies the adsorbate vibration (i.e., the "sloshing" of charge in and out of the metal in synchronism with the molecule's motion). This involves the electronic ground state only and will be referred to as susceptibility modulation. McCall and Platzman (1980) employed the last concept to calculate the effect on the Raman cross section of modulating the susceptibility of the underlying metal by the periodic injection and withdrawal of electrons accompanying the adsorbate's vibration. The discussion is in terms of a diatomic adsorbed on a flat jellium surface. Chemical binding to the surface is an explicit feature of this model; consequently it is a "chemical" contribution to SERS.

Writing the Raman cross section as

$$d\sigma/d\Omega = \tfrac{1}{3}k^4 \left| \frac{\partial \alpha}{\partial r} \delta r \right|^2 ,$$

one can estimate the change in polarizability of an elementary volume δv of metal due to charge injection and withdrawal to be

$$\delta v \frac{\partial \chi}{\partial q} \cdot \frac{\partial q}{\partial r} \delta r ,$$

where χ is the metal's susceptibility, q the charge injection into the metal, and r a normal displacement of the molecule. Hence

$$d\sigma/d\Omega = \tfrac{1}{3}k^4 \left| \delta v \frac{\partial \chi}{\partial q} \cdot \frac{\partial q}{\partial r} \delta r \right|^2 . \tag{16}$$

In Eq. (16) δr is estimated at 0.1 Å from the RMS value of the atomic displacement of an adsorbed atom bound by a harmonic potential. $\partial q/\partial r$ is assumed to be $0.2e/$Å. In estimating the quantity $d\chi/dq$, one assumes a Drude metal—i.e., $\varepsilon_M = 1 - \omega_p^2/\omega^2$, while $\chi = (\varepsilon_M - 1)4\pi$ and $\omega_p^2 = 4\pi ne^2/m$. If one writes $n = N/\delta v$, where N is the total charge in volume δv, it is clear that $\partial \chi/\partial q = \partial \chi/\partial N = e^2/m\omega^2\delta v$. Substituting into Eq. (16) and using the expression $ck = \omega$, one obtains

$$d\sigma/d\Omega = \frac{1}{3}\left[\frac{e}{mc^2}\right]^2 (\partial q/\partial r)^2(\delta r)^2$$

$$= 10^{-29} \text{ cm}^2 .$$

Since a strongly chemisorbed diatomic was assumed in the calculation, the authors (McCall and Platzman, 1980) speculated that the model may be applicable to CN^- chemisorbed on Ag. Free CN^- is isoelectronic with N_2, for which the gas-phase Raman cross section is approximately 5×10^{-31} cm^2. Hence the susceptibility modulation produces roughly an order-of-magnitude enhancement, a not unreasonable figure for the chemical effect.

B. Inelastic Mie scattering

A variant of this effect was presented by Abe et al. (1981) and suggested qualitatively by Creighton et al. (1979). The salient difference between this and the model of McCall and Platzman is that charge injection and withdrawal by adsorbate on a small colloidal metal sphere is considered. The result is to modulate the polarizability of the sphere by shifting its surface-plasma resonance synchronously with the adsorbate vibration. The effect is to create sum and difference side bands on the Mie-scattered light corresponding to the Raman effect. In its original form (Abe et al., 1981) the charge injection and withdrawal were considered to affect the electron concentration in the whole colloidal sphere. This was criticized (Metiu, 1983) as not taking screening into effect. What follows is a somewhat modified model in which the susceptibility modulation is restricted to a spherical shell of width d at the surface of the metal.

Consider a spherical metal colloidal particle of radius R covered with a monolayer of adsorbate. Assume that coupling between the adsorbate molecules causes them to vibrate in phase. Although this is a well-known phenomenon in surface infrared spectroscopy (Hammaker et al., 1965; Shigeishi and King, 1976; Moskovits and Hulse, 1978), it is clearly one of the criticizable features of this model. SERS evidence for coupling among adsorbate is provided by Garroff and Sandroff (1983), who find a shift in the C-S stretching frequency of 1-hexadecane thiol adsorbed on a silver-island film with surface coverage. As in analogous surface ir experiments, such a shift signals the presence of vibrational coupling among the adsorbate molecules. As before,

$$d\sigma/d\Omega = \frac{1}{3}k^4\left|\frac{\partial \alpha}{\partial Q}\delta Q\right|^2, \tag{17}$$

where Q is a normal coordinate of the coupled adsorbate layer.

One assumes that at an arbitrary point along Q the colloidal particle may be described by a metal sphere of dielectric function $\varepsilon_3(\omega)$ coated with a metal shell of width d and dielectric function $\varepsilon_2(\omega)$, which differs from $\varepsilon_3(\omega)$ in that its value of ω_p', the plasma frequency, is increased or reduced according to the quantity of charge injected or withdrawn into the shell at that value of Q. At $Q = 0$, $\varepsilon_3 = \varepsilon_2$ and the colloidal particle reverts to being a simple metal sphere.

The polarizability of a coated sphere is given by

$$\alpha = R^3\frac{(\varepsilon_2-\varepsilon_1)(\varepsilon_3+2\varepsilon_2)+f^3(2\varepsilon_2+\varepsilon_1)(\varepsilon_3-\varepsilon_2)}{(\varepsilon_2+2\varepsilon_1)(\varepsilon_3+2\varepsilon_2)+f^3(2\varepsilon_2-2\varepsilon_1)(\varepsilon_3-\varepsilon_2)}, \tag{18}$$

where $f = (R-d)/R$.

The desired quantity is

$$\frac{\partial \alpha}{\partial Q}\bigg|_{Q=0} = \frac{\partial \alpha}{\partial \varepsilon_2}\frac{\partial \varepsilon_2}{\partial \omega_p^2}\frac{\partial \omega_p^2}{\partial q}\frac{\partial q}{\partial Q}, \tag{19}$$

where $\partial \alpha/\partial \varepsilon_2$ is calculated at $\varepsilon_2 = \varepsilon_3$.

From Eq. (18) $(\partial \alpha/\partial \varepsilon_2)|_{\varepsilon_2=\varepsilon_3} = 3R^3(1-f^3)\varepsilon_1/(\varepsilon_3+2\varepsilon_1)^2$. When one writes $\varepsilon_2 = \varepsilon_b - \omega_p^2/(\omega^2+i\omega/\tau)$, where $\varepsilon_b - 1$ is the interband contribution to ε_2, the quantity $\partial \varepsilon_2/\partial \omega_p^2 = -(\omega^2+i\omega/\tau)$, while $\partial \omega_p^2/\partial q = 4\pi e^2/mV$, where V is the volume of the spherical shell, and $V = 4\pi R^2 d$ if $d \ll R$. Since we assume vibrational synchronism among the adsorbate molecules q, the total charge injected, is the sum of charge contributed by each adsorbate. Hence $q = Nq_1$, where N is the total number of adsorbate molecules on the surface and q_1 is the charge that each contributes.

Gathering terms, one has

$$\frac{\partial \alpha}{\partial Q} = \left[\frac{9\varepsilon_1}{(\varepsilon_3+2\varepsilon_1)^2}\right]\left[\frac{-1}{\omega^2+i\omega/\tau}\right]\frac{e^2}{m}N(\partial q_1/\partial Q), \tag{20}$$

where $1-f^3$ was assumed to be $\simeq 3d/R$. The first two terms in Eq. (20) must be evaluated at $\omega = \omega_0 - \omega_v$, where ω_0 and ω_v are the incident laser frequency and frequency of vibration.

Substituting (20) into (17), one can estimate the Raman cross section. A 200-Å-diam silver colloidal particle is assumed for which $N \sim 10^4$ molecules, assuming roughly one surface site for each surface-silver atom.

In order to compare our results with McCall and Platzman, we assume with them that $\delta Q \sim 0.1$ Å, $\partial q_1/\partial Q = 0.2e/$Å, $e^2/m\omega^2 = 1.8 \times 10^{-23}$ cm^3 ($i\omega/\tau$ was neglected with respect to ω^2). We also assume that we are at surface-plasma resonance; hence $\varepsilon_3 + 2\varepsilon_1 = \text{Im}(\varepsilon_3) = 0.28$ (Johnson and Christy, 1972) when ε_1 is taken to be unity. With these parameters and $k = 20000$ cm^{-1}, one obtains

$$d\sigma/d\Omega = 9 \times 10^{-21} \text{ cm}^2 .$$

This is 8 orders of magnitude larger than for the non-resonant case considered by McCall and Platzman. Four orders of magnitude of the difference are contributed by the first term in Eq. (20), i.e., by assuming surface-plasma resonance, and 4 more orders of magnitude result from the fact that by assuming coherent vibrational motion among the adsorbate the Raman signal scales as N^2 [reminiscent of super-radiance (Dicke, 1954)].

For uncoupled adsorbate molecules the quantity $\partial q/\partial Q$ becomes proportional to $\sqrt{N}$ and the Raman intensity scales as N. This is the expected state of affairs at very low coverage. Hence the coverage dependence of SERS is not expected to go as θ^2 (where θ is the coverage), since at low coverage there will be only weak coupling among adsorbate molecules; therefore on the average, $\sqrt{N}$ of these will be moving in more or less the same direction at any given moment. At low coverage, the SERS intensity is therefore expected to be proportional to θ switching to θ^2 near full coverage, and eventually saturating at $\theta = 1$.

Since inelastic Mie scattering is due to the metallic particle, while the em model assumes scattering by the adsorbate, the two mechanisms are additive rather than multiplicative. Hence for one to see it at all it would have to be stronger than the em effect. And as with the other chemical effects this mechanism is only pertinent to chemisorbed molecules.

It is difficult to say for certain whether the SERS spectrum of chemisorbed molecules is in fact due to inelastic Mie scattering. Certainly many of the observations attributed to the chemical effect are consistent with it. These include the different degrees of enhancement associated with different bands in a SERS spectrum of a molecule. Within the framework of the model this simply reflects the different charge-donating ability of the molecule in different vibrational modes. Moreover, because of the second term of the right-hand side of Eq. (20), the calculated excitation profile associated with inelastic Mie scattering follows the surface-plasmon resonance of the metal particle in much the same manner as in the em model; and the degree of enhancement at the maximum is proportional to $[\text{Im}(\varepsilon)]^{-4}$, suggesting that the group Ia and Ib metals should be the best enhancers.

The quadratic dependence of the Raman cross section on N may also provide a rationale for the much greater SERS ability of aggregated colloids. This suggests, however, that when two colloidal particles aggregate their coating of adsorbate vibrates coherently. Since some aggregates contain as many as five hundred particles, the effect could be spectacular. At the same time the imagination is taxed by the thought of all the molecules adsorbed on so large a structure vibrating coherently. In addition it is known, based on the fact that a grating effect was not observed with the SERS signal, that the Raman scattering from individual ellipsoids in the previously discussed lithographically produced sample (Liao et al., 1981) is emitted incoherently. This contrasts with second-harmonic generation, which did produce a grating effect. That observation, while reinforcing doubt, does not preclude coherent scattering in aggregated colloidal particles

in which individual particles are touching and presumably conducting. In the lithographic sample the particles are spaced a thousand Å or so apart. Despite these positive aspects, this model has not generally met with a favorable response. Naturally, this model is not intended as a replacement for the em model but rather as a mechanism operating alongside it.

A quantum-mechanical model having certain elements in common with inelastic Mie scattering has recently been proposed by Lippitsch (1984) and named "ground-state charge transfer." Briefly, the enhancement is attributed to vibronic coupling of the molecular ground state to metal states with molecular vibrations modulating, as before, the amount of ground-state charge transfer. While the author has managed to account qualitatively for a large number of aspects of SERS with this model and has enunciated a system of SERS selection rules based on it, the calculation of excitation spectra remains a difficult task.

C. Surface polarizability modulation

An elegant model related to the previous two is due to Jah et al. (1980), who have developed it as one of two contributions to SERS from molecules adsorbed on sinusoidal metal gratings. The authors calculate the surface charge density from the Poisson equation, in which the field had previously been calculated for the grating by perturbation theory (Jah et al., 1982). The expression for the surface charge density so obtained is a δ function localized at the surface, resulting from the fact that the authors assumed a step discontinuity in ε at the surface. In order to make the model more realistic, the authors replace the δ function by an exponentially decaying function of distance. The decay coefficient is assumed to include explicit contributions from the molecules taken to be a collection of partial atomic charges. In the presence of molecular vibrations the atomic positions are expanded to first order about their equilibrium positions, yielding expressions for the decay coefficients linear in atomic displacement. The zz-component of the surface polarizability β_{zz} is then calculated, and the cross section of the Stokes-scattered light that is proportional to $|\partial\beta_{zz}/\partial R_i|^2$ is calculated using the conventional expression.

The authors show that enhancements exceeding 10^8 are possible with proper choice of parameters, a most critical one being the distance between the oscillating charge and the image plane.

D. Parametric excitation model

Li (1982) proposed another mechanism to explain SERS, which, briefly, regards SERS to be due to the instability of the Raman mode of the molecular dipole caused by the coherent superposition of the laser field and the surface field induced by the light scattered by the molecule. Since the scattered field further induces motion of the dipole, an unstable feedback is established, with the

SERS signal growing with time. Li calculates that the time taken to achieve 10^6 enhancement may range from a millisecond to two hours depending on the separation of the admolecule (taken to be CN^-) from the surface. The mechanism also relies on the nonlinearity of the dipole's response to the field. SERS should then be a nonlinear phenomenon. The predicted growth has not been seen even for oscillators somewhat removed from the surface. Neither has a quadratic dependence of the SERS signal on the laser field. Thus although thought provoking, this mechanism is probably not a contributor to SERS.

E. Super-radiance model

Another interesting proposal is due to Hu and Huang (1982), who consider the consequence of having several of the adsorbed molecules emitting in phase. As with super-radiance (Dicke, 1954), molecules contained within a region of space small with respect to the wavelength are considered a single quantum-mechanical unit. Under those circumstances the authors conclude that if the final level involved in the Raman process is populated either by absorption or by the Raman process itself, then the scattering cross section is increased roughly by a factor equal to the number of molecules in that state (i.e., the Raman intensity would be proportional to the square of the number of molecules in the final level). The model suffers from several drawbacks. First, the mechanism for cooperative emission is not specified; second, it is not obvious why adsorption onto certain metals such as silver should produce a strong SERS signal, while with other metals only a weak effect is detected, etc.

F. Microensemble model

Another interesting model is due to Robinson (1980,1981), who considers the molecule and its surroundings including the metal a microensemble. Zero-order product states such as ψ(molec)ψ(surface), including excited electronic states, couple through dipole-dipole interactions. These mixed states are inserted into the resonance Raman scattering equation which is obtained from second-order perturbation theory for the substrate, and the part of this scattering which is derived from the small molecular component of the mixed eigenstates is identified as the SERS effect. Although this model is suggestive of the charge transfer model, it has the added interesting feature that it attempts to account for the role of roughness in SERS. Roughening is assumed to break up the surface into microdomains *in* which the electrons move freely but *between* which motion is curtailed. It is the exchange-dipole interactions between the admolecule and one of these metallic domains that give rise to SERS, in the view of this model. If the microdomain is too large and the conductivity of the metal is high, then a large dipole moment cannot be induced in the vicinity of the metal; however, the probability of interaction with the radiation field is higher for a large metallic microdomain. For

a smaller microdomain the dipole moment becomes larger but the coupling to the radiation field is reduced. There must therefore be an optimum size for the roughness. This optimum size must clearly be smaller than the electronic mean free path of the bulk metal, since this model counts greatly for its efficiency upon a serious reduction of the effective conductivity of the metal with decreasing size of roughness. For silver the electronic mean free path is approximately 300 Å, and indeed the most intense SERS is obtained with systems in which the metal feature size is in the neighborhood of 100—200 Å.

The model has not been developed sufficiently to allow a thorough appraisal. SERS excitation spectra are calculated (Robinson, 1981) with "reasonable" parameters rather than ones based on the metal involved. Moreover, while the model is not expressed in terms of the excitation of surface plasmons, it is not clear that when considering a small particle, its surface-plasmon excitation is not one of the electronic states of the metal that enter into the sum in the expression for the Raman cross section.

VI. CONCLUSIONS

Before attempting to draw conclusions about SERS one must define precisely what one means by surface-enhanced Raman scattering. The notoriety that the effect generated has prompted individuals to include a large class of phenomena under that sobriquet that includes almost any detectable Raman signals from adsorbates interacting with a wide variety of surfaces. So, in addition to SERS from molecules on metals, "SERS" from molecules on NiO, TiO_2 (Yamada and Yamamoto, 1983), and polyacetylene (Batchelder et al., 1981) have been reported. It appears doubtful that all systems benefit from the same physical mechanism in producing detectable Raman emissions. I will therefore adopt the following operational definition for SERS: it is the effect that caused all the fuss when first reported by Van Duyne and Creighton. Defined in that way, SERS derives its enhancement, I conclude, almost entirely from molecular coupling to electromagnetic resonances of small, coupled metal particles. To be sure, the electromagnetic effect operates on the system that actually exists at the surface and that may be modified in interesting and significant ways through bond formation with surface adsorption sites. This may alter, among other things, the Raman polarizability of the system. Nevertheless, it seems more correct to think of the chemical effects as changing the nature and identity of the adsorbate while the em effect actually produces the enhancement. One of the most persuasive witnesses to this statement does not come from SERS at all but from enhanced nonlinear effects, such as second-harmonic generation, which are almost impossible to account for in terms other than the em model. It is clear that the frequency shifts and changes in relative intensity of the bands in a SERS spectrum brought about by perturbations such as increasing coverage, varying the electrode

potential, or adsorbing competitive adsorbates suggest that SERS is potentially a sensitive tool (albeit one limited to a restricted set of systems) for studying surface chemical properties such as the geometry and orientation of the adsorbate on the surface and changes in orientation brought about by external variables, the nature of the surface bonding site, the nature of the chemisorptive bond, and even surface chemical reactions. Ironically, the proponents of the chemical-enhancement mechanism have discouraged to some extent detailed investigation of the surface chemistry in SERS-active systems by focusing on the putative role of chemistry in the enhancement mechanism. It has become difficult to discuss surface chemistry, or the nature of chemisorption sites, consequently, without being drawn into the quagmire of the enhancement controversy. Nevertheless, SERS has been and is currently being applied to a large number of fascinating surface chemical problems, among them the study of catalytic processes. Chang and co-workers (von Raben et al., 1983; Dorain et al., 1981) showed that oxygen-covered silver powders can convert SO_2 to surface SO_2^{2-} that can be further oxidized to SO_4^{2-} when heated in oxygen. Likewise, NO and NO_2/N_2O_4 gave rise to NO_2^- and NO_3^- on oxygenated silver powders (von Raben et al., 1983; Dorain et al., 1981). The products in both cases were detected by SERS. Wood and Zwemer (1981) and Wood, Klein, and Zwemer (1981b) attempted to see intermediates in the catalytic oxidation of ethylene by silver using SERS. Sandroff and Herschbach (1982) have applied SERS to the study of sulfur compounds adsorbed on silver colloid as models for surface processes involved in lubrication. Sandroff et al. (1984) also used SERS to study the effect of high pressure on the spectrum of pyridine adsorbed on gold colloid and explained the observed frequency shift in terms of pressure-induced changes in the force constants resulting from the contraction of bond lengths in pyridine with increasing hydrostatic pressure. Again, Sandroff et al. (1983) and Moskovits and Suh (1985) applied SERS to the determination of the conformations of long chain molecules adsorbed on colloidal particle surfaces.

One of the richest applications of SERS has been to the study of electrode processes. This has been extensively reviewed (Chang and Laube, 1984). Recent reports indicate that these studies can be extended to semiconductor surfaces (Van Duyne and Haushalter, 1983).

SERS is also being used to follow the thermal decomposition of a number of halocarbons on silver. Clear evidence of intermediates is visible (Moskovits and DiLella, 1982b). Recently the decomposition of fluorobenzene to fluoroacetylene (DiLella, 1985) has been reported, as has the decomposition of ammonia to NH_2 (Schulze et al., 1984). In both cases silver was the substrate and SERS was the spectroscopic tool used to detect the reagents and products.

A two-dimensional phase transition was reported (Suh et al., 1983) on the basis of a SERS study. In it, para-aminobenzoic acid was seen to interconvert between two forms on the surface of silver colloid. Creighton (1983)

and Moskovits and Suh (1984) have used data derived from SERS spectra to determine the orientation of several molecules on colloidal silver surfaces.

Some of the most exciting reports do not involve SERS at all but are derivative of SERS studies; for example, Weitz and Oliveria (1984) studied the geometry of aggregated aqueous colloidal systems and concluded that they are fractal objects. The mass of the aggregate was found to scale as L^D, where L is the size and D the fractal dimension. Since D was found to be near 1.75, they were able to conclude that the irreversible aggregation process proceeded as a homogeneous glutination of clusters of all sizes rather than as a diffusional process of single particles onto a seed. The foregoing is clearly a highly curtailed list.

It is clear, as I write this, that the noisy and giddy early days of SERS are over. It is no longer the habit to have at least one session on SERS at every APS, ACS, and AVS meeting. But even as the old guard is filing out of the field, there is indication that some new souls are entering it, seeking possible applications of the effect in such disciplines as biology and analytical chemistry. In their hands, perhaps, SERS will be transformed into something new once again.

ACKNOWLEDGMENTS

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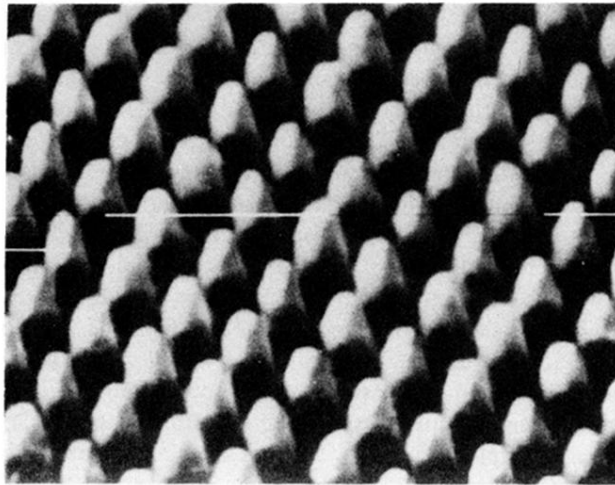
FIG. 1. Electron micrograph of silver particle array produced by evaporating silver onto SiO_2 posts produced by microlithography. The bar is 1.0 μm in length (Liao *et al.*, 1981).
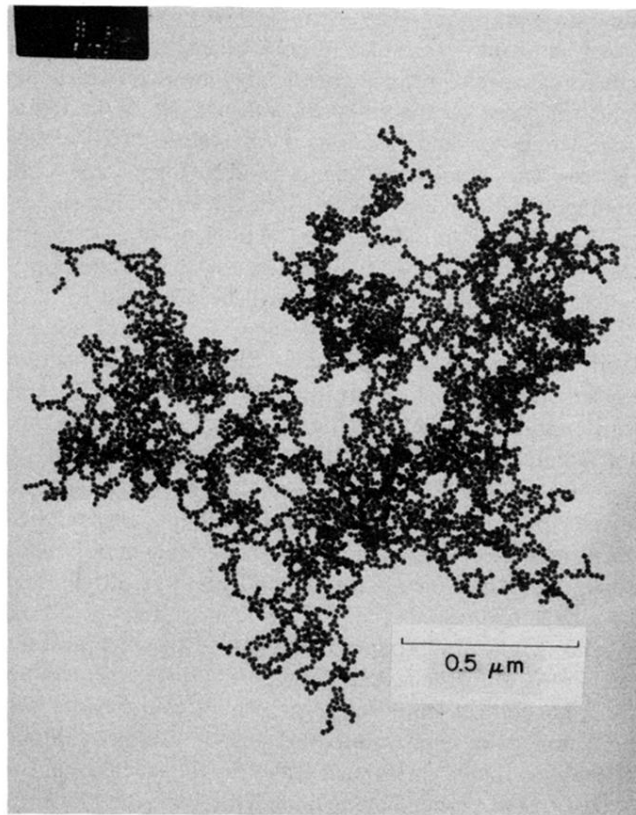
FIG. 2. TEM image of gold colloid aggregate containing 4739 gold particles (Weitz and Oliveria, 1984).