Surface-Enhanced Raman Spectroscopy: a Brief Perspective

Martin Moskovits

Department of Chemistry and the California Nanosystems Institute,
University of California, Santa Barbara, CA 93105
mmoskovits@ltsc.ucsb.edu

1 Introduction

Surface-enhanced Raman spectroscopy (SERS) was first observed by *Fleischman* et al. in 1974 [1], and discovered by *Jeanmarie* and *Van Duyne* [2] and *Albrecht* and *Creighton* [3] in 1977. I make the distinction between observation and discovery because, when first observed for pyridine adsorbed on an electrochemically roughened silver electrode [1], the unusual intensity of the Raman signals was attributed to the increased surface area of the rough substrate. It was Van Duyne and Creighton who pointed out that the intensification of the effective Raman cross section was far in excess of the increased number of molecules interrogated as a result of the surface's roughness factor. In 1978 I had the good fortune of proposing that the huge increase in Raman cross section was a result of the excitation of surface plasmons [4]. That insight immediately led to a number of predictions such as the expectation that SERS should be observable in metal colloids and the hierarchy of intensification that should be observed, all else being equal, with silver and the alkali metals providing the most intense SERS signals followed by gold and copper in that order, then other good conductors such as aluminum, indium and platinum, and finally the transition metals and the other more poorly conducting metals. Of course one had to factor into all of this such important parameters as the excitation wavelength, the polarization of the exciting and scattered radiation with respect to symmetry axes of the nanostructures illuminated, the precise structural features of the SERS-active system and so on. Within a few years of the discovery of SERS, essentially all of these predictions were shown to be true. The very close qualitative agreement between the SERS enhancement and the intensity and quality factor of the surface plasmon is a baseline feature of essentially everything that has been learned about SERS over the last 30 years, a fact that needs to be borne in mind as new theories of SERS are proposed.

Work in SERS reached a plateau approximately 10 years ago and became invigorated once again by the reports by *Kneipp* and coworkers [5,6,7,8,9,10] and *Nie* and coworkers [11, 12, 13, 14, 15, 16] who simultaneously and independently reported that intense enough SERS emissions could be recorded under favorable circumstances to detect single molecules, that together with the quest for high-sensitivity molecular- and especially biomolecular-sensing

platforms, has returned SERS as a research field to the front burner so that there are arguably now more people working in SERS than ever before. An indirect barometer of its recent popularity can be gauged from the fact that the review article I wrote in 1985 [17] has had more citations in 2005 than in any previous year. Moreover, two active fields can arguably be said to have evolved largely out of SERS: near-field optics [18] and plasmonics [19]. And all of this has benefited from the increased availability of high-performance computing that has allowed large-scale and high-level computations to be carried out on large nanoparticle aggregates, rough-surface models and other nanostructured systems pertinent to SERS.

2 The Electromagnetic Theory of SERS

The simplest model that translates the excitation of surface plasmons into a SERS mechanism is the so-called electromagnetic model simultaneously enunciated in 1980 by *Gersten* [20, 21], *Gersten* and *Nitzan* [22, 23] and *McCall* et al. [24, 25] and expanded upon by *Kerker* et al. [26, 27, 28, 29, 30] who consider the electromagnetic fields surrounding a small illuminated metal particle. Although a survey of the SERS literature leads to the conclusion that SERS from a single, isolated metal nanoparticle has likely never been credibly reported, a preliminary analysis of the fields surrounding a small isolated metal nanoparticle is useful in defining some of the basic criteria one needs to fulfill in order to see intense SERS.

A small, isolated, illuminated metal sphere will sustain oscillating surface plasmon multipoles of various order induced by the time-varying electric-field vector of the light. The surface plasmons are collective oscillations of the conduction electrons against the background of ionic metal cores [17]. In addition, light can induce a host of other excitations in the metal particle including interband transitions. For a particle much smaller than the wavelength of the exciting light, all but the dipolar plasmon can be ignored. Systems with free or almost free electrons will sustain such excitations; and, the freer the electrons the sharper and the more intense the dipolar plasmon resonance will be. When the exciting laser light is resonant with the dipolar plasmon the metal particle will radiate light characteristic of dipolar radiation [31]. This radiation is a coherent process with the exciting field and is characterized by a spatial distribution of field magnitudes (that reaches steady state a few femtoseconds after the light is turned on) in which the light intensity from certain portions of space surrounding the particle is depleted, while the intensity at certain portions near the metal particle is enhanced. Although this has been known for a very long time, the recent images of this process produced by *Käll* and coworkers [32, 33] illustrate this process vividly.

Let us call the field enhancement averaged over the surface of the particle g. The average magnitude of the field radiated by the metal particle E_s will be: $E_\mathrm{s} = gE_0$, where E_0 is the magnitude of the incident field. One should

keep in mind that E_s is the average local *near field* at the particle surface. The average molecule adsorbed at the surface of the metal particle will therefore be excited by a field whose magnitude is E_s, and the Raman-scattered light produced by the molecule will have a field strength $E_R \propto \alpha_R E_s \propto \alpha_R g E_0$, where α_R is the appropriate combination of components of the Raman tensor. (The arguments in this section are meant to give a clear pictorial idea of the SERS enhancement process. To carry out the problem correctly one must carry out the tensor product properly, taking into account the vectorial nature of the fields involved that includes both their wave and polarization vectors.)

The Raman-scattered fields can be further enhanced by the metal particle in exactly the same manner as the incident field was. That is, the metal particle can scatter light at the *Raman-shifted* wavelength enhanced by a factor g'. (The prime is used to indicate the fact that the field enhancement at the Raman-shifted wavelength will, in general, differ from its value at the incident wavelength.) The amplitude of the SERS-scattered field will therefore be given by $E_{\text{SERS}} \propto \alpha_R g g' E_0$, and the average SERS intensity will be proportional to the square modulus of E_{SERS}. That is, $I_{\text{SERS}} \propto |\alpha_R|^2 |gg'|^2 I_0$, where I_{SERS} and I_0 are the "intensities" of the SERS-scattered and incident fields, respectively. For low-frequency bands when $g \cong g'$ the SERS intensity will be enhanced by a factor proportional to the fourth power of the enhancement of the local incident near field, i.e., $|E_L|^4 = |g|^4$. (For higher-frequency Raman modes the SERS intensity will be a more complicated function of the plasmon resonant properties of the metal particle according to the precise wavelengths at which the incident and Raman-scattered light fall. Likewise, it has been shown by *Stockman* and others [34, 35, 36, 37] that for fractal aggregates the correct sum over the cluster leads to a $|E_L|^3$ rather than the fourth power of the local field.) It is helpful to define the "SERS enhancement" G as the ratio of the Raman-scattered intensity in the presence of the metal particle to its value in the absence of the metal particle $G = \left| \frac{\alpha_R}{\alpha_{Ro}} \right| |gg'|^2$ where α_{Ro} is the Raman polarizability of the isolated molecule.

Three important points must be noted. 1. The major contribution to SERS is scattering *by the metal particle* rather than by the molecule whose Raman spectrum is, however, reflected in the SERS spectrum of the light scattered by the metal. 2. Although the SERS intensity (for low-frequency Raman modes) varies as the fourth power of the local field, the effect is a linear optical effect, which depends on the first power of I_0. (Of course, nonlinear optical phenomena are also enhanced [38]. But these will not be discussed here.) However, the fourth-power dependence on g is key to the inordinate enhancements SERS provides. For silver at $400 \, \text{nm}$, for example, g is only ~ 30, yet that implies a Raman enhancement $G \sim 8 \times 10^5$ assuming the Raman polarizability to be unchanged from that of the isolated molecule. (In fact the field enhancement by an isolated particles is likely one or more orders of magnitude lower than that on account of physical aspects that are often omitted in carrying out this calculation, such as the fact that retarded

fields must be used and nonlocal dielectric function values for the metal [17].)
3. Although one speaks loosely of α_R as the Raman polarizability "of the molecule", in fact it is the Raman polarizability of the scatterer that includes the molecule but, when the molecule is adsorbed on the metal particle's surface, will include contributions from the metal and may, as a result, be greatly altered both in its magnitude, symmetry and resonant properties from the Raman polarizability of the isolated molecule. This will be particularly important in systems where metal-to-molecule or molecule-to-metal charge transfer occurs, altering dramatically the resonances of the system thereby contributing to so-called chemical enhancement. Experience shows that such resonances often occur. 4. SERS excitation is a near-field phenomenon. The near field, especially near a metal surface, will have spatial components that decay more rapidly with distance than the spatial variation in the far field (where the spatial "structure" in the field is of the order of the wavelength). Hence, one expects to see (and indeed does see) effects such as relaxation of dipole-selection rules [39, 40, 41], which causes normally forbidden vibrational modes to occur in the SERS spectrum and dipole-forbidden fluorescences to be observed [42, 43, 44]. This point needs to be taken into account also in the description of the field response of the particles themselves, especially when (as will be discussed below) one deals with electromagnetic and other physical phenomena such as quantum-mechanical tunneling taking place in interparticle gaps and interstices that are much smaller than the wavelength, in which the spatial variation of the electromagnetic field could be very large over a rather small distance.

The foregoing contains all of the seminal characteristics of SERS. It indicates that essentially all systems possessing free carriers can show SERS; hence, the observation of SERS from "unusual" systems such as Si or transition metals is not unexpected (if one excites with light of the appropriate wavelength). The intensity of such emissions will depend, to zeroth order, on the magnitude of g, which will be much larger that unity for metals such as silver, gold and the alkalis, larger, but not much larger than unity for other good conductors (Al, In, Pt) and only a little larger than unity for most other metals (in all cases we assume optimal choice of excitation wavelength). Improvements in the throughput of Raman spectrometers and in multiplex spectroscopic detection, have made SERS measurements from most metals, indeed, all Raman measurements, enhanced or otherwise, far more accessible nowadays.

SERS is one of the few phenomena that can truly be described as nanoscience. This is because for it to occur, the metal particles or metal features responsible for its operation must be small with respect to the wavelength of the exciting light. This normally means that the SERS-active systems must ideally possess structure in the 5 nm to 100 nm range. Likewise, the dimensions of the active structure cannot be much smaller than some lower bound, which is normally larger than the average molecule. The upper dimensional bound of the SERS-active system is determined by wavelength.

As features of the order of the wavelength or larger are used, the optical fields no longer excite dipolar plasmons almost exclusively; instead progressively higher-order multipoles are excited. Unlike the dipole, these modes are nonradiative, hence they are not efficient in exciting Raman (or other dipole-driven excitations). Accordingly, the SERS efficiency drops until, for large enough particles, so much of the exciting radiation is locked up in higher-order plasmon multipoles that SERS is all but extinguished.

At the other end of the dimensional scale as the nanostructure responsible for SERS becomes too small, the effective conductivity of the metal nanoparticles diminishes as a result of electronic scattering processes at the particle's surface [45, 46, 47]. As a result, the quality factor of the dipolar plasmon resonance is vitiated and the reradiated field strength reduced. When the metal particle becomes small enough, the pseudo bulk description implicit in the definition of the surface plasmon no longer applies. Instead, one needs to treat the metal particle as a fully quantum object whose electronic properties show so-called quantum-size effects. Reducing the size of the metal particle even further so that the particle is composed of only a few metal atoms, one passes into a regime in which a molecular description expresses the particles' properties best.

Some of these points are illustrated using the following rudimentary model. The polarizability of a small metal sphere with dielectric function $\varepsilon(\lambda)$ and radius R, surrounded by vacuum is given by:

$$\alpha = R^3 \frac{\varepsilon - 1}{\varepsilon + 2} \, . \tag{1}$$

Combining this expression with the expression for the dielectric function of a Drude metal slightly modified for interband transitions we obtain:

$$\varepsilon = \varepsilon_{\mathrm{b}} + 1 - \frac{\omega_{\mathrm{p}}^2}{\omega^2 + \mathrm{i}\omega\gamma} \, , \tag{2}$$

in which ε_{b} is the (generally wavelength-dependent) contribution of interband transitions to the dielectric function, ω_{p} is the metal's plasmon resonance whose square is proportional to the electron density in the metal and γ is the electronic-scattering rate that is inversely proportional to the electronic mean-free-path and therefore also inversely proportional to the metal's DC conductivity. Substituting (2) into (1) yields the expression

$$\alpha = \frac{R^3(\varepsilon_{\mathrm{b}}\omega^2 - \omega_{\mathrm{p}}^2) + \mathrm{i}\omega\gamma\varepsilon_{\mathrm{b}}}{[(\varepsilon_{\mathrm{b}} + 3)\omega^2 - \omega_{\mathrm{p}}^2] + \mathrm{i}\omega\gamma(\varepsilon_{\mathrm{b}} + 3)} \, . \tag{3}$$

The real and imaginary parts of the expression for α given in (3) have a pole when the frequency ω is equal to $\omega_{\mathrm{R}} = \frac{\omega_{\mathrm{p}}}{\sqrt{\varepsilon_{\mathrm{b}}+3}}$. The width of that resonance is given by $\gamma(\varepsilon_{\mathrm{b}} + 3)$.

Hence, when γ is large either because of the inherent poor conductivity of the metal or due to the fact that the metal nanofeatures are so small
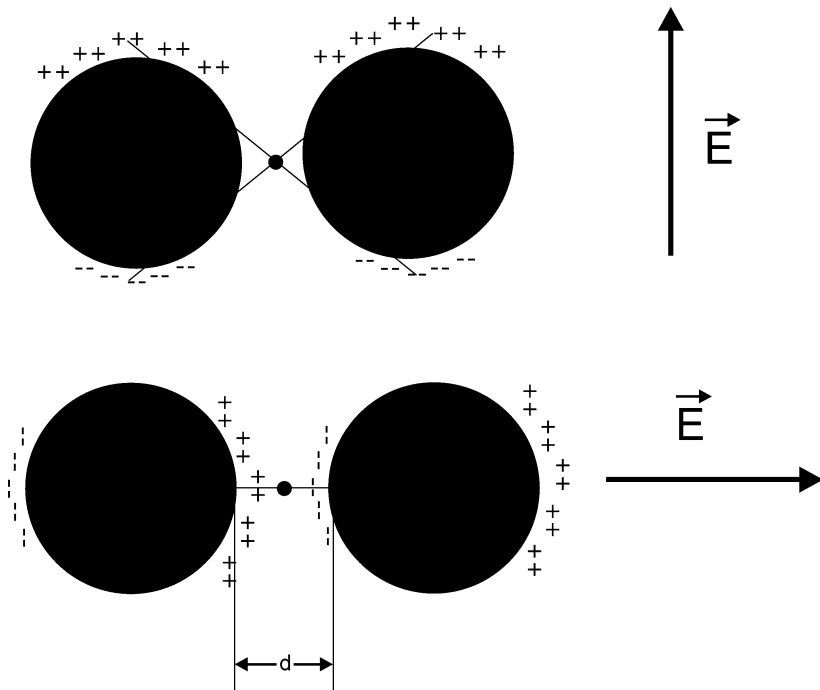
Fig. 1. Simple graphical illustration of the reason that light polarized with the **E**-vector along the interparticle axis can result in huge enhancements in the gap between the two nanoparticles while the orthogonal polarization cannot. For light polarized along the interparticle axis the proximity of the charges (induced by the optical fields) to the molecule can be made arbitrarily small and hence the field sensed by the molecule commensurately large as the nanoparticles are brought closer together. That capability is not available for light polarized orthogonally to the interparticle axis

that electronic scattering at the particle's surfaces become the dominant electron-scattering process, the quality of the resonance is reduced and with it the SERS enhancement. Likewise, for metals whose dielectric properties are greatly modified by interband transitions in the wavelength range under consideration, i.e., for which the value of the function ε_b is large, the width of the resonance is increased and the SERS-enhancement decreases. This explains why, all things being equal, the SERS enhancement of silver exceeds that of gold, which, in turn, exceeds that of copper. The participation of interband transitions in the dielectric function of those metals in the visible range of the spectrum increases in that order. Most transition metals are poor SERS enhancing systems because, for them, the two effects combine to reduce their SERS enhancement ability, i.e., their conductivity is low (γ is large) and the interband contribution to the dielectric function is great (ε_b is large).

The interband contribution to the dielectric function also affects the location of the dipolar plasmon resonance. The quantity $\omega_p \sim 9$ eV for the coinage metals, but the dipolar surface resonance ω_R occurs in, or near the visible for Cu, Ag and Au as a result of the contribution of ε_b in $\omega_R = \frac{\omega_p}{\sqrt{\varepsilon_b + 3}}$.

Summarizing, for a given metal system the SERS intensity will depend, to first order, on the size of the nanostructure responsible for its enhancement. It will be optimal when this size is small with respect to the wavelength of the exciting light so long as that size is not much smaller than the electronic mean free path of the conduction electrons. For the coinage metals this optimal range will span ~ 10 nm to 100 nm.

3 Assemblies of Interacting Nanostructures: The Ubiquitous SERS-Active Systems

The foregoing considered the situation for a single metal particle. Almost all effective SERS-active systems, however, consist of assemblies of interacting particles. Examples are nanoparticle aggregates, rough metals surfaces and island films. More recently, the quest has been for closely spaced, well-engineered systems of interacting metal nanostructures (either particles or cavities) that fulfill the double goals of providing high field enhancement and doing so with highly reproducible and controllable SERS platforms [48,49,50]. For assemblies of isolated particles the interaction is through-space electromagnetic coupling that will be dominated by dipolar coupling, but will include multipolar coupling for closely spaced particles. A firm understanding that the SERS intensity can be greatly enhanced when two or more nanoparticles are brought closely together was already in place in the early 1980s though the work of *Metiu* and coworkers [51,52,53] and of *Nitzan* and coworkers [54], who showed that at an appropriate wavelength and polarization and for a small enough interparticle gap, Raman enhancements $\sim 10^{10}$ could be obtained for molecules localized in a small volume within the interparticle interstice. Others have added seminally to our understanding of these interparticle-coupling effects [55, 56], in some cases including a treatment in which the role of the adsorbed molecules is considered as more than a bystander in the enhanced fields [57, 58, 59]. Those calculations carried out in the 1980's were of a high level, taking account of the effect of multipoles out to order 60 or more. This type of calculation was repeated recently by *Käll* and coworkers [32,33] and others whose evocative figures show that when two nanoparticles are brought close together the optical field strength in the interstitial "hot spot" can reach $\sim 10^{11}$ or more, provided the two nanoparticles are brought within ~ 1 nm or less, light of the appropriate wavelength is used and the exciting electric field vector is polarized along the interparticle axis. This giant enhancement, which exceeds that at isolated metal particles by ~ 6 orders of magnitude, falls off rapidly as the interparticle gap increases.

For light polarized across the interparticle axis, the enhancement is almost negligibly different from its value at a single, isolated particle.

These sorts of calculations were recently performed for core-shell particles [60, 61, 62, 63, 64, 65] composed of a dielectric inner core surrounded by a thin continuous metal shell, which show that the further localization achievable in this geometry can make the SERS enhancement within the interparticle hot spot greater still by some 3 orders of magnitude potentially resulting in enhancements of 10^{13} or more. These predictions should be looked upon with some skepticism since a number of physical requirements such as those listed previously have been ignored. I also note that the (local) dielectric function for silver or gold is seldom corrected for the reduction in electronic mean free path, an effect that will be rather pronounced in thin metal shells. In constructing experimental versions of these core-shell particles one also needs to take care that the assumption of a continuous and smooth metal shell (as assumed in the calculation) is in fact realized. Discontinuous and rough metal features may result in rather intense SERS activity, but not of a kind that is consistent with the analogous calculation. Moreover, since such experiments are carried out in the name of replacing the previously studied, random SERS-active systems with well-designed and properly engineered SERS platforms, spurious roughness on these more regular structures simply replaces one type of random system with another. This is a rather general caveat. A number of "engineered" or lithographically produced SERS active systems that are described in terms of their *designed* properties probably show SERS activity that is an amalgam of those "designed" properties plus the effect of spurious roughness, where, at times, the latter is the dominant component.

A number of seminal aspects of the effect of interparticle coupling can be understood in terms of some very simple physics. Referring to Fig. 1, a molecule (indicated by a small circle in the figure) located in the interstice between two metal nanospheres is flanked by two sets of (time-varying) conjugate charges arising from the polarization of the individual nanoparticles. (The model also describes the two-dimensional component of any system through which a planar cut is represented by two circles, as for example for two parallel nanowires.) As the nanoparticles are brought closer together, the proximity of these charges to the molecule can be made arbitrarily close and hence the capacitive field sensed by the molecule commensurately large. The mutual interaction of the two nanospheres (or nanowires) also leads to an increase in the magnitude of the dipole induced in each component of the two-component nanosystem. The dipole induced in each nano-object arises from the combined field of the incident light and the intense field of its partner, which, in this configuration, leads to an amplification of the polarization. If this problem is solved naively as one of simple electrostatics involving two polarizable nanoparticles, then for light polarized along the interparticle axis, the enhancement increases approximately as d^{-8} where d is the gap size between the two nanowires.

Contrariwise, when the light is polarized in the other direction, illustrated in Fig. 1 (top), that is, normal to the axis joining the centers of the two nanospheres, a molecule in the interstitial region will not benefit from proximity to the induced charges, however closely the nanoparticles are brought together. Nor is there any other location where the field benefits distinctly from the fact that one has a system of two particles rather than one. Additionally, the mutual polarization of each of the two nanoparticles as a result of the field emitted by the other is not favorable.

Bringing two particles together also brings about other effects that one needs to be mindful of, for example, the plasmon resonance splits into two polarization-sensitive components [32, 33, 51, 52, 53], one of which has a resonance that depends strongly on the separation of the two nanospheres. Hence, as the two nanoparticles are separated, the SERS enhancement will diminish and the resonance condition will simultaneously change.

Further aggregation into larger clusters will create opportunities for other "hot" interstitials each of which with its own characteristics of polarization and field strength. Likewise one can modify this effect further by, for example, aggregating core-shell particles.

Is there a geometrical configuration of nanoparticles (of a given metal and given size or multiple metals and several sizes) that leads to the maximal field enhancement? And if so, how much larger would that field be (for comparable sizes of the interstitial spaces) as compared to that in the particle dimer? Although this problem is not yet solved, instinctively one feels that although perhaps another order of magnitude may be achievable by constructing a cluster of optimal geometry, the dimer configuration already accounts for the lion's share of the extra enhancement due to aggregation.

Another question that is worth asking and has not yet been solved is the dependence of the enhancement per interstitial site in a cluster of N nanoparticles. That is if one brings together N nanoparticles by linking them with M ligands (where $N \sim M$), and ignoring for the moment the problem of ensuring that every one of the ligands can profit from the appropriate polarization, is the enhancement per ligand less than or greater than its value when a single ligand molecule links two nanospheres? For a periodic structure such as a system of nanoparticles arranged on a square lattice connected by a single ligand linking neighboring nanoparticles, that enhancement per ligand is likely to be lower than that in a dimer but one that converges rapidly with increasing cluster size. But the situation for the cluster or arbitrary geometry arranged specifically with the aim of maximizing the per-ligand enhancement has not been solved.

The precise structure of the nanoparticle cluster has yet another important aspect that one needs to be mindful of. For highly (geometrically) symmetric aggregates, the degeneracies of the normal modes describing the surface-plasmon excitations (the problem is, to first order, isomorphic with a normal mode analysis of coupled oscillators, except that in common vibrational problems one deals with nuclear motion, while here the oscillators

involved collective motion of electrons) will be such that they will generally be characterized by relatively narrow excitation spectra; while clusters with lower geometrical symmetries will have much broader excitation spectra. This will strongly affect resonance conditions.

The enhancement in an important class of large clusters – fractals – needs special mention. Nanoparticle aggregates grown by self-assembly from monomers in solution often show scaling symmetry either as self-similar (or, when deposited on a substrate) self-affine systems [66, 67]. *Stockman* and *Shalaev* [34, 35, 36, 37] have shown through a long series of papers that, due to the symmetry breaking that arises from the fact that the exciting field does not possess scaling symmetry while the cluster does, a form of energy localization arises that can lead to the formation of electromagnetic hot spots with field strengths that are often of the same magnitude as those discussed above for the nanoparticle dimer. What is more, the lack of translational symmetry in the nanoparticle aggregate leads to very broad excitation spectra ensuring resonance over a very broad range of wavelengths (although, of course, each resonance will correspond to a different set of hot spots, with fairly adjacent wavelengths often corresponding to very disparate patterns of hot spots). The existence of such hot spots has been shown experimentally both for Rayleigh and Raman scattering [67, 68]. Figure 2 shows an example of hot spots measured on a self-affine system of silver nanoparticles allowed to condense gravitationally out of solution. The images were obtained using a near-field optical fiber probe to obtain Raman maps of three SERS bands of phthalazine (or its photochemical products) adsorbed on a self-affine silver film [67, 68]. Also shown is a topographic map taken using shear-force microscopy of the region of the film at which the Raman maps were measured. The irregular distribution of SERS intensity over the surface of the self-affine silver film is clearly visible. Moreover, the pattern varies according to the Raman band probed, each of which corresponds to a different absolute wavelength. Although tedious, since the signal was weak and many points had to be probed to construct the map, the measurements were reproducible.

There are other electromagnetic mechanisms that can augment the SERS enhancement (and also modify the wavelength response of the system). Prime among them is the creation of structures such as ellipsoids and nanowires with regions of very large curvature [26, 27, 28, 29, 30]. This is sometimes referred to as the lightning-rod effect.

The reason SERS is seldom reported from single isolated nanoparticles is therefore easy to understand. With dimers and larger nanoparticle clusters capable of producing enhancements 5 or 6 orders and magnitude larger than those of single isolated particles even a handful of particle dimers or small clusters (or structures that are equivalent to small clusters, such as closely spaced nanoroughness features at a metal surface) will overwhelm the SERS signal from many thousands of isolated particles. As a result, all reports of SERS spectra claiming to originate from single, isolated particles must be looked upon with suspicion, even if rather compelling TEM images are
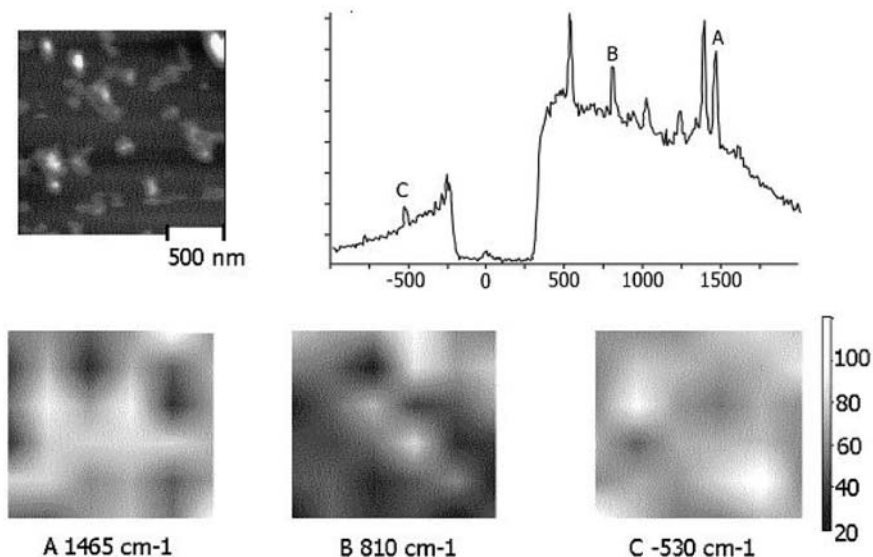
Fig. 2. *Top left:* Shear-force topographic image of a silver film produced by collapsing phthlazine-covered silver-nanoparticle aggregates gravitationally onto a pyrex cover slide. *Top right:* The near-field SERS spectrum of phthalazine measured on the film imaged in the previous panel. A, B, C: Near-field intensity maps of the SERS bands shown in the previous spectrum measured over a $3\,\mu\text{m} \times 3\,\mu\text{m}$ portion of the nanostructured silver film. Reprinted with permission from [69]

reproduced showing the presence of virtually only monomers. One cannot be certain that in the optical experiment the laser did not excite some of the very few clusters present in the sample.

It is also clear based on the foregoing, and the fact that essentially all SERS studies so far have utilized ensembles of strongly interacting metal particles such as aggregated metal nanoparticles or the closely spaced surface features present at cold-deposited metal films [70, 71], that in almost every instance, the average SERS enhancement $\sim 10^6$ is, in fact, an average over a very broad distribution of enhancements present within the portion of the SERS-active sample probed by the laser, which can range from values near unity to values exceeding 10^{11}.

A number of misconceptions exist regarding the em enhancement. A number of workers assume either that the em model implies the quasistatic approximation, in which the em fields are essentially those obtained by solving the Poisson equation, i.e., by assuming the problem is one of electrostatics, or that one needs to make the quasistatic approximation. Neither of these is correct, and in fact many studies, including even rather early studies, were carried out using electromagnetic formalisms that do not make the quasistatic approximation. Moreover, the recent interest in the excitation and propaga-

tion of optical signals generated or mediated by plasmons, referred to as plasmonics, or in photonic crystals, as well as in the near-field optics that often involve subwavelength geometrical features has resulted in many electromagnetic calculations of the fields in the vicinity of slits of various geometries, aperture arrays, and nanoparticle assemblies whose optical response cannot be described in terms the quasistatic approximation and are therefore treated by more general methods. Although not always presented as such, the results of those calculations are often pertinent to SERS of molecules residing in or near those structures. Because the quasistatic approximation leads to acceptably accurate results only for nanosystems with structural dimension much smaller than the wavelength of light (i.e., smaller than $\sim 40\,\mathrm{nm}$) this point is particularly important these days when engineered nanostructures [48,49,50], and other structures such as nanowires [72, 73] with somewhat larger structural dimensions are used.

It is clear that despite often misleading statements to the contrary, the em model is successful both in accounting for the major observations in SERS and as a prescriptive approach towards predicting the outcome of experiments. It is clearly not a complete account of all of the rich assortment of phenomena that can occur for molecules residing at a metal interface. To some extent these other effects are the most interesting since it is through them that the specificity of interaction between molecule and metal is expressed. Additionally, the time is ripe for the development of alternative expressions of the em model so as to take account of the quantum-mechanical nature of the problem, thereby better describing both the dynamics of the electrons in the metal and their interaction with the adsorbed molecule. This is not a new quest, but one that is not yet complete. Recent forays in that direction by *Brus* and coworkers [74, 75] and others point the way.

4 Possible Extensions of the Electromagnetic Model

Since most SERS signals come from fields that are concentrated in very small volumes of space it is also worth considering if we need to expand the basic approach to the calculation of field intensities in such restricted volumes due to the fact that the optical fields are rapidly varying both temporally as well as spatially. A preliminary gauge of the problem is demonstrated by the equation for the dipole moment induced in a particle placed in an inhomogeneous electromagnetic field:

$$\mu_\alpha = \alpha_{\alpha\beta}E_\beta + \tfrac{1}{3}A_{\alpha\beta\gamma}\frac{\partial E_\beta}{\partial \gamma} + G_{\alpha\beta}B_\beta + \cdots , \tag{4}$$

in which $\{\alpha,\ \beta,\ \gamma\}$ stand for $\{x,\ y,\ z\}$, the tensor convention is assumed on repeated subscripts, the tensors $\boldsymbol{\alpha}$, $\boldsymbol{A}$ and $\boldsymbol{G}$ are, respectively, the electric–dipole–electric–dipole, electric–dipole–electric–quadrupole, and electric–dipole–magnetic–dipole tensors and $\boldsymbol{E}$ and $\boldsymbol{B}$, are, respectively, the electric

and magnetic optical fields [76]. In the far field, and for a particle small compared to the wavelength of light, only the first term of 1 contributes significantly because both the optical electric and magnetic fields vary slowly over the body of a small particle. However, for a particle or a molecule in the near field, especially in the field of a hot spot in the interstice between nanoparticles where the field amplitude varies greatly over a small distance, the contributions due to the second and third terms to the induced dipole could be significant. This sort of contribution will not only affect the spectroscopic selection rules of the molecules being examined (since the $\boldsymbol{A}$ and $\boldsymbol{G}$ tensors span different irreducible representation from these of the $\boldsymbol{\alpha}$ tensor), but the "field-gradient" terms will also contribute to the dipolar plasmon fields radiated by the metal particles. That is, the electric dipole induced in a metal particle excited by the near field of a neighboring metal particle could have a significant contribution due to the interaction of the former's *quadrupole moment* with the gradient (or more correctly the dyadic tensor $\boldsymbol{\nabla E}$) of the field of the latter. Hence, even somewhat larger particles, with significant plasmon quadrupole moments that would normally not be implicated in the dipolar radiation by the particle, might under these circumstances produce sizable radiating dipolar plasmons both as a result of the more familiar first term of 1 as well as through one or both of the second and third terms.

Other formulations of the em theory of SERS might be attempted that would better conform to the structural details of the SERS-active system. Nowadays most of these consist of systems of interacting nanoparticles or other nanostructures displaying hot spots, especially systems in which one attempts to achieve a greater level of structural control than before. One can, for example, regard two closely spaced metal nanoparticles illuminated by an optical field as a radiating dipole antenna with a time-varying current traversing its gap that is driven by quantum tunneling whose intensity would be commensurately large as a result of excitation of the localized plasmon. Quantum states of molecules residing in the gap would constitute possible resonant energy-loss channels (as in inelastic tunneling spectroscopy [77, 78, 79]) that would, in turn, show their presence by the appearance of sidebands (i.e., Raman emissions) in the radiation field of the dipole antenna. Extending the antenna analogy to larger clusters, one could immediately determine the relative SERS enhancement and polarization properties of clusters of various shapes and sizes by determining which of the cluster's current modes are dipolar in character.

5 Conclusions

The em theory of SERS, despite its physical simplicity, can account for all major SERS observations including 1. the need for a nanostructured material as the SERS-active system, 2. the observation that some metals form good SERS-active systems while others do not, as well as predicting which

are which, 3. the observation that strongly interacting metal nanoparticles result in very much more effective SERS-active systems than isolated single particles, and 4. the observed polarization sensitivity shown by nanoparticle aggregates. By extending the ideas inherent in the em model one can also understand the seminal features reported for single-molecule SERS, including the puzzling observation that only a few silver "particles" in an ensemble are "hot" (they are appropriately structured nanoparticle clusters), that for a hot particle once one is able to observe SERS, adding more adsorbate does not significantly alter the intensity (once the em hot spot is occupied, adding adsorbate to other sites on the nanoparticle cluster will not add greatly to the observed intensity). However, the em model does not account for all that is learned through SERS. Molecular resonances, charge-transfer transitions and other processes such as ballistic electrons transiently probing the region where the molecule resides [74,75] then modulating electronic processes of the metal as a result, certainly contribute to the rich information SERS reports; and by virtue of the fact that these contributions will vary from molecule to molecule, they will constitute among the most interesting aspects reported by SERS. But, the overall reason why SERS produces such inordinate enhancements is largely an electromagnetic property of nanostructures.

References

[1] M. Fleischman, P. J. Hendra, A. J. McQuillan: Chem. Phys. Lett. **26**, 123 (1974)
[2] D. L. Jeanmaire, R. P. Van Duyne: J. Electroanal. Chem. **84**, 1 (1977)
[3] M. G. Albrecht, J. A. Creighton: J. Am. Chem. Soc. **99**, 5215 (1977)
[4] M. Moskovits: J. Chem. Phys. **69**, 4159 (1978)
[5] K. Kneipp, H. Kneipp, I. Itzkan, R. R. Dasari, M. S. Feld: Chem. Phys. **247**, 155 (1999)
[6] K. Kneipp, H. Kneipp, R. Manoharan, E. B. Hanlon, I. Itzkan, R. R. Dasari, M. S. Feld: Appl. Spectrosc. **52**, 1493 (1998)
[7] K. Kneipp, H. Kneipp, V. B. Kartha, R. Manoharan, G. Deinum, I. Itzkan, R. R. Dasari, M. S. Feld: Phys. Rev. E **57**, R6281 (1998)
[8] K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. R. Dasari, M. S. Feld: Phys. Rev. Lett. **78**, 1667 (1997)
[9] K. Kneipp, Y. Wang, H. Kneipp, I. Itzkan, R. R. Dasari, M. S. Feld: Phys. Rev. Lett. **76**, 2444 (1996)
[10] K. Kneipp, H. Kneipp, R. Manoharan, I. Itzkan, R. R. Dasari, M. S. Feld: J. Raman Spectrosc. **29**, 743 (1998)
[11] J. T. Krug, G. D. Wang, S. R. Emory, S. Nie: J. Am. Chem. Soc. **121**, 9208 (1999)
[12] S. R. Emory, W. E. Haskins, S. Nie: J. Am. Chem. Soc. **120**, 8009 (1998)
[13] W. A. Lyon, S. Nie: Anal. Chem. **69**, 3400 (1997)
[14] S. Nie, S. R. Emory: Science **275**, 1102 (1997)
[15] W. E. Doering, S. Nie: J. Phys. Chem. **106**, 311 (2002)
[16] D. J. Maxwell, S. R. Emory, S. Nie: Chem. Mater. **13**, 1082 (2001)

[17] M. Moskovits: Rev. Mod. Phys. **57**, 783 (1985)
[18] M. A. Paesler, P. J. Moyer: *Near-Field Optics: Theory, Instrumentation and Applications* (Wiley, New York 1996)
[19] N. Halas (Ed.): *Plasmonics: Metallic Nanostructures and Their Optical Properties* (SPIE 2003)
[20] J. I. Gersten: J. Chem. Phys. **72**, 5779 (1980)
[21] J. I. Gersten: J. Chem. Phys. **72**, 5780 (1980)
[22] J. I. Gersten, A. Nitzan: J. Chem. Phys. **73**, 3023 (1980)
[23] J. I. Gersten, A. Nitzan: J. Chem. Phys. **75**, 1139 (1981)
[24] S. L. McCall, P. M. Platzman: Phys. Rev. B **22**, 1660 (1980)
[25] S. L. McCall, P. M. Platzman, P. A. Wolff: Phys. Lett. **77A**, 381 (1980)
[26] M. Kerker: Appl. Opt. **18**, 1180 (1979)
[27] M. Kerker, O. Siiman, O. S. Wang: J. Phys. Chem. **88**, 3168 (1984)
[28] M. Kerker, D. S. Wang, H. Chew: Appl. Opt. **19**, 4159 (1980)
[29] D. S. Wang, M. Kerker: Phys. Rev. B **24**, 1777 (1981)
[30] D. S. Wang, M. Kerker: Phys. Rev. B **25**, 2433 (1982)
[31] J. D. Jackson: *Electromagnetic Theory*, 3rd ed. (Wiley, New York 1998)
[32] H. X. Xu, M. Käll: Chem. Phys. Chem. **4**, 1001 (2003)
[33] H. Xu, J. Aizpurua, M. Käll, P. Apell: Phys. Rev. B **62**, 4318 (2000)
[34] M. I. Stockman: Phys. Rev. E **56**, 6494 (1997)
[35] V. M. Shalaev, R. Botet, J. Mercer, E. B. Stechel: Phys. Rev. B **54**, 8235 (1996)
[36] V. M. Shalaev, A. K. Sarychev: Phys. Rev. B **57**, 13265 (1998)
[37] S. Gresillon, L. Aigouy, A. C. Boccara, J. C. Rivoal, X. Quelin, C. Desmarest, P. Gadenne, V. A. Shubin, A. K. Sarychev, V. M. Shalaev: Phys. Rev. Lett. **82**, 4520 (1999)
[38] see, for example, Sect. III D in [17]
[39] M. Moskovits, D. P. DiLella, K. Maynard: Langmuir **4**, 67 (1988)
[40] J. K. Sass, H. Neff, M. Moskovits, S. Holloway: J. Phys. Chem. **85**, 621 (1981)
[41] M. Moskovits: J. Chem. Phys. **77**, 4408 (1982)
[42] M. Moskovits, D. P. DiLella: J. Chem. Phys. **77**, 1655 (1982)
[43] E. J. Ayars, H. D. Hallen, C. L. Jahncke: Phys. Rev. Lett. **85**, 4180 (2000)
[44] H. D. Hallen, C. L. Jahncke: J. Raman Spectrosc. **34**, 655 (2003)
[45] U. Kreibig, C. Von Frags: Z. Physik **224**, 307 (1969)
[46] U. Kreibig, P. Zacharia: Z. Physik **231**, 128 (1970)
[47] M. J. Dignam, M. Moskovits: J. Chem. Soc. Faraday Trans. 2 **69**, 65 (1973)
[48] T. A. Kelf, Y. Sugawara, J. J. Baumberg, M. Abdelsalam, P. N. Bartlett: Phys. Rev. Lett. **95**, 116802 (2005)
[49] J. J. Baumberg, T. A. Kelf, Y. Sugawara, S. Pelfrey, M. Adelsalam, P. N. Bartlett, A. E. Russell: Nano Lett. **11**, 2262 (2005)
[50] N. M. B. Perney, J. J. Baumberg, M. E. Zoorob, M. D. B. Charlton, S. Mahnkopf, C. M. Netti: Opt. Express **14**, 847 (2006)
[51] P. K. Aravind, A. Nitzan, H. Metiu: Surf. Sci. **110**, 189 (1981)
[52] P. K. Aravind, H. Metiu: J. Phys. Chem. **86**, 5076 (1982)
[53] P. K. Aravind, H. Metiu: Surf. Sci. **124**, 506 (1983)
[54] N. Liver, A. Nitzan, J. I. Gersten: Chem. Phys. Lett. **111**, 449 (1984)
[55] M. Inoue, K. Ohtaka: J. Phys. Soc. Jpn. **52**, 1457 (1983)
[56] M. Inoue, K. Ohtaka: J. Phys. Soc. Jpn. **52**, 3853 (1983)
[57] M. L. Xu, M. J. Dignam: J. Chem. Phys. **100**, 197 (1994)

[58] M. L. Xu, M. J. Dignam: J. Chem. Phys. **99**, 2307 (1993)

[59] M. L. Xu, M. J. Dignam: J. Chem. Phys. **96**, 7758 (1992)

[60] C. E. Talley, J. B. Jackson, C. Oubre, N. K. Grady, C. W. Hollars, S. M. Lane, T. R. Huser, P. Nordlander, N. J. Halas: Nano Lett. **5**, 1569 (2005)

[61] C. Oubre, P. Nordlander: J. Phys. Chem. B **109**, 10042 (2005)

[62] S. J. Oldenburg, R. D. Averitt, S. L. Westcott, N. J. Halas: Chem. Phys. Lett. **288**, 243 (1998)

[63] J. Jackson, N. J. Halas: J. Phys. Chem. B **105**, 2743 (2001)

[64] S. J. Oldenburg, J. B. Jackson, S. L. Westcott, N. J. Halas: Appl. Phys. Lett. **111**, 2897 (1999)

[65] E. Prodan, C. Radloff, N. J. Halas, P. Nordlander: Science **302**, 419 (2003)

[66] V. M. Shalaev: *Nonlinear Optics of Random Media: Fractal Composites and Metal-Dielectric Films* (Springer, Heidelberg, Berlin, New York 2000)

[67] V. P. Drachev, S. V. Perminov, S. G. Rautian, V. P. Safonov: Nonlinear optical effects and selective photomodification of colloidal silver aggregates, in V. Shalaev (Ed.): *Optical Properties of Nanostructured Random Media* (Springer, Heidelberg, Berlin, New York 2002) pp. 113–147

[68] V. A. Markel, V. M. Shalaev, P. Zhang, W. Huynh, L. Tay, T. L. Haslett, M. Moskovits: Phys. Rev. B **59**, 10903 (1999)

[69] M. Moskovits, L. Tay, J. Yang, T. Haslett: SERS and the single molecule, in V. Shalaev (Ed.): *Optical Properties of Nanostructured Random Media* (Springer, Berlin Heidelberg New York 2002) pp. 215–226, copyright 2002 Springer Verlag

[70] C. Douketis, T. L. Haslett, Z. Wang, M. Moskovits, S. Iannotta: J. Chem. Phys. **113**, 11315 (2000)

[71] C. Douketis, Z. Wang, T. L. Haslett, M. Moskovits: Phys. Rev. B **51**, 11022 (1995)

[72] C. Douketis, Z. Wang, T. L. Haslett, M. Moskovits: J. Phys. Chem. B **108**, 12724 (2004)

[73] A. R. Tao, P. D. Yang: J. Phys. Chem. B **109**, 15687 (2005)

[74] A. M. Michaels, J. Jiang, L. Brus: J. Phys. Chem. B **104**, 11965 (2000)

[75] J. Jiang, K. Bosnick, M. Maillard, L. Brus: J. Phys. Chem. B **107**, 9964 (2003)

[76] A. D. Buckingham: Adv. Chem. Phys. **12**, 107 (1967)

[77] D. J. Scalapino, S. M. Marcus: Phys. Rev. Lett. **18**, 459 (1967)

[78] J. Lambe, R. C. Jaklevic: Phys. Rev. **165**, 821 (1968)

[79] M. G. Simonsen, R. V. Coleman, P. K. Hansma: J. Chem. Phys. **61**, 3789 (1974)

Index