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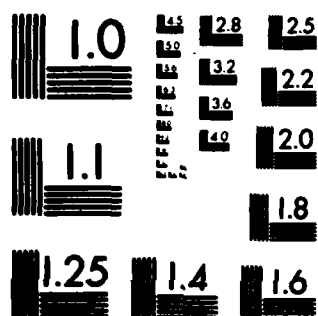
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Theoretical understanding of the origins of strong Raman signals from molecules near roughened Ag, Cu, and Au surfaces has progressed to the point where the action of two very different types of process are recognized. There is "chemical" enhancement that is apparent only for chemisorbed species, as for example, specifically adsorbed anions on Ag electrodes. The chemical mechanism is poorly understood, however, ingenious ideas and concepts have been advanced, including localization of electron-hole pair states and optically driven charge transfer between adsorbate and metal, to model aspects of the chemical

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enhancement. The second and best understood process is the enormous enhancement of the incoming and outgoing radiation fields at the surface resulting from lightening rod geometries and the excitation of localized surface plasmon modes. Calculations show that for special geometries, very high (approximately 10^6-10^8) enhancement factors are possible in confined regions.

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THEORY OF SURFACE ENHANCED RAMAN SPECTROSCOPY:
A PROSPECTIVE VIEW

by

Michael R. Philpott

Presented at

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Research Report

THEORY OF SURFACE ENHANCED RAMAN SCATTERING: A PROSPECTIVE VIEW

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THEORY OF SURFACE ENHANCED RAMAN SCATTERING:
A PROSPECTIVE VIEW

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Abstract. Theoretical understanding of the origins of strong Raman signals from molecules near roughened Ag, Cu, and Au surfaces has progressed to the point where the action of two very different types of process are recognized. There is "chemical" enhancement that is apparent only for chemisorbed species, as for example, specifically adsorbed anions on Ag electrodes. The chemical mechanism is poorly understood, however, ingenious ideas and concepts have been advanced, including localization of electron-hole pair states and optically driven charge transfer between adsorbate and metal, to model aspects of the chemical enhancement. The second and best understood process is the enormous enhancement of the incoming and outgoing radiation fields at the surface resulting from lightening rod geometries and the excitation of localized surface plasmon modes. Calculations show that for special geometries, very high (approximately 10^6–10^8) enhancement factors are possible in confined regions.

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I. INTRODUCTION

Surface enhanced Raman scattering (SERS) was originally observed from silver electrodes immersed in aqueous electrolytes.[1-3] At first, it was thought that the effect was due to high surface areas produced by repeated oxidation-reduction cycles (ORCs).[1] This idea was dispelled by Van Duyne et al.[2] and Creighton et al.[3] who independently showed that the greatest signal was obtained after a few ORCs. Van Duyne[4] clearly recognized the enormity of the enhancement 10^4 to 10^6 and together with Schatz proposed the first widely discussed image theory.[5]

To provide a prospective view, we will first review an elementary formulation of vibrational Raman scattering with the idea of seeking clues to mechanisms that provide for giant enhancements. This approach is possible since at least some of the answers are now available. Then we will separately examine the several classes of theory that provide insight into the chemical and physical origins of SERS. Space and time do not permit an exhaustive review of either the literature or a compilation of references. For these, the reader is referred to several excellently readable reviews.[5,7-9]

II. RAMAN SCATTERING

In vibrational Raman scattering, a photon collides inelastically with a molecule either picking up a vibrational quantum or depositing one within the molecule. Thus, monochromatic light traversing a medium emerges with a series of discrete side bands. The quantum mechanical transition rate for this process is

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$$t_{if} = \frac{2\pi}{\hbar} (m_{if})^2 \delta(E_i - E_f) \qquad (1)$$

where m_{if} is the second order matrix element

$$m_{if} = <i|VG_0(E_i)V|f> = \sum_j \frac{<i|V|j><j|V|f>}{E_i - E_j} . \qquad (2)$$

Here $|i>$, $|j>$, and $|f>$ represent the initial, all intermediate and the final state respectively. The operator V describes the interaction between the scatterer and the electromagnetic (EM) field, its simplest form being $-\mu.E$ the scalar product of the molecular dipole μ and electric field operator E. Simple analysis of Eq. (1) shows that the rate is proportional to $|E_{in}|^2|E_{out}|^2$, *i.e.*, the fourth power in the field, and likewise in the molecular dipole operator.

There is a difference between E and μ since the former can be represented quite adequately by a classical field, whereas the latter is evaluated via its matrix elements. As a result, the contribution of μ to m_{if} occurs through a derivative of a polarizability-like tensor. When the incident photon is near an electronic transition of this tensor, the cross section gets large, this is called resonance Raman scattering in isolated molecules. In general, Eqs. (1) and (2) can admit three types of enhancement. First, the local EM field experienced by the molecule may be amplified by surface plasmon, image dipole, *etc.*, effects. Second mixing of molecular states with metal states may bring about a large effective polarizability derivative as a result of coupling of molecule and metal polarizabilities. Third, the mixing with metal states may result in a localized electronic resonance at optical frequencies. In general, the last two chemical mechanisms are not completely separate. Coupling of polarizabilities can be regarded as an effect from the numerator, whereas the creation of the localized electronic resonance will be felt primarily through a near vanishing of the denominator.

The operation of three approximately multiplicative enhancement mechanisms will be strongly influenced by surface morphology, chemisorption bond strength, electronic structure of molecule and metal surface, and exciting photon energy. Therefore, it is not surprising to find a wide range of enhanced Raman scattering intensities. However, the dominant mechanism seems generally to be the EM affect with enhancements variously estimated in the range 10^4 to 10^6. The chemical mechanisms (types 2 and 3 above) appear to contribute a combined factor in the range 10 to 10^2.

III. THE CHEMICAL EFFECT

Historically, the association of SERS with electrochemical interfaces focussed attention on chemi or physisorption as the main source of the enhancement. Only after the iconoclastic experiments of Murray *et al.*[10] did attention swing to EM enhancements. The theories of SERS up to 1979 have been admirably reviewed by Furtak and Reyes,[6] the reader should consult this work for details not given here.

The central problem in understanding the chemical contribution to the overall enhancement reduces to the calculation of the effective polarizability of the adsorbate-metal surface complex. We call this entity the active site. Models given the active site vary greatly. The simplest being a single ligand attached to an ideal surface. In more complicated models, the core of the active site may involve one or more metal adatom to which the adsorbate is attached, thereby resembling distorted coordination complexes of a silver cluster attached by metal-metal bonds to the surface atoms of the electrode.

According to the image theory of SERS, if the active site is modelled as a point molecule with polarizability $\alpha(Q)$ centered a distance z above the metal surface, the effective polarizability of the scatterer is[5,9]

$$\alpha_{eff}(Q) = \alpha(Q)\left[1 - \frac{2\alpha(Q)}{(2z)^3}\left(\frac{\epsilon_b - \epsilon_a}{\epsilon_b + \epsilon_a}\right)\right]^{-1} . \qquad (3)$$

Here ϵ_a and ϵ_b are the dielectric functions for electrolyte and metal respectively at the incident light frequency. Large values of α_{eff} and consequently large Raman enhancements occur for small denominators. In practice, z was treated as a free parameter in order to obtain Raman enhancements in the 10^4–10^6 range. This procedure results in values of z that are unrealistically small. On the positive side, this simple treatment does permit useful correlations for scattering from different metals because of the flat surface dielectric factor $(\epsilon_b - \epsilon_a)(\epsilon_b + \epsilon_a)^{-1}$. It explains why free electron metals give the greatest enhancements (real and large negative ϵ_b) and why Ag works for all visible light and Cu and Au only in the red (i.e., at energies less than the interband transitions).

Image theories have undergone many refinements including the introduction of electronic resonances in $\alpha(Q)$ due to metal-molecule interactions and nonlocal dielectric functions $\epsilon_b(\omega,k)$ for the metal. Both these effects are important sources of enhancement. The first will be dealt with separately later. The second recognizes the potential importance of electron-hole pair transitions within the metal in contributing to $\alpha_{eff}(Q)$. These transitions are not described using the long wavelength limit function $\epsilon_b(\omega)$. Whereas these ideas and concepts are interesting, there is presently no way of testing for their contribution to the observed enhancement in a given experiment.

Quite a different approach was described by Otto[11] who suggested that modulation of the surface charge density of the metal at vibrational frequencies by coulombic interactions between metal and molecule. This idea entails modulation of the metal polarizability. McCall and Platzmann[12] attempted a key step in treatment of chemisorbed ligands by considering the deformation of surface charge by the motion of electrons in and out of the surface through the chemisorption bond. Their very rough estimates based on a pill-box model of the band yielded enhancement factors in the range 10–10^2.

Yet, other developments include Otto and coworker's[13] forceful discussions of those structural features of the active site important for large enhancements. In particular, the idea that a metal adatom acted as a relay or amplifier of the modulation imposed by the vibration of the ligand. These ideas and those developed independently by Burstein *et al.*[14] constituted an important platform for the rationalization of results from diverse systems, and attempted to define the role played by large scale surface roughness. Basically, it was hypothesized that the active site consisted of an adatom (or perhaps even and adcluster) with one or more ligands attached. The adatom acts as an element of small or atomic scale roughness causing localized breakdown in the selection rules for electron-hole pair excitations. The large scale roughness was important for coupling of incident light into the metal. Once the light, as a mixed photon-surface plasmon state entered the surface it was able to excite localized electron-hole pair transitions. These ideas explained many of the qualitative features of SERS, namely the scales of roughness, the dominance of free electron metals and the polarization characteristics of the Raman light. They also explained the continuous part of the emission spectrum as due a Raman continuum due inelastic scattering of excited electrons and holes by the rough surface. However, the existence of slow component in the emission spectrum raised the problem of the ratio of fluorescence to Raman intensity.[15]

Burstein and coworkers[14] also classified the interactions between adsorbate and metal that could be at work in SERS. Four mechanisms were proposed: (i) excitation energy transfer between vibronic states of ligand and electron-hole (e-h) pair states in the vicinity of the active site mediated by direct coulombic interaction. (ii) exchange overlap between photoexcited e-h pairs and ligand orbitals. (iii) charge transfer with the formation of a charged pair state with hole (electron) on ligand and electron (hole) or metal. (iv) formation of polaron-like states by strong mixing of e-h pair states near the active site. In this last case, it was hypothesized that the creation of a localized polaron will involve significant nuclear shifts within the active site and the possibility of a vibrational Raman spectrum with distinct mode spectrum.

There have been several attempts to incorporate some of these concepts into a theory for the Raman cross section. We describe here two that are particularly interesting because of the physical insight they offer and the possibility of connections with real experiments.

The contribution from charge transfer transitions to the enhanced Raman scattering was treated in a clever way by Persson.[16] The model Hamiltonian used was

$$H = [\epsilon_a(Q) - edE_z]a^+a + \sum_k \epsilon_k a_k^+ a_k$$

$$+ \sum_k (V_{ak}a^+a_k + V_{ak}^* a a_k^+) + \hbar\Omega b^+b + H_{rad} \tag{4}$$

where a^+ and a_k^+ are adsorbate and metal electron creation operators. and b^+ the molecular phonon creation operator. Transforming to a diagonal representation ($|\alpha> = c_\alpha^+|0>$) for the electronic part of the Hamiltonian gives $H = H_0 + V$ where,

$$H_0 = \sum_\alpha \varepsilon_\alpha c_\alpha^+ c_\alpha + \hbar\Omega b^+ b + H_{rad} \tag{5}$$

$$V = \left[\varepsilon_a'(0)Q - edE_z\right]\sum_{\alpha\beta} <\beta|a><a|\alpha>c_\alpha^+ c_\beta \,. \tag{6}$$

and $|a>$ is the adsorbate orbitals. Note that for the electron-phonon and electron-photon interactions are separate in V. Consequently, the transition rate is

$$t_{if} = \frac{2\pi}{\hbar} \left|<\phi_i,0|VG_0VG_0V|\phi_f,0>\right|^2 \delta(E_i - E_f) \tag{7}$$

where ϕ_i and ϕ_f are the initial and final states of the phonon and phonon fields, $|0>$ signifies the electronic ground state, and $G_0 = (E+i\gamma-H_0)^{-1}$ is the Green's operator. The trick in evaluating the electronic part of Eq. (7) is to express all integrals over electron-hole pair states in terms of an adsorbate density of state function

$$\rho_a(\varepsilon) = [\Gamma(\varepsilon)/\pi]\left\{\left[\varepsilon - \tilde{\varepsilon}_a(\varepsilon)\right]^2 + \left[\Gamma(\varepsilon)\right]^2\right\}^{-1} \tag{8}$$

This represents the broadening of the adsorbate level $\varepsilon_a(0)$ upon chemisorption. Ultimately the chemical enhancement factor is expressed as

$$\eta_{chem} = \left|\frac{(ed)^2\varepsilon_a'(0)\mathscr{G}(\omega,\omega')}{1/2\,\alpha'(0)}\right|^2$$

where $\alpha'(0)$ is the derivative of the electronic polarizability of the isolated molecule and $\mathscr{G}$ is expressed in terms of integrals over $\rho_a(\varepsilon)$, and is evaluated numerically. A typical estimate is $\eta_{chem}\simeq 30$, for a ligand like CO or CN on Ag at $\hbar\omega_L = 2.4$ eV. For small Γ ($\simeq 0.12$ eV) a clear peak occurs in $|\mathscr{G}|$ at $\hbar\omega_L\simeq|\tilde{\varepsilon}_a - \varepsilon_F|$ which signifies the existence of a well defined charge transfer state.

Although this theory is highly simplified, it does represent an attempt to estimate an important contribution to the enhancement arising from chemisorption and clearly can be extended to include other physical and chemical factors. This model has been used to interpret some features of the potential dependence of SERS intensities for electrochemical systems, and thereby postulate the existence of photoexcited charge transfer transitions at the electrodes surface.[8]

A more elaborate theory has been developed by Arya and Zeyber,[17] who approached the whole problem from a more rigorous but more abstract many body theory viewpoint. Space does not permit discussion of mathematical details, except for the following. The Anderson-Newns Hamiltonian for metal-adsor ᵗᵉ syr ₄ plus a phonon and full radiation field and interaction was

used. The calculation consisted of picking out the Raman terms contributing to the self energy of the full photon propagator using diagrammatic expansions. This method, in principle, allows the surface topography to be arbitrary provided the appropriate classical Green's function equations can be solved. At the simplest levels of approximation for the vertex functions, it was found that the chemical and physical factors contributing to the enhancement were multiplicative. Although there are differences in the specialization of the Anderson-Newn's Hamiltonian to the SERS problem compared to Perrson,[16] the many body formulation is general enough to withstand many modifications to accommodate the essential physics of diverse SERS systems. Arya and Zeyher[17] reported calculations for flat and corrugated surfaces. Local field effects, *e.g.*, those due to Coulombic interactions, gave enhancements in the range $10-10^2$, and chemisorption effects similar factors. No charge transfer resonance like that described by Perrson[16] was observed because of the way the Hamiltonian was specialized, *i.e.*, the model problem solved in sample calculations was different. The greatest effect was due to electromagnetic field enhancement when plasma surface polaritons were excited on a grating surface. This physical factor gave a maximum enhancement of 10^4. So that the combined total enhancement including local field, chemical and electromagnetic factor had a maximum of 10^8. These model calculations described by Arya and Zehyer[17] are extremely interesting and their approach appears well worth developing for more realistic models.

In conclusion, it appears that chemical and local field effects (like image interactions for physisorbed species, are responsible for enhancements in the range 10 to 10^3. The upper limit is not high enough to make active sites visible without further enhancement in electrochemical systems. This further enhancement arising from the increased EM field amplitudes is discussed next.

III. THE PHYSICAL EFFECTS

The importance of purely physical effects in form of electromagnetic field enhancements received impetus from the experiments of Murray *et al.*[10] in which the Raman scatterers were physically separated from the silver surface by polymer films. The importance of enhanced EM fields at rough surfaces was first formulated by Moskovits[18] who used a Maxwell-Garnet-like formulation of the surface field problem to relate Raman intensity and reflectivity to the wavelength of the exciting light. The Maxwell-Garnet formulation gives an effective field for Raman scattering. After Murray's experiments, rapid development of EM enhancement mechanisms occurred, with important contributions from numerous authors including Gerstein *et al.*,[19] Kerker *et al.*,[20] Wolff *et al.*,[21] Barber *et al.*,[22] Kirtley *et al.*[23] and numerous others that space does not permit to list separately. The principal effects are outlined below.

On a flat surface, the field amplitudes of plasmon surface polaritons excited by prisms or grating couplers can be enhanced by factors as high as 10. Therefore, utilizing surface polaritons for input and output can give rise to large ($\leq 10^4$) enhancements for physisorbed species.

Roughened electrodes or vacuum deposited island films may be likened to a collection of particulate-like objects. The sphere is the simplest such geometry for which Maxwell's equations can be solved exactly. For spheres smaller than $\lambda/15$, the electrostatic limit suffices in calculating the electronic field intensity generated in the vicinity of the sphere by an incident EM wave. In the dipole approximation, the field outside the sphere is the same as that generated by a point dipole of magnitude

$$\vec{\mu}_{SP}(\omega) = a^3 \left(\frac{\varepsilon_b - \varepsilon_a}{\varepsilon_b + 2\varepsilon_a} \right) \vec{E}_i(\omega, r_0)$$

where a is the radius of the sphere and $\vec{r}_0$ its position. Note that $\vec{\mu}$ is proportional to the volume of the sphere which can be millions of times greater than that of a molecule and has a resonance when the denominator $\varepsilon_b + 2\varepsilon_a$ is smaller or zero. This relation determines the frequency of the dipole resonance, the so-called Mie mode. For a free electron plasma sphere, this resonance occurs at

$$\omega_{SP} = \omega_p (1 + 2\varepsilon_a)^{-1/2} .$$

The effect of placing a small metallic sphere in the electromagnetic field is to "suck-in" the field lines, there-by concentrating the field near the surface.

The fields around prolate ellipsoids and near cones have been calculated, as to have those near to hemispherical bosses. In particular, we refer to the calculations of Gerstein and coworkers[9] and Ruppin[24] who show that the ratio $|E/E_0|^4$ can become extremely large. For larger objects the dipole modes are reduced and higher modes contribute important fields. Consequently, it is important to assess their influence. Detailed calculations for isolated prolate ellipsoids have been reported by Barber, Chang, and Massoudi.[22] They find agreement with the electrostatic limit theories at small dimensions and as the size of the particle increases significant differences in the magnitude of the field. Enhancements are considerably lower on two counts. First, if $|E/E_0|^4$ is averaged over the geometrical area, and second, for objects with large dimensions where the higher multipole fields act to reduce the dipole part.

It seems clear that even more calculations, like those of Barber et al.[22] exploring the limits of the physical effect are needed in order to correctly ascertain the measurement of the physical enhancement inherent in the experiments of Murray et al.[10] and Liao et al.[25]

IV. OUTLOOK

While a lot of progress has been made in the last few years, much remains to be done to clarify the details of the mechanisms contributing to enhanced Raman scattering. The area of greatest utility for SERS is and will be for some time the electrochemical interface. For this class of system, there is only one other spectroscopic probe with molecular specificity, namely IR. It is important, therefore to concentrate on those aspects that will make SERS more of a tool. SERS utilizing the

enhancements of PSPS on flat surfaces, initially with polycrystalline but ultimately with single crystal surfaces needs to be vigorously pursued.[26] The use of voltage or light polarization modulation techniques to provide addition surface sensitivity will certainly be necessary, in order to lift the surface signals above the Raman continuum due to water. With this lead, the theory should concentrate more on chemical mechanisms since the major EM enhancement is simply that due to flat surfaces which is intrinsically simpler than that of other topographies.

The structural models of the active sites will be simpler too, since the Raman scattering is from majority surface species and not those generated by oxidation reduction cycles. In turn, models of the double layer incorporating more molecular details will be needed. If flat SERS from electrodes cannot be made to work, then in electrochemistry, the phenomenon will reduce to a study of active site chemistry. Since these sites are a minority, they will not be part of the main stream of electrochemical science.

In UHV, basic studies of the active sites on well defined surface topographies are possible because of the multitude of surface tools currently available. Elucidation of active site structure will be a great help in understanding the spectra and dynamics of electrochemical active sites. Though as mentioned, this does not appear to be a mainstream activity. The theoretical problems appropriate to the UHV SERS experiments that should be vigorously pursued are the following: EM calculations that better define the limits of physical field enhancements for well defined topographies like spheroids, gratings, and bosses. It is also important to understand the field distributions in compound systems like ellipsoids over planes, small groups of ellipsoids and arrays of ellipsoids.

ACKNOWLEDGMENTS

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