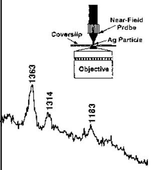
CHEMICAL SOCIETY REVIEWS



Surface-enhanced Raman scattering

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We present an introduction to surface-enhanced Raman scattering (SERS) which reviews the basic experimental facts and the essential features of the mechanisms which have been proposed to account for the observations. We then review very recent fundamental developments which include: SERS from single particles and single molecules; SERS from fractal clusters and surfaces; and new insights into the chemical enhancement mechanism of SERS.

1 Introduction

Surface-enhanced Raman scattering (SERS) was discovered twenty years ago. The field developed aggressively, even explosively, for the first decade or so and then settled down a bit as it entered its teenage years. Interest shifted from fundamentals to applications and a steady stream of papers was published in diverse fields which included electrochemistry, analytical chemistry, chemical physics, solid state physics, biophysics and even medicine, for example. As SERS enters its third decade there has been a renewed interest in fundamentals, especially in the short-range or chemical mechanism, and single molecule detection has been achieved. Few scientists 25 years ago would have bet that Raman spectroscopy, notorious for its difficulty and insensitivity at that time, would have joined the ranks of single molecule spectroscopies before the end of the century.

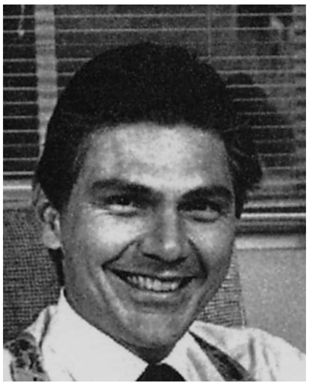
We present here a contemporary review of SERS with two objectives in mind. First, we wish to provide an introduction to the field for scientists (and for students, in particular) who may wish to conduct research in the area or use SERS techniques in their own research in other fields. Second, we wish to highlight new areas of SERS research which we feel are particularly exciting and show promise for further development. Our goal is to provide the reader with sufficient background, orientation and perspective to permit him or her to read the primary reviews and the original literature more easily. In keeping with the spirit of the Journal only the briefest historical development will be presented and the reader is referred to other review articles, rather than the original literature, for elaboration and further discussion. We acknowledge here the important contributions made by an enormous number of scientists from around the world over the past twenty years and regret that the format of this review does not permit us to recognize many individual contributions.

The review is organized as follows. (We assume that the reader is familiar with the elementary aspects of Raman scattering; if not, the monograph by Long[1] is recommended.) A short history of the discovery of SERS is followed by a summary of the key experimental facts. Two classes of SERS mechanisms, electromagnetic and chemical, are introduced and it is shown how these mechanisms account for the experimental observations. Most of the features of the electromagnetic mechanism can be understood by examining the electrostatics of a polarizable metal sphere in a uniform external electric field; that model, therefore, will be discussed in some detail. Evidence that the electromagnetic mechanism is not the whole story will be presented to motivate a discussion of the chemical mechanism.

Three areas of contemporary interest and activity are then reviewed in some detail. Recent advances in microscopy have made it possible to use single particles as SERS substrates and to obtain the Raman spectra of single molecules adsorbed on them; an introduction to this field and selected examples are presented. The importance of interparticle interactions is illustrated nowhere better than by fractal clusters. Recent advances in theory and computational techniques have provided a quantitative understanding of the localization of electromagnetic energy and its effects on both linear and nonlinear spectroscopies. Finally, very recent studies on systems which show chemical enhancement without electromagnetic enhancement have provided a new and more detailed level of understanding about this mechanism. We conclude with mention of two areas of application which we find particularly promising and our assessment of the future of the field.

2 History and fundamentals

SERS was discovered, though not recognized as such, by Fleischmann *et al.*[2] in 1974 who observed intense Raman scattering from pyridine adsorbed onto a roughened silver



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electrode surface from aqueous solution. The motivation for this work was to develop a chemically specific spectroscopic probe which could be used to study electrochemical processes *in situ*; Fleischmann's approach was to roughen the electrode to increase its surface area and, hence, the number of adsorbed molecules available for study. Jeanmaire and Van Duyne[3] and Albrecht and Creighton[4] recognized independently that the large intensities observed could not be accounted for simply by the increase in the number of scatterers present and proposed that an enhancement of the scattered intensity occurred in the adsorbed state. Interestingly enough, these papers presaged a debate about the SERS mechanism which ran furiously for nearly a decade and about which research is still being conducted. Jeanmaire and Van Duyne tentatively proposed an electric field enhancement mechanism whereas Albrecht and Creighton speculated that resonance Raman scattering from molecular electronic states, broadened by their interaction with the metal surface, might be responsible. As we shall see, they were both right in concept, though not in detail.

SERS research accelerated dramatically in the early 1980s with contributions from chemists, physicists and engineers from around the world. It is not hard to see the motivation for such interest. The effect was large, completely unexpected, hard to understand and of enormous practical utility if it could be understood and exploited. By 1985, certainly, the experimental facts were generally agreed upon as were the essential features of the mechanisms.

2.1 Experimental observations

SERS has been observed for a very large number of molecules adsorbed on the surfaces of relatively few metals in a variety of morphologies and physical environments. Silver, copper and gold have been far and away the dominant SERS substrates but work has been reported on the alkali metals and a few others. The largest enhancements occur for surfaces which are rough on the nanoscale (10–100 nm). These include electrode surfaces roughened by one or more oxidation–reduction cycles, island films deposited on glass surfaces at elevated temperatures, films deposited by evaporation or sputtering in vacuum onto cold (100 K) substrates, colloids (especially aggregated colloids), single ellipsoidal nanoparticles and arrays of such particles prepared by lithographic techniques. It had been thought that surface roughness, either atomic scale or nanoscale, was required for SERS. Recent results, discussed below, show that roughness is not a requirement, however.

SERS differs in a number of ways from ordinary Raman spectroscopy of molecules and solids and even from unenhanced surface Raman spectroscopy.[5] The intensities of the bands observed generally fall off with increasing vibrational frequency; C–H stretches, for example, tend to be relatively weak in SERS. Overtones and combination bands are not common. Selection rules are relaxed resulting in the appearance of normally forbidden Raman modes in the surface spectra. The spectra tend to be completely depolarized, in contrast to solution spectra and those taken from molecules adsorbed on atomically smooth, flat surfaces. Excitation profiles differ from the ω^4 dependence of nonresonant scattering; the broad resonances observed may be characteristic of the substrate, the adsorbate or the combined system. Excitation profiles depend upon electrode potential in electrochemical experiments and may be different for different vibrational modes. The enhancement may be remarkably long ranged, extending tens of nanometers from the surface, depending upon the substrate morphology.

Many mechanisms were proposed in the early days of SERS to account for the experimental facts mentioned above. A number of them turned out simply to be wrong and those that survived were quickly sorted into two classes which were called electromagnetic and chemical. As their names imply, the former focus on the enhanced electromagnetic fields which can be supported on metal surfaces with appropriate morphologies and the latter on changes in the electronic structure of molecules which occur upon adsorption and which can lead to resonance Raman scattering. We review briefly the salient features of these mechanisms below.

2.2 Electromagnetic enhancement

The collective excitation of the electron gas of a conductor is called a plasmon; if the excitation is confined to the near surface region it is called a surface plasmon. Surface plasmons can either be propagating, on the surface of a grating, for example, or localized, on the surface of a spherical particle, for example. Surface roughness or curvature is required for the excitation of surface plasmons by light. Perhaps the most familiar example of this phenomenon is Wood's anomaly, in which the reflectivity of a grating dips sharply at the frequency which excites the surface plasmon. The electromagnetic field of the light at the surface can be greatly enhanced under conditions of surface plasmon excitation; the amplification of both the incident laser field and the scattered Raman field through their interaction with the surface constitutes the electromagnetic SERS mechanism.

There have been many versions of the electromagnetic theory developed over the years which treat physical situations of varying complexity at different levels of completeness. Model systems which have been treated include isolated spheres, isolated ellipsoids, interacting spheres, interacting ellipsoids, randomly rough surfaces treated as collections of hemispherical bumps or gratings and fractal surfaces, for example. These systems have been analyzed with different degrees of sophistication. The simplest treatments invoke the electrostatic approximation using sharp boundaries and local, bulk dielectric functions for the substrate. Full electrodynamic calculations have been carried out for the simpler systems and the effects of a nonlocal dielectric response have been discussed. These issues have been critically reviewed in the comprehensive article by Moskovits.[6]

The essential physics which underlies the electromagnetic mechanism is well-illustrated by the textbook example of a metal sphere in an external electric field. For a spherical particle whose radius is much smaller than the wavelength of light, the electric field is uniform across the particle and the electrostatic (Rayleigh) approximation is a good one. The field induced at the surface of the sphere is related to the applied, external (laser) field by eqn. (1) where $\varepsilon_1(\omega)$ is the complex, frequency-dependent dielectric function of the metal and ε_2 is the relative permittivity of the ambient phase.

$$E_{\mathrm{induced}} = \{[\varepsilon_1(\omega) - \varepsilon_2]/[\varepsilon_1(\omega) + 2\varepsilon_2]\}\, E_{\mathrm{laser}} \qquad (1)$$

This function is resonant at the frequency for which Re $(\varepsilon_1) = -2\varepsilon_2$. Excitation of the surface plasmon greatly increases the local field experienced by a molecule adsorbed on the surface of the particle. A very physical way to visualize this phenomenon is to consider the particle as having localized the plane wave of the light as a dipole field centered in the sphere which then decays with the dipole decay law away from the surface in all directions. The particle not only enhances the incident laser field but also the Raman scattered field. It acts as an antenna which amplifies the scattered light intensity. It is easy to see from the above discussion why small increases in the local field produce such large enhancements in the Raman scattering; the overall enhancement scales roughly as E^4!

This simple model rationalizes, at least qualitatively, most of the experimental observations. While we have focused on the sphere for simplicity, the arguments which follow apply generally to the wide variety of surface morphologies which have been used in SERS research; the numerical factor of 2 in the resonance equation will simply be different for different structures. The dominance of the coinage metals and the alkali metals as SERS substrates arises simply because the resonance condition is satisfied at the visible frequencies commonly used for Raman spectroscopy. Other metals have their surface plasmon resonances in different regions of the electromagnetic spectrum and can, in principle, support SERS at those frequencies. In addition, the imaginary part of the dielectric function (which measures losses in the solid) for the coinage and alkali metals is very small at the resonance frequency. Low loss materials sustain sharper and more intense resonances than those where scattering and other dissipative mechanisms are important. The materials requirement is fulfilled simply by selecting an excitation frequency for which Re ε_1 satisfies a resonance condition and Im ε_1 is as close to zero as possible.

The model explains many of the other observations mentioned above. Since the Raman scattered light is of a different frequency than the incident laser the enhancement really goes as $E^2_{\text{laser}}\ E^2_{\text{Raman}}$. This means that both fields can be nearly resonant with the surface plasmon only for small frequency shifts. This fact explains the fall off in intensity observed for high frequency vibrational bands; the surface plasmon is excited by either the laser field or the Raman field but not both. The dipole decay law explains the range dependence of the phenomenon and the early controversy over that issue. The enhancement falls off as $G = [r/(r + d)]^{12}$ for a single molecule located a distance d from the surface of a sphere of radius r, or $G = [r/(r + d)]^{10}$ for a monolayer of molecules. For large radii of curvature the effect looks long-ranged whereas for small radii it can appear to be a surface effect. That the enhancement can be long ranged provided strong evidence for the electromagnetic mechanism. The depolarization is easily explained by considering a SERS-active surface to be a heterogeneous collection of roughness features of different sizes and shapes onto which the molecules adsorb in a variety of orientations. The lack of motional averaging and the opportunity for multiple scattering both contribute to depolarization.

2.3 Chemical enhancement

Several lines of evidence suggest that there is a second enhancement mechanism which operates independently of the electromagnetic mechanism; for systems in which both mechanisms are simultaneously operative the effects are multiplicative. As discussed below, it has been very difficult to separate these effects on systems which support electromagnetic enhancement. The early evidence for the existence of chemical enhancement was, therefore, mostly inferential.

Electromagnetic enhancement should be a nonselective amplifier for Raman scattering by all molecules adsorbed on a particular surface yet the molecules CO and N_2 differ by a factor of 200 in their SERS intensities under the same experimental conditions. This result is very hard to explain invoking only electromagnetic enhancement. The polarizabilities of the molecules are nearly identical and even the most radical differences in orientation upon adsorption could not produce such a large difference. A second line of evidence in support of a chemical mechanism comes from potential-dependent electrochemical experiments. If the potential is scanned at a fixed laser frequency, or the laser frequency is scanned at fixed potential, broad resonances are observed.

These observations can be explained by a resonance Raman mechanism in which either (*a*) the electronic states of the adsorbate are shifted and broadened by their interaction with the surface or (*b*) new electronic states which arise from chemisorption serve as resonant intermediate states in Raman scattering. The evidence to date supports the latter hypothesis. It is not uncommon that the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the adsorbate are symmetrically disposed in energy with respect to the Fermi level of the metal (Fig. 1). In this case charge-transfer excitations (either from the metal to the molecule or *vice versa*) can occur at about half the energy of the intrinsic intramolecular excitations of the adsorbate. Molecules commonly studied by SERS typically have their lowest-lying electronic excitations in the near ultraviolet which would put the charge transfer excitations of this simple model in the visible region of the spectrum. Lombardi *et al.*[7] have developed a theory which accounts for the potential-dependent excitation profiles mentioned above; it is very physical (based upon the standard second-order perturbation theory of Raman scattering), easy to understand and useful for extracting molecular information from SERS spectra. Their article is also a good source of references for both the experiments which motivated the theory as well as earlier theoretical treatments of the problem.

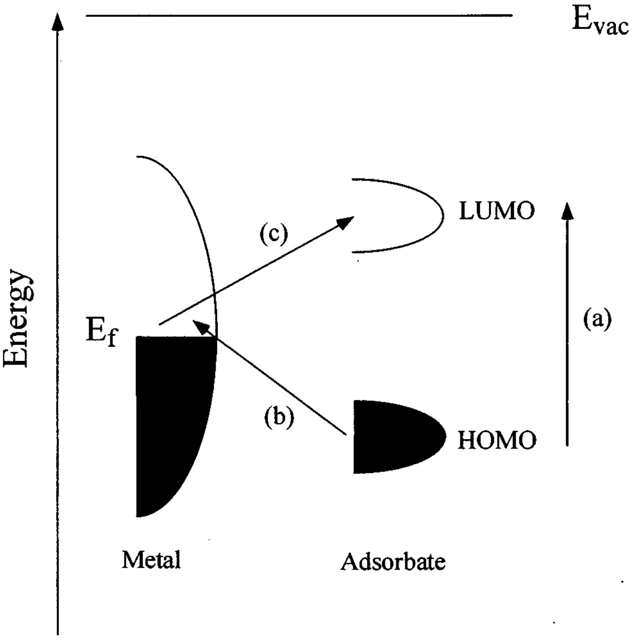


Fig. 1 Typical energy level diagram for a molecule adsorbed on a metal surface. The occupied and unoccupied molecular orbitals are broadened into resonances by their interaction with the metal states; orbital occupancy is determined by the Fermi energy. Possible charge transfer excitations are shown.

In this section we have provided a brief introduction to SERS. For readers interested in a comprehensive review of surface-enhanced processes (including luminescence and photochemistry) emphasizing the physical aspects of the phenomena, the excellent review by Moskovits[6] is warmly recommended. There is a wonderful collection of reprints of original articles in the field, carefully chosen and compiled by Kerker,[8] which provides a sense of the excitement, controversy and dynamics of the subject that is hard to convey in a review article. Two keynote issues of the *Journal of Raman Spectroscopy*,[9,10] one published in 1991 and the second currently in preparation, are also good collections of articles which include several reviews. Other useful references to which the reader is referred for more detail on various aspects of the subject include: Birke *et al.*[11] (general), Pettinger[12] (electrochemistry), Cotton *et al.*[13] (biomolecules), Nabiev *et al.*[14] (medical applications) and Vo Dinh[15] (sensors). We hope that these articles will provide the reader with easy access to the relevant literature of interest.

3 Single particles and single molecules

There has been tremendous interest recently in the properties of nanoparticles, in optical microscopies which provide greatly enhanced depth (confocal microscopy) and lateral (near field microscopy) resolution and in the ability to detect and characterize single molecules. Nanoparticles (with dimensions of the order of nanometers) can have properties which are intermediate in character between molecular and bulk; mesoscopic physics and the accompanying materials science are hot areas of current research. Similarly, the new optical microscopies bridge the gap between the few micron length scale of conventional light microscopes and the atomic resolution of scanning tunneling and atomic force (AFM) microscopes. A very exciting new area of SERS research has drawn upon these fields recently in an attempt to better understand the electrodynamics of small particles, and the SERS which results, and to exploit this understanding to obtain the vibrational spectra of single molecules. Single molecule spectroscopy must certainly be the Holy Grail of analytical chemistry and the addition of a vibrational spectroscopy, with its superior structural characterization, to the electronic spectroscopies already developed is an important achievement.

As mentioned in the introduction, the possibility of using Raman spectroscopy, of all things, for single molecule spectroscopy seems almost ludicrous. Ordinary Raman cross sections are of the order 10^{-30} cm^2 $molecule^{-1}$ sr^{-1} so even a watt of laser power focused into a square micron would produce only one scattered photon every few hours from a single molecule. Enormous enhancements must be created to make single molecule Raman spectroscopy a reality. Two groups have achieved this goal recently using very different approaches. Kneipp *et al.*[16] reported the detection of single molecules of cresyl violet adsorbed on aggregated clusters of colloidal silver. They used near-infrared excitation which is not resonant with any intramolecular optical transitions of the dye but efficiently excites the plasmons of the fractal aggregate (*vide infra*). Nie and Emory,[17,18] on the other hand, combined surface and resonance enhancement (SERRS) to produce the required sensitivity to detect a dye molecule adsorbed on the surface of a single silver particle.

Nie and Emory used standard citrate reduction techniques to produce silver sols which comprised a heterogeneous collection of mostly unaggregated particles of various sizes and shapes. Surprisingly, a small number of these particles showed extraordinarily high enhancements; they have been labelled 'hot' particles. These particles can be imaged by bandpass filtering the Raman scattering of adsorbed Rhodamine 6G. Combined optical and AFM measurements showed that most of these particles were isolated, of dimension *ca.* 100 nm and have shapes which ranged from spherical to rod-like (Fig. 2). In agreement with the general features of the electromagnetic mechanism, more intense scattering was observed when the laser polarization was aligned along the long axis of an ellipsoidal particle which is the most polarizable direction. Size selective fractionation through nanoporous membranes allows the enrichment of particles in a certain size range; in general agreement with the electromagnetic theory is the result that the resonance frequency is a function of particle size. The large enhancement factors observed cannot be accounted for solely by electromagnetic theory, however, and it is very hard to see why so few particles are 'hot' and why the distribution is so peaked about certain particle sizes for a given laser excitation wavelength. This behavior is in contrast to the situation for fractal surfaces in which the localization of electromagnetic energy at 'hot spots' is understood.

Single molecule Raman spectra excited both in the near field and in the confocal mode are shown in Fig. 3. Samples were prepared which had fewer than one adsorbed molecule per particle, on average, by using appropriately dilute solutions based upon the known adsorption isotherm for the system. Confirmation that near field excitation does not dramatically alter the selection rules for SERS is shown by the similarity of the spectra. The increased signal-to-noise ratio observed for the confocal spectrum arises because the laser power is more efficiently transferred to the sample in this configuration. The total enhancement estimated for the system is an astonishing 10^{14}–10^{15} which can be converted to a 'Raman quantum yield' of essentially unity! The authors suggest that this large enhancement factor can be reconciled with the more commonly measured values of 10^8–10^{10} for SERRS by considering the averaging that occurs in conventional measurements. They estimate that only one out of a hundred or a thousand particles is 'hot' and, in addition, that only about one in ten thousand surface sites leads to efficient enhancement. Support for the latter conclusion comes from the rapid saturation of the effect with surface coverage. The SERS signal is fully developed with only 3–4 molecules per particle. Recent microscopic examination of these particles shows well-developed facets which provide a variety of sites of atomic scale roughness and thus

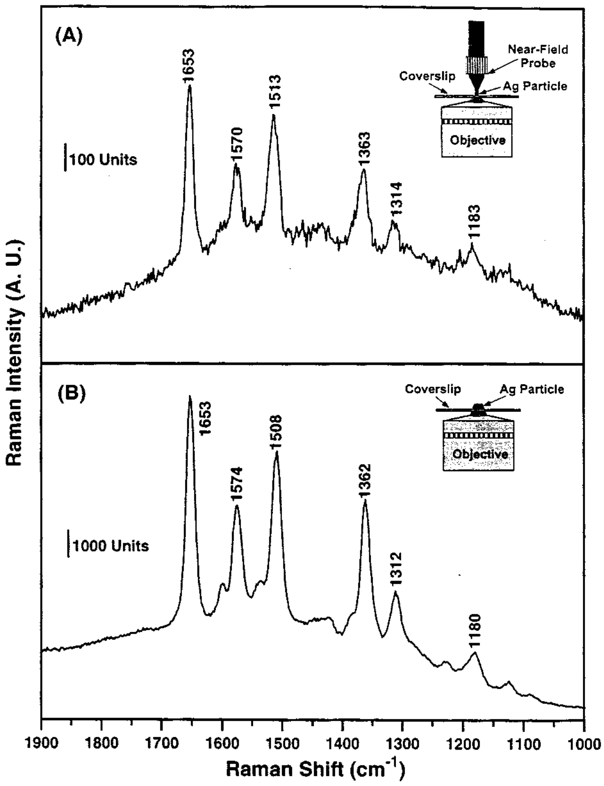


Fig. 3 Near-field (A) and confocal (B) SERS spectra of Rhodamine 6G adsorbed on single silver nanoparticles. (Reproduced from Ref. 18 by permission).

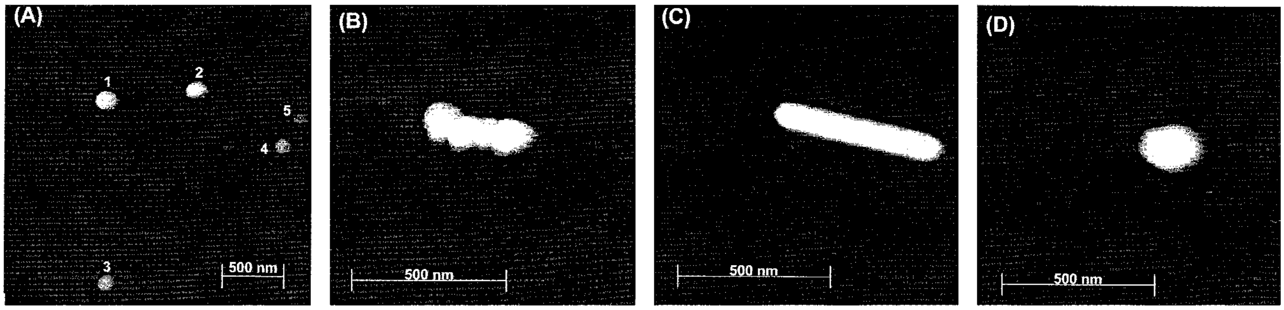


Fig. 2 Tapping mode atomic force microscopy images of selected silver nanoparticles. (A) Particles 1 and 2 showed significant Raman enhancement, the rest did not. (B) A four-particle hot aggregate. (C) A rod-like hot particle. (D) A faceted hot particle. (Reproduced from Ref. 17 by permission).

various possibilities for adsorption. Although the extraordinarily large enhancement factors have been reported by two research groups for two very different physical systems a detailed understanding of the various contributions made by the several mechanisms operating is not yet in hand and promises to be a very interesting area for study.

This field is moving very quickly and we can expect rapid advances on both the fundamental and applied fronts. Single silver nanoparticles have already been used to modify the tips of near field fiber probes in an effort to do near field SERS microscopy. Numerous schemes are being evaluated, employing various combinations of near- and far-field excitation and detection, to try and develop this technique. When perfected, this single molecule vibrational spectroscopy will be a very powerful tool indeed.

4 Fractals

It was recognized early in SERS research that systems of interacting particles produced the largest enhancements and a great deal of effort has been directed towards the study of the electrodynamics of coupled systems. It was also recognized early on that aggregated silver colloids produced fractal clusters.[19] Concepts from these fields of inquiry have been brought together recently to analyze both the linear and nonlinear optical properties of fractals, including, of course, SERS. Powerful new theoretical approaches have been developed and combined with near-field optical microscopy to investigate these phenomena in great detail. SERS has once again revitalized interest in a venerable subject, the optical properties of small particles, and stimulated research in areas outside its specific domain.

A fractal object looks very much the same when examined at different magnifications. This property is called dilation symmetry. Fractals are characterized by the concepts of scale invariance and self-similarity. Unlike geometrical objects, physical fractal structures (mountains, clouds, clusters, and surfaces, for example) follow scaling laws only over a limited range of length scales, the limits of which are determined by real physical constraints. These could be the size of the sample, at the macroscopic limit, or the size of the molecule, on the microscopic end, for example. Fractals which obey different scaling laws in different directions, or achieve self-similarity by anisotropic dilation, are called self-affine. There are a number of good monographs in the general area of the physics of fractals; we have found the book by Gouyet[20] to be very helpful.

The averaged optical properties of composite systems have been well understood for a number of years using Maxwell–Garnett and more sophisticated effective medium theories. The measured long-wavelength optical absorption of these systems often exceeds the calculated values by many orders of magnitude, however, and a number of suggestions have been offered to explain the differences. Among these is that electromagnetic fields can become localized in the interparticle regions of clusters resulting in greatly enhanced absorption and other optical properties. This is the essential mechanism by which fractal aggregates produce a rich variety of interesting optical phenomena, both linear and nonlinear.

Fig. 4 shows a typical fractal cluster of colloidal silver particles prepared by reducing silver nitrate with sodium borohydride. The number of particles in a cluster of gyration radius R_C is given by $N = (R_C/R_0)^D$ where R_0 is a characteristic separation between colloidal particles and D is the fractal dimension. For this particular cluster the particles have typical diameters of 20 nm and $D = 1.78$. The contour diagrams in Fig. 4 show the computed intensity of the electric field which results when this cluster is illuminated with 500 nm light. Note the remarkable localization and greatly enhanced intensity which results from the fractal character of the aggregate. The local intensity enhancement can be as high as 10^3 and it is important to recognize that the fluctuations in the intensity can be as large as the intensity itself. This fact has important consequences for the spectroscopy and photochemistry of molecules adsorbed on the surfaces of these aggregates.

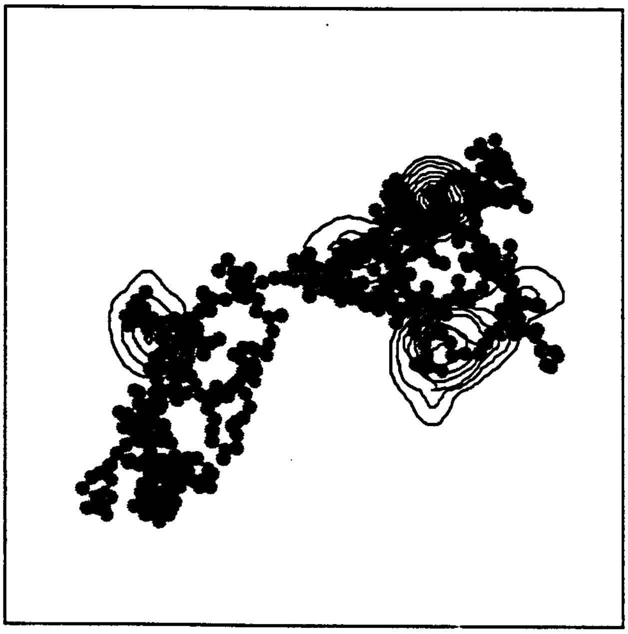


Fig. 4 Local field intensities calculated for a simulated cluster of fractal dimension $D = 1.78$. (Reproduced from Ref. 22 by permission).

There has been a tremendous body of theoretical work developed recently which is directed towards achieving a quantitative understanding of these phenomena. The excellent review by Shalaev[21] summarizes this work in great detail. We highlight a few key developments to orient the reader. The field intensities shown in Fig. 4 are the results of a simulation based upon a scaling theory applied to ‘diluted’ aggregates which contain a few hundred particles. The theory clearly accounts, at least qualitatively, for the frequency and polarization dependent localization of electromagnetic energy in fractal clusters as demonstrated recently by its good agreement with the results of direct imaging of the fields using photon scanning tunneling microscopy.[22]

A more general theory has been presented recently[21] which provides solutions to the coupled dipole equations using the exact (electrodynamic) operator for the dipole interaction rather than that of the static limit. Furthermore the theory is capable of examining much larger systems (up to 10^4 particles) which more realistically model the aggregates studied by experiments. A particularly nice result of these calculations which illustrates the essential physics is shown in Fig 5. Fig. 5 shows the wavelength-dependent local field enhancement factor calculated by simulation for three different kinds of 500-particle aggregates, a fractal cluster (CCA), a system of close-packed spheres (CPSP) and a gas of spherical particles (RGP). The excitation of the surface plasmon of isolated spheres is clearly seen as the sharp feature below 400 nm for the gas and there is very little interaction among the particles, as shown by the weak, featureless response above that wavelength. For the crystalline system (CPSP), the single particle excitation is attenuated and intensity appears in the long-wavelength region of the spectrum as a result of the interparticle interactions. The largest enhancements in the local field intensity clearly occur for the fractal system (CCA) however. The symmetry breaking results in localization of the energy in regions of the aggregate which depend sensitively on wavelength and polarization and the additional enhancement can be huge, factors of 10^3 or so. The fluctuations are large which means that the intensity of the electric field averaged over the aggregate ($\langle E^2 \rangle$) is greater

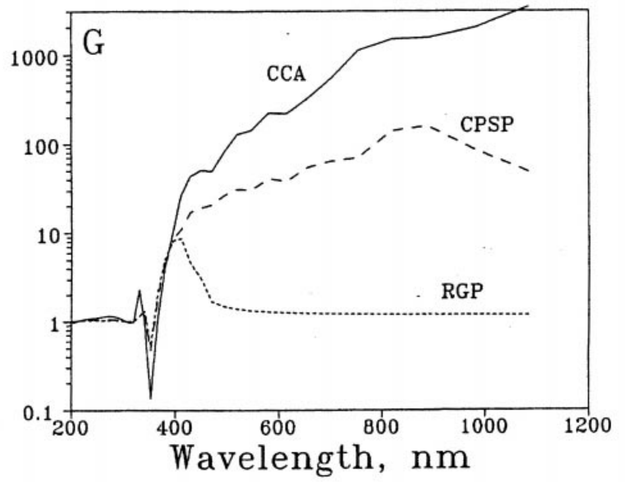


Fig. 5 Wavelength dependence of the averaged local field intensity for a gas of spherical particles (RGP), a close-packed crystal of spherical particles (CPSP) and a fractal aggregate (CCA). (Reproduced from Ref. 21 by permission).

than the square of the field averaged over the aggregate ($<E>^2$). Recall that Fig. 5 illustrates this phenomenon for the linear optical response; the effect is even more pronounced for nonlinear responses which include four-wave mixing, third harmonic generation and, of course, SERS. Excellent agreement has been reached between theory and experiment for SERS excitation profiles for molecules adsorbed on colloidal silver clusters.

Although we have not discussed them in this review, there is a similarly impressive body of work on self-affine surfaces, important examples of which are the cold deposited silver films often used in SERS. The studies which have been carried out on both fractal clusters and self-affine surfaces have provided beautiful illustrations of the physics of these interesting systems as well as stimulated new theoretical approaches to study the electromagnetic properties of systems which are inhomogeneous on the nanometer length scale. The consequences of these discoveries for analytical applications of SERS are potentially significant. If signals arise largely from regions of the surface or cluster where the electromagnetic field is intense due to its spatial localization the possibility that the environment being sampled is not typical certainly exists and photochemical considerations may also become important.

5 Chemical enhancement on smooth surfaces

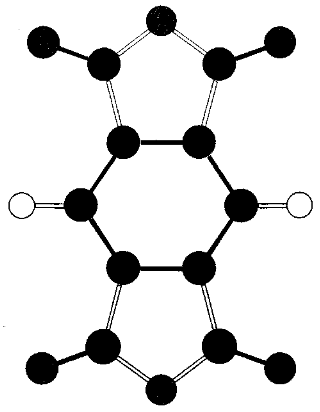
5.1 Introduction

It has proved to be very difficult to study the chemical enhancement mechanism selectively for two reasons. First, it is generally thought to contribute only a factor of $10–10^2$, compared to factors of $10^4–10^7$ for electromagnetic enhancement. Second, almost any experimental parameter which can be varied to probe a system will have an influence *via* both mechanisms, making the separation of effects difficult, if not impossible. It is extremely important, however, to understand the chemical mechanism for both fundamental reasons and for its relevance to analytical applications. Since the effects are multiplicative, unexpected chemical enhancement could lead to analytical conclusions which are not only quantitatively wrong but even qualitatively wrong.

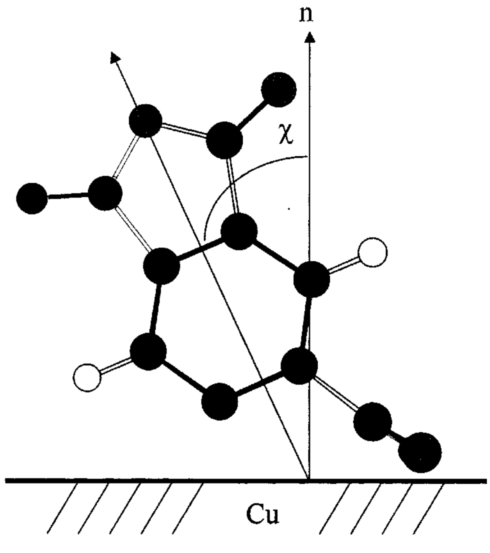
The earliest experimental evidence which suggested a connection between SERS and charge transfer excitations has been reviewed by Avouris and Demuth.[23] They describe ultrahigh vacuum (UHV) experiments in which both SERS and a charge transfer excitation were observed for a Ag(111) surface onto which a grating was etched to allow for surface plasmon excitation. We reported[24] shortly thereafter, however, that molecules physically adsorbed onto atomically smooth surfaces showed no enhancement apart from the small electromagnetic effect expected from the surface simply acting as a mirror. This suggested to us (and others) that atomic scale roughness was a requirement for SERS though it was not clear whether the roughness merely provided chemisorption sites or also chemical enhancement. A systematic series of experiments was conducted to test this idea—atomic scale roughness was created on otherwise flat surfaces which provide only minor electromagnetic enhancement—but proved ultimately inconclusive. We rationalized our failure to observe the charge transfer mechanism for SERS directly by pointing out that the very large homogeneous linewidths of the transitions observed would result in only very small enhancements. We had, in fact, abandoned this line of inquiry when the adventitious discovery[25] of SERS from pyromellitic dianhydride (PMDA) adsorbed on Cu(111) provided us with a new opportunity to investigate this problem of longstanding interest in an especially incisive way.

5.2 PMDA/Cu(111): experimental results

Fig. 6 shows PMDA as both the free molecule and as the adsorbed carboxylate. As shown in Fig. 6, the molecule chemisorbs as a carboxylate by elimination of CO from one anhydride ring; the plane defined by the aromatic ring and the second anhydride group is oriented perpendicular to the surface. Fig. 7 shows the Raman spectrum of PMDA adsorbed on Cu(111) in UHV at 100 K, excited at 647 and 725 nm. The 647.2 nm spectrum is clearly enhanced; the count rates of the most



Pyromellitic dianhydride
(PMDA)



Adsorbed carboxylate

Fig. 6 Pyromellitic dianhydride as the free molecule and as the adsorbed carboxylate intense peaks are *ca.* 2000 cts $s^{-1}W^{-1}$compared with the typical unenhanced count rates we observe of *ca.* 20 cts $s^{-1}W^{-1}$.

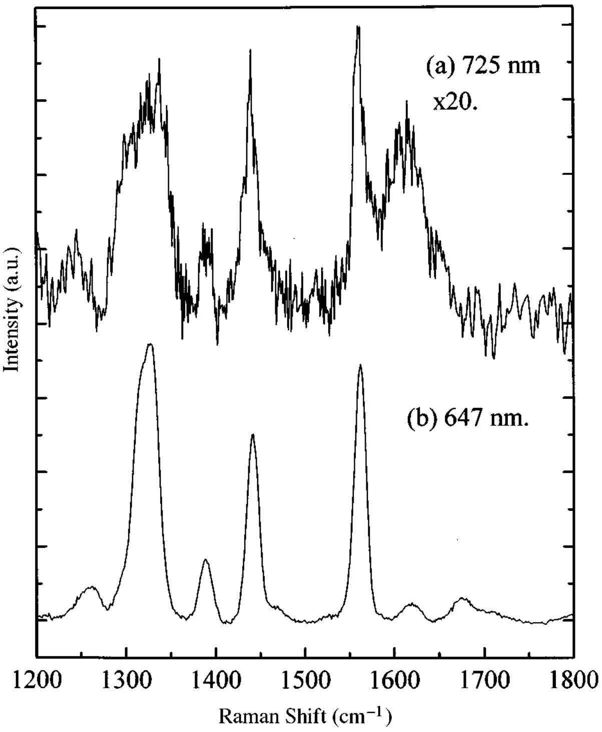


Fig. 7 Raman spectra of pyromellitic dianhydride adsorbed on Cu(111) excited at 725 nm (a) and 647 nm (b)

To see if any new electronic excitations resulted from chemisorption, we measured the electronic absorption spectrum of PMDA/Cu(111) using EELS (Fig. 8). Note the intense, narrow transition at 1.9 eV which appears only in the monolayer spectrum. The intrinsic intramolecular excitations of PMDA, a colorless compound, occur in the ultraviolet and are observed in both the monolayer spectrum and with increased intensity in the spectra of condensed multilayers (not shown here). These results clearly demonstrate that a new low-energy electronically excited state is created when PMDA adsorbs on copper.

To connect the results of our Raman scattering experiments with those of the EELS experiments it is necessary to show that the Raman excitation profile (dependence of intensities upon incident laser frequency) is related to the charge transfer absorption. Fig. 10 shows that the low-energy side of the excitation profile tracks the EELS spectrum well; experiments are underway to extend these measurements to higher energies. We discuss below the simulated spectra shown in Fig. 10.

The PMDA/Cu(111) system provided a case in which the enhancement factor was large enough, and the resonant behavior obvious enough, that it was easy to conclude that chemical enhancement occurs. How do we establish the existence of chemical enhancement, and determine its magnitude, for weaker interactions? The answer is to apply a more sophisticated analysis. In the absence of coverage-dependent reorientations, the relative intensities of all bands should show the same coverage and frequency dependence for unenhanced spectra; deviations from this behavior can be taken as evidence for chemical enhancement.

Flat, single crystal surfaces allow us to investigate the role of surface structure and to conduct polarization experiments to learn more about the nature of the excited state. We have observed significant differences in the spectra obtained from the Cu(111) and Cu(100) surfaces . It is reasonable to expect some differences even in the absence of SERS. The bonding configurations could be different on each surface and the combined effects of the anisotropic molecular polarizability and surface screening would produce different spectra. For PMDA on copper, however, we could not rationalize the differences observed using such simple arguments and the results led us to consider the idea that the charge transfer states were different on the two surfaces.

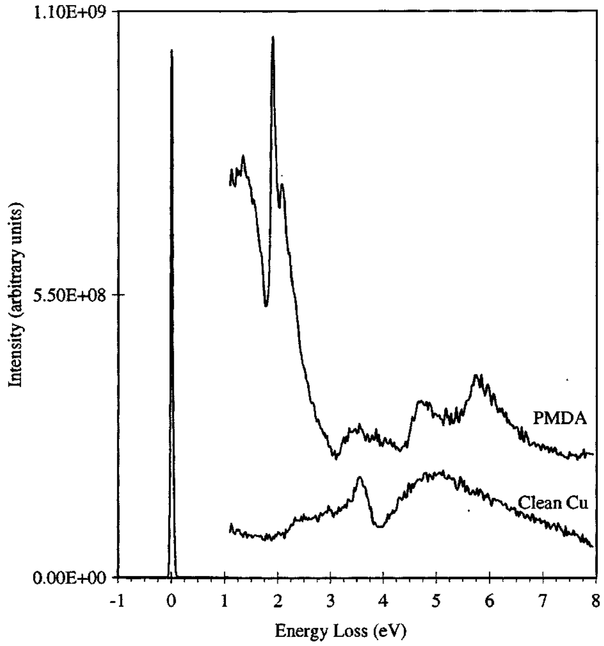


Fig. 8 Electron energy loss spectrum of pyromellitic dianhydride (PMDA) adsorbed on Cu(111); the spectrum of clean Cu(111) is shown for comparison

The Raman spectra obtained from both surfaces looked superficially similar but closer inspection revealed significant differences. The spectrum recorded from the (111) surface was *ca.* 2–3 times more intense than that from the (100) surface when excited with p-polarized (parallel to the plane of incidence) light and even the relative intensities were quite different for each crystal face. In addition, both the total intensities and the relative intensities change markedly with laser polarization in a manner which is inconsistent with the predictions of classical electrodynamics. In particular, the intensities observed with s-polarized (perpendicular to the plane of incidence) excitation were too high to be accounted for by consideration of the optical properties of metal surfaces alone. Clearly, the surface electronic structure plays an important role in determining the character of the charge transfer state responsible for the chemical enhancement in SERS.

5.3 Theory and simulations

To gain additional insight into the scattering mechanism we have carried out molecular spectroscopy simulations[26] using the dynamical approach of Heller and coworkers.[27,28] Equivalent results could be obtained using second order perturbation theory but we prefer the dynamical approach for its physical insight and computational convenience. The chemical enhancement mechanism of SERS can be considered a variation of ordinary resonance Raman scattering, the differences being that the excited states are not purely intramolecular, and that the screening, orienting, and damping properties of the metal surface must be considered. Within this framework, the Raman intensity is determined by a few simple parameters which include: the energy and linewidth of the excited state, the displacement and curvature of the excited state potential energy surface (PES) along each normal coordinate and the magnitude of the transition moment component normal to the surface.

Vertical excitation of the molecule from the ground vibrational level of the ground electronic state to the excited electronic state results in a vibrational wavepacket which is not an eigenfunction of the excited state Hamiltonian. It therefore evolves in time and later returns to the ground electronic state. As for ordinary resonance Raman scattering, the excited state PES must be shifted significantly along some normal coordinate for that mode to be enhanced *via* Franck–Condon activity. Larger displacements produce greater overlaps between the vibrational wavefunctions of the ground and excited states.

The intensity of Raman scattering follows a profile similar to that of the absorption spectrum of the charge transfer state. The largest enhancement occurs, of course, on resonance; the intensity and spectral width of the excitation profile is determined in part by the oscillator strength and lifetime of the excited state. The functional form of this dependence was discussed in the article by Lombardi *et al.*[7] referred to earlier.

Fig. 9 shows the results of a simulation of the Raman spectrum of adsorbed PMDA, compared with the actual spectrum and Fig. 10 shows the results of the simulation of the EEL spectrum and the Raman excitation profile compared with the experimental results. A consistent set of parameters was used for all of the simulations; these included the vibrational frequencies and charge transfer absorption energy obtained from experiment and the width of the excited state resonance and a reference shift in the PES chosen to fit the spectra. The quality of the fits is excellent and allows us to reach certain conclusions about the excited states on the two surfaces.

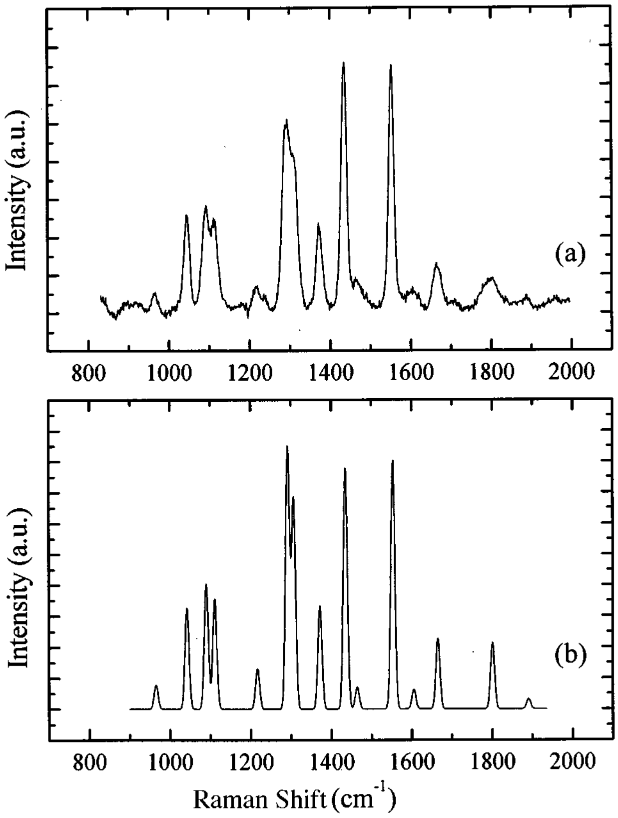


Fig. 9 Experimental (a) and simulated (b) Raman spectra of pyromellitic dianhydride adsorbed on Cu(100) for 647 nm excitation

Franck–Condon activity is clearly shown by the vibronic shoulder observed in the EEL spectra and in the simulations. The differences in frequencies and relative intensities observed for the two surfaces (not shown here) tell us that the PES on Cu(111) is displaced more and of greater curvature than that on Cu(100). That the s-polarized spectra are more intense than predicted by the classical model suggests that the relevant transition dipole moments are oriented nearly parallel to the surface. Since the intensity of the p-polarized spectra relative to the s-polarized spectra is smaller for Cu(100) we conclude that the transition dipole moment is oriented more closely toward the surface for the PMDA/Cu(100) system than for PMDA/Cu(111). The latter conclusion also explains why the absolute intensity of the scattering is greater on the (111) surface. Metal surfaces screen the tangential components of electric fields and enhance normal components; all other things being equal, systems in which the transition dipole moment is oriented along the surface normal will have the largest enhancements. The results of these experiments and simulations show clearly that the microscopic details of surface bonding and their effects on the electronic structure of the adsorbate are critical in determining chemical enhancement.

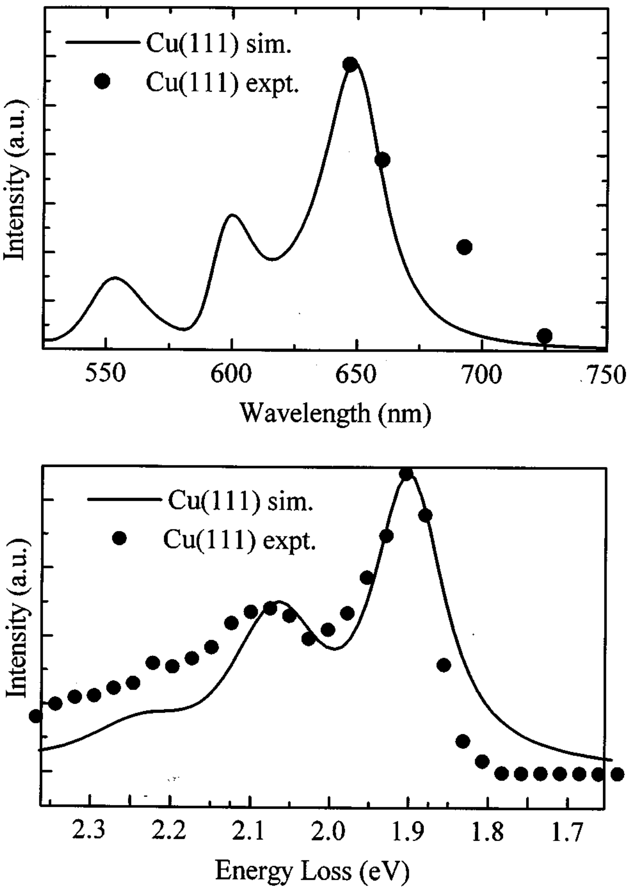


Fig. 10 Experimental and simulated Raman excitation profiles (top) and EEL spectra (bottom) for pyromellitic dianhydride adsorbed on Cu(100)

5.4 The nature of the charge transfer state

Although we have referred to the resonant intermediate state as a charge transfer state, for consistency with the literature and because it is hard to see what else it could be, we have only recently obtained definitive evidence of its character. We also discovered, quite unexpectedly, evidence for the spatial localization of these states.

It is clear from Fig. 1 that changing the Fermi energy (or work function) without affecting the adsorbate orbital energies would shift the wavelength of the charge transfer transition. This idea was the basis for the interpretation of the potential-dependent electrochemical SERS experiments with the Fermi energy controlled by the applied potential. It has been known for some time that doping a surface with very small amounts of either electropositive or electronegative elements can also shift its Fermi energy significantly; this doping is easily accomplished in UHV experiments by dosing the appropriate elements onto the surface. Perturbations which shift the energy of the low energy state without affecting the adsorbate's intramolecular excited states would provide strong evidence of a dynamic, or photon driven, charge transfer. In addition, the direction of charge transfer is determined by the relation between the applied change in Fermi energy and the resulting shift in the transition energy. A red shift which results from raising the Fermi energy would mean that the charge transfer occurs from a filled metal orbital to an empty adsorbate orbital; a blue shift means the opposite.

Our recent experiments show that doping the copper surface with a few percent of a monolayer of Cs results in the attenuation of the 1.9 eV peak in the EEL spectrum of adsorbed PMDA and the appearance of a new peak at 2.5 eV. The blue shift observed immediately establishes that the charge transfer is molecule → metalin nature. The surprising result is that the energy of the new peak is independent of Cs coverage, in contrast to what would be expected if doping produced a uniform increase in the Fermi energy of the entire surface. The intensity of the new peak does, however, increase with increasing Cs coverage. These observations have been taken as evidence that the alkali metal produces a local change in the metal work function which affects only nearby PMDA molecules. We estimate that a single Cs atom can influence the electronic structure of about four neighboring molecules. These experimental results are consistent with recent work on electron localization near ground state adsorbed atoms but provide the first evidence of which we are aware for the effect upon excited molecular states. These results are reported in detail elsewhere.[28]

6 Applications

There have been of the order of a thousand SERS papers published in the last five or six years and so it is clearly impossible to try and review them even in broad classes here. SERS has been used to investigate a wide variety of problems in science and the only unifying theme has been the use of a common technique. We would like to mention, however, a couple of lines of inquiry which we have found particularly interesting and which we feel may interest a general chemical audience. We also feel that they may make SERS more widely applicable as a tool in surface physics and chemistry.

Natan's group has published an interesting series of papers recently on the development of novel SERS substrates based upon the self assembly of gold colloids.[30] Important characteristics of these systems include ease of preparation, reproducibility, stability, compatibility with biomolecules and the important ability to tune the electromagnetic characteristics of the surface by controlling particle size and spacing. These workers have also prepared gold colloids overcoated with silver as useful SERS substrates. The versatility of this approach is a promising development for analytical applications.

Weaver's group has found a way to extend the SERS technique to transition metal surfaces by electrodepositing the metal of interest on a suitably prepared enhancing gold substrate. Although this idea had been tried before, the inability to make pinhole-free overlayers prevented the technique from being generally useful. High quality films have been prepared by depositing slowly at constant cathode current rather than the more rapid constant potential deposition method formerly used. These films must be thick enough to behave chemically as the bulk metal of interest yet thin enough to support the electromagnetic enhancement of the underlying substrate. Promising applications of this *in situ* method to study gas phase heterogeneous catalytic reactions and electrocatalytic processes have recently been reported[31] and the future of this area of application looks promising.

7 Conclusions and outlook

SERS research continues at a brisk pace; hundreds of papers are published each year. Fundamental aspects of the phenomenon are still under investigation. The ability to isolate and characterize single particles and small clusters has provided us with a powerful new approach to the study of electromagnetic enhancement. Advances in computational techniques have allowed us to simulate accurately the electrodynamic response of very complicated structures. And the discovery of SERS from molecules adsorbed on flat single crystal surfaces has allowed us to study the chemical mechanism selectively.

These advances, together with revolutionary developments in instrumentation, promise a bright future for SERS. Instrumental advances include: compact, efficient spectrometers, based upon holographic filter and grating technology; charge-coupled device detectors, with nearly unit quantum efficiency and Raman microscopes operating in both near-field and confocal modes. We believe that a comprehensive, quantitative understanding of the mechanisms will be achieved during the next few years and that applications of this powerful molecular spectroscopy will be found in areas not yet imagined.

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