Surface Spectroscopy

Surface Enhanced Optical Processes

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The observation [1] of intense spontaneous Raman spectra from monolayers of molecules adsorbed on suitably roughened silver surfaces has resulted in much activity, both theoretical and experimental, to understand the phenomena. Many theoretical models [2] have been proposed utilizing many effects. For example, image field effects, adatom effects, adsorption induced resonances, interaction between adsorbed molecules and electron hole pairs, and localized plasmon modes have been speculated as the source of the giant enhancement of 10^6 often observed. One of the most successful models has been the localized plasmon or particle plasmon theory [3]. In this model the enhancement is due to the simultaneous amplification of the incident optical field and the re-radiated Raman field by the localized plasmon resonance of a bump or particle on the silver surface. The importance of plasmon resonances has been demonstrated by experiments [4] on silver gratings. Substantial increases in Raman signal intensity was observed when the angle of incidence was such as to satisfy the phase matching conditions for launching a surface plasmon. However, the largest enhancements occur with localized particle plasmons. For example, if one models the surface as composed of isolated silver ellipsoids whose dimensions are small compared to optical wavelengths, one finds the amplification of the Raman intensity, due to the localized particle plasmon, is

$$|f(\omega_L)f(\omega_S)|^2 = \left| \frac{\varepsilon(\omega_L)-1}{1-[1-\varepsilon(\omega_L)]\left(A-i\frac{Vk_L^3}{6\pi}\right)} \, \frac{\varepsilon(\omega_S)-1}{1-[1-\varepsilon(\omega_S)]\left(A-i\frac{Vk_S^3}{6\pi}\right)} \right|^2 ,$$

where ω_L and ω_S are the laser and Stokes frequency respectively, ε is the dielectric constant of silver, V is the volume of the particle and A is the depolarization factor $0<A<1$ which characterizes the particle eccentricity. Experiments have been performed which verify most aspects of this model and these experiments will be discussed.

Because the particle plasmon process produces increased local electromagnetic fields, one also obtains enhancement of all other electromagnetic processes, such as second harmonic generation, luminescence, and inelastic acoustic light scattering [5]. Enhancement of these effects has been verified by experiments.

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Nonlinear Optical Detection of Adsorbed Monolayers and Monolayer Spectroscopy

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The usual techniques for the study of interfaces are often limited in their capacity for spectral and temporal resolution. Optical methods are therefore attractive, but they do not generally exhibit any intrinsic surface sensitivity. However, the second-order nonlinear optical processes are forbidden by symmetry in centrosymmetric media and, hence, tend to be highly surface-specific. We have shown that second-harmonic generation (SHG) has indeed the sensitivity of detecting monolayers of adsorbates on surfaces. We have applied it to study molecular adsorption and desorption at the silver-liquid interface in an electrolytic solution. We have also succeeded in demonstrating the possibility of doing spectroscopic work on adsorbed monolayers on smooth surfaces by nonlinear optical techniques.

Because of the strong local-field enhancement, molecular monolayers adsorbed on a roughened silver electrode in an electrolytic solution can be easily detected by SHG. From the observed signals, we can deduce an average second-order nonlinear polarizability for the adsorbed molecules. The results indicate that the molecule-metal interaction can greatly affect the nonlinear polarizability, especially in cases where the molecules are centrosymmetric. Variation of the signal as a function of the concentration of molecules in the solution yields an adsorption isotherm, from which an adsorption free energy for the particular adsorbates on silver can be deduced.

Spectroscopy of adsorbed molecules on smooth substrates is one of the most important problems in surface science. We have succeeded, for the first time, in obtaining spectra for monolayer adsorbates by a second-order nonlinear optical method. In the experiment, samples of rhodamine 110 and rhodamine 6G molecules adsorbed on smooth fused silica substrates at a surface density of $5\times10^{13}/\mathrm{cm}^2$ are used. The second-harmonic spectra of the $S_0\rightarrow S_2$ electronic transition of the adsorbates are actually obtained using a pulsed dye laser as the tunable source. The results show a clear shift in the spectral peaks of the two adsorbates.From the polarization dependence of the SH signal, information about the orientation of the adsorbed molecules can also be obtained. We find that the dye molecules have an isotropic orientational distribution in the surface plane, but have their molecular plane titled from the surface. A value for the previously unknown second-order polarizability of the rhodamine dyes can also be determined.

Spectroscopy of Adsorbed Molecules Using Silver-Island Films

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The enhancement of optical scattering phenomena from molecules adsorbed at rough metal interfaces offers considerable potential for performing novel spectroscopy at surfaces and for altering the free state branching to the deexcitation channels available to adsorbed molecules. In order to assess this potential, we have studied how the electrodynamic interactions at rough silver interfaces affect some of the optical processes which occur. Our emphasis has been on the spectroscopic implications of the techniques and thus we have performed a careful determination of the relative enhancement for normal Raman scattering, resonance Raman scattering and fluorescence. We find a heiarchy of enhancement ratios that is ideal for spectroscopic purposes. A model for the interactions of the plasma resonances localized on the roughness features of the surface with the various excitations of the adsorbates accounts for the observations. Competition between an increased radiative emission rate and an increased nonradiative damping rate due to the electromagnetic coupling between the emitting molecule and the rough surface is found to also play a crucial role in determining the effectiveness of other deexcitation channels including photochemical degradation and intermolecular energy transfer.

Silver-islands films make an ideal rough surface for our studies. They are easily and reproducibly made and their optical properties are simple to measure and well understood [1]. Furthermore, the excitation of the local plasma resonances and their role in the enhanced optical scattering processes has been determined [2, 3]. An accurate and quantitative measure of the magnitude of the enhancement due to the silver can be simply obtained by comparing the signal from equal coverages of molecules on an island film to a bare silica substrate, which is essentially electromagnetically "inert".

We have measured the increase in the scattered intensity on the island film for normal Raman scattering, resonance Raman scattering and fluorescence. For a monolayer of nitrobenzoate, the normal Raman scattering is enhanced by $\gtrsim 5 \times 10^5$. For resonance Raman scattering from Rhodamine 6 G (R6G) or basic Fuchsin, the enhancement varies from $\sim 10^2$ to $\sim 10^4$, depending on the thickness of the coverage and the excitation wavelength. The enhancement of fluorescence depends very strongly on the quantum efficiency (QE) of the molecule. Basic Fuchsin and R6G have similar absorption bands in solution, but the QE of Fuchsin is less than 0.01 while atht of R6G is nearly 1. On an island film, the emission from Fuchsin is increased by ~ 10 while that of R6G is decreased by ~ 3. Furthermore, most of the emission from a Fuchsin coated sample comes from molecules lying near the islands, while most of the emission from an R6G coated sample comes from molecules lying between the islands.

By extending the treatment of enhanced Raman scattering at rough surfaces to include molecular resonances and the damping processes of the silver the relative magnitudes of the enhancements observed can be accounted for [4]. The heiarchy of enhancements is ideal for surface spectroscopic applications. For normal RS, as much enhancement as possible is beneficial, while resonance RS is inherently more intense and thus the enhancement of this process is not as essential for probing surface adsorbed layers. However, the ability to enhance the resonant Raman signal above the fluorescence signal is crucial. We find that for high QE molecules, resonance RS is increased by $\sim 10^5$ over fluorescence. Finally, the enhancement of the effective yield of fluorescence from molecules with otherwise low QE is helpful for fluorescence spectroscopy.

The coupling between the emitting dipole of the adsorbed molecule and the silver island also alters the branching ratios into the various deexcitation channels of the system. As in the case of basic Fuchsin, the probability of decay into nonradiative channels such as internal conversion is decreased in favor of the decay of the coupled molecule-island system. Other inter- and intramolecular processes, such as photochemical degradation are also altered by the electrodynamics of the rough interface. Examples of these effects will be presented as will illustrative examples of new spectroscopy made possible by the heiarchy of surface enhancements.

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Reflectivity of Silver Particle Arrays Exhibiting Surface Enhancement

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A recently developed theory of dipolar interactions between metal particles is used to calculate the reflectivity of silver particle arrays as a function of wavelength, angle, and polarization. Experimental results verify the theoretical prediction that particle plasmon resonances can be tailored by changing the particle interactions.

Recent interest has been focused on the enhancement of a variety of electromagnetic processes on suitably prepared silver and gold surfaces. Following the observation of enhanced Raman scattering, it was shown that harmonic generation as well as one- and two-photon absorption can be strongly enhanced. Metal island films are often used in these studies, as their enhancement properties can be varied by changing the film thickness.

An electromagnetic particle plasmon model has been used to explain a large number of experimental observations. For metal island films, the model must be extended to include the dipolar interactions between the metal particles, which shift and broaden the plasmon resonance. The influence of these dipolar interactions can be studied in a controlled manner by using regular arrays of silver particles. The particles are supported by structures of ≈ 1000 Å dimensions produced by microlithographic techniques. Such surfaces have proved to be strongly enhancing various nonlinear electromagnetic phenomena.

The reflectivity of a metal particle surface is derived and expressed as a product of a factor proportional to ω^2, and the local intensity enhancement factor. The latter is calculated using the electrostatic particle plasmon model, extended to include the effects of retarded dipolar interactions and radiation damping. Experimentally determined particle sizes and shapes are used. The calculated reflectivity is of the correct order of magnitude; it varies between $\approx 5\%$ and $\leqq 100\%$. A pronounced wavelength dependence is predicted which depends on array dimensions and incidence angle, as well as particle shape and surrounding medium.

A regular two-dimensional array of freely suspended, identical Ag spheroids was approximated as follows. A quartz wafer was patterned to produce a square array of tall SiO_2 posts, 2500 Å apart. Silver particles were deposited onto the tips by oblique evaporation. The whole structure was then immersed in a liquid index-matched to quartz. The interface between the substrate and the surrounding medium is thereby eliminated, such that the silver particles appear to be suspended in a homogeneous medium.

The reflectivity exhibits indeed the strong wavelength dependence predicted by theory. The pattern changes drastically when incidence angle or polarization are varied. By producing particles of different excentricity, depositing them onto the posts with their long axis either parallel or perpendicular to the wafer plane, and by rotating the wafer relative to the plane of incidence, we obtain complete control over the plasmon resonance frequency of the array. The concept of tailoring an array capable of resonating two wavelengths simultaneously, which would maximize the enhancement in surface Raman scattering, is thereby confirmed.

Enhanced Raman Spectra of Metal-Molecule Clusters

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Surface enhanced Raman Scattering (SERS) is usually observed with molecules adsorbed on roughened metal surfaces. It is mostly investigated with silver, but has also been reported for copper, gold, platinum, nickel, and mercury.

Two effects seem to contribute to the Raman enhancement:

I) a classical electric field enhancement resulting from surface plasmons and

II) a chemical enhancement due to excitation of localized electronic states induced by chemisoprtion.

Measurements on silica supported nickel and platinum catalysts demonstrate that the Raman enhancement strongly depends on diameter and shape of the metal particles [1]. To get a better understanding of the geometric effects and to study the chemical contribution alone, we started to investigate small silver and copper clusters containing only a few atoms. Luminescence and Raman-spectra of the pure metal clusters and of molecules (e.g. pyridine) adsorbed to these clusters are reported.

The particles are produced by matrix isolation technique, i.e. the metal, the adsorbed molecules, and a rare gas (argon or xenon) are cocondensed on a copper substrat which is cooled to below 10 K. Typical evaporation rates of the metal are smaller than 3 Å/min at a gas pressure of about 10^{-5} mbar which could be kept constant by a needle valve. The luminescence and Raman spectra were measured in back scattering geometry at power levels less than 20 mW.

With the excitation wavelength $\lambda = 351$ mm or $\lambda = 413$ mm of the krypton laser pure Ag_m-clusters ($m = 1, 2, 3$) give a broad blue luminescence which is superimposed by many vibrational progressions [2]. When pyridine is cocondensed with silver the blue luminescence disappears and a strong red luminescence is observed instead. The copper particles show a similar luminescence. It is always accompanied by a strong CuO-luminescence which probable results from the oxygen impurities of the xenon gas. Attempts to avoid the oxygen contamination were only partially successful so far.

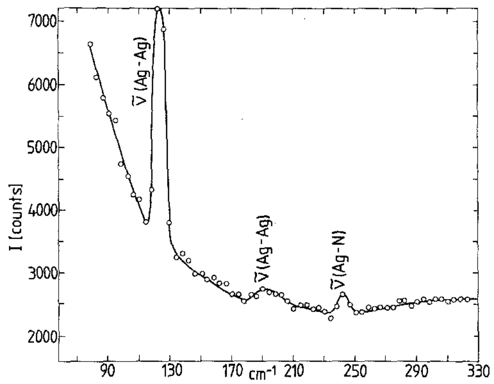

Fig. 1

The Raman spectra of the pure metal clusters can be used to identify by group theoretical selection rules the geometrical configuration of the metal particles. The Raman spectra of pyridine molecules bounded to the metal particles resemble those of pyridine adsorbed on roughened metal surfaces. The strongest modes are the pyridine breathing modes. As an example Fig. 1 shows the low wavenumber Raman spectrum of Ag_m-pyridine clusters ($m = 1, 2, 3$) condensed into an argon matrix.

The lines at $120\,cm^{-1}$ and $190\,cm^{-1}$ can be assigned to the ν (Ag–Ag) stretching vibrations of Ag_3 and Ag_2 particles, respectively, and are only insignificantly shifted with respect to the pure silver particles. The line at $242\,cm^{-1}$ characterizes the strength of the Ag-pyridine bond.

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Stimulated Emission of Surface Plasmons In Metal-Insulator-Heavily Doped *P*-Type Semiconductor Structures

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Radiative emission from both metal-barrier-metal (M.B.M.) and metal-insulator-semiconductor (M.I.S.) junctions has demonstrated the possibility of surface plasma excitation by tunneling electrons [1, 2]. The spontaneous emission spectrum is both tunable and broadband with an upper cutoff frequency given by $\omega_c = eV_0/h$, V_0 being the applied bias. Spontaneous emission from M.B.M. junction structures has been considered theoretically [3] and stimulated emission of the anti-symmetric plasmon mode has been proposed using such tunneling structures [4]. The plasmon mode has also been considered in conjunction with negative resistance in the current-voltage characteristic [5]. In the former case the attendant absorption, not considered in [4] but also allowed by the tunneling process, of the slowly propagating anti-symmetric plasmon mode makes net gain difficult if not impossible to achieve in such structures. In addition coupling such plasmon modes to the external field is also difficult.

We show, however, that net gain of the anti-symmetric surface plasmon mode can be achieved in metal-insulator-heavily doped *p*-type semiconductor junctions (M.I.S.(P^{++})). In- Ga_2O_3-GaAs(p^{++}) is shown to be a suitable combination of materials. Further, localized doping of the semiconductor can be utilized to couple the junction mode to guided optical modes and to minimize the effects of free carrier loss. This would be the first demonstration of a coupling to the antisymmetric gap mode.

For the appropriate band structure and bias situation shown in Fig. 1, the relevant initial electron energy E_1 is between the valence band edge of the semiconductor, E_V; and E_{FM}, the Fermi level of the metal, and absorptive transitions of energy $h\omega < E_C - E_{FS} - eV_0$ are forbidden due to the bandgap, E_G, of the semiconductor. Further, noting that the higher E_1, the greater the tunneling probability, emissive transitions with E_1 greater than $E_V (E_V < E_1 < E_{FM})$ dominate over the allowed absorptive transitions with E_1 less than E_V. This implies that a net emission of surface plasmons is possible provided dielectric (including free carrier) losses can be overcome.

Using the method of Lasher and Stern [6], the absorption (emission) coefficient due to the net stimulated emission as a function of energy has been calculated. The absorption due to the free carrier scattering within the semiconductor is the dominating loss mechanism and is given by the imaginery part of the complex propagation constant of the antisymmetric mode. It is believed that contributions from phonon scattering in the insulator, surface states, coupling to the plasmon mode from the external field, and impurities in the insulator, will be less significant and that these can be largely overcome by appropriate fabrication processes.

Using a single electron model with appropriate effective masses, the net gain has been evaluated for In–Ga_2O_3–GaAs(p^{++}) at $T = 300\,K$, $h\omega < E_C - E_{ES} - eV_0$ and a hole density of $p = 5 \times 10^{20}\,cm^{-3}$. Gain is predicted over a large bandwidth (Fig. 2). In the low frequency approximation this gain can be shown to be directly related to negative resistance in the current-voltage characteristic [12]. This has been previously observed by Esaki and Stiles in M–O–S (p^{++}) structures [7]. At higher frequencies purely quantum aspects enter and will be discussed.

The proposed class of coherent sources utilizing tunneling to pump the anti-symmetric plasmon mode in metal-barrier-*p* type semiconductor junctions is extremely attractive for submicron dimensions and provides a large cross-section for interaction with the well confined anti-symmetric plasmon mode.

Experimental efforts underway to demonstrate the gain will be discussed. Junctions have been fabricated and the spontaneous emission is presently being studied.

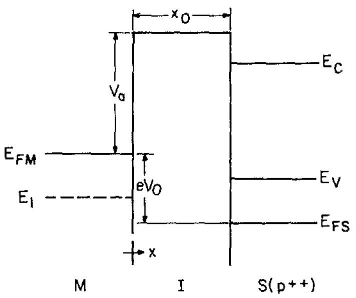

Fig. 1. Band diagram for idealized M–O–S(p^{++}) tunneling structure proposed for pumping the anti-anti-symmetric plasmon mode

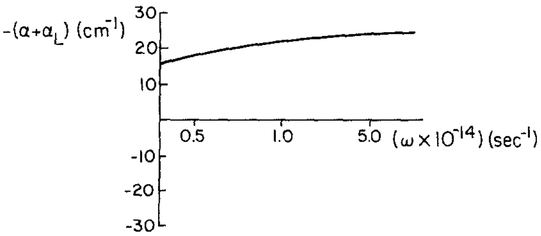

Fig. 2. Predicted gain for In–Ga_2O_3–GaAs(p^{++}) for a hole concentration of $5 \times 10^{20}\,cm^{-3}$ and a bias voltage of 1.4 V

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