

Role of Electromagnetic Resonances in the Surface-Enhanced Raman Effect

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The magnitude of the plasma-resonance contribution to surface-enhanced Raman scattering on silver-island films has been measured with use of an experimental arrangement in which the resonance can be suppressed. The measured reduction in Raman scattering is ~ 300 , but theoretical analysis indicates that there may remain an additional unsuppressed factor $\lesssim 3$. The data show that plasma resonances are not essential for observation of Raman scattering by molecular monolayers using standard detection techniques.

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We report experiments in which we have measured for the first time the contribution of local plasma resonances to the surface-enhanced Raman scattering (SERS) of molecules adsorbed on a rough metal surface. Thus we distinguish between the resonant part of the classical electromagnetic enhancement mechanism and all other possible mechanisms.

SERS has attracted the attention of many workers during the past few years, following the discovery¹⁻³ that under certain conditions, molecular monolayers adsorbed on metal surfaces could exhibit Raman scattering enhanced by many orders of magnitude. In addition to its obvious utility as a technique for studying surfaces and monitoring surface reactions, SERS has had an attraction as an unexpected and unexplained phenomenon, when we thought we knew almost everything knowable about the optical properties of metals and molecules. For a recent review of the topic, see the collection of articles edited by Chang and Furtak.⁴

One of the most popular models for explaining and calculating SERS is the plasma-resonance model.⁵⁻⁷ At a perfectly planar metal surface, light cannot excite the surface plasma modes, but with some roughness there arise local, and excitable, plasma resonances, analogous to the well understood resonances of isolated metal spheres. At resonance, for small isolated spheroids, the local electric field near the metal surface can be enhanced by a large factor, and an adsorbed molecule can use this multiplying factor⁷ both in adsorbing and in radiating. Much effort has therefore been expended in the attempt to calculate local fields in realistic situations only remotely resembling the ideal isolated me-

tal sphere,⁸⁻¹⁰ as well as in the experimental study of systems more nearly resembling a calculable ideal.¹¹⁻¹⁵

In this work, we have studied one of the standard nonideal SERS surfaces, the silver-island film,¹⁴ and have attempted to measure the enhancement obtained from its plasma resonances, as directly as possible. Our scheme is to poison the resonances with a nearby lossy dielectric medium, in this case graphite. Our principal finding is that Raman signals are reduced, in the nearby presence of graphite, by a factor of a few hundred. Remaining enhancement mechanisms, not depending on plasma resonances, must therefore account for the remaining factor in the neighborhood of one thousand. An immediate consequence of this conclusion is that many other metals, beyond metals with strong plasma resonances (the noble metals), ought to have useful and interesting SERS properties. Our work differs from that of Furtak and Kester,¹⁵ who damped the silver resonances by alloying with Pd, in two respects; first, our lossy medium is external to the metal particles and acts only on external fields, and second, we achieve a quantitative measure of the importance of plasma resonances alone.

On fresh-cleavage surfaces of highly oriented pyrolytic graphite, we evaporated thin wedges of SiO₂, as shown in Fig. 1, leaving some of the graphite surface uncovered, and keeping the SiO film thin enough (~ 200 Å) to avoid any optical interference effects. The thicknesses of the SiO films were measured by calibrating the deposition rate (~ 200 Å/min) with an Inficon XTM deposited-mass monitor. Finally, we produced the silver-island films by evaporating enough silver

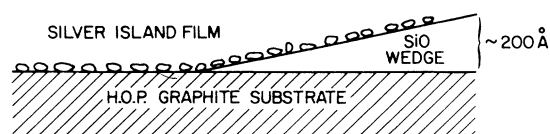


FIG. 1. Schematic diagram of the samples. The figure is not drawn to scale in that the actual angle of the SiO wedge is of the order of microradians.

for a uniform 50-Å layer, as measured by the same thickness monitor, and with substrates both at room temperature and heated to 150°C.

We examined our silver-island films by scanning electron microscopy. Those evaporated on cool substrates showed characteristic island diameters of 200–600 Å, with slightly more numerous and smaller islands in the regions on the SiO film. Silver-island films formed at higher temperatures showed smaller and more uniform islands, with diameters near 200 Å, and again somewhat more coverage on the SiO film. We conclude from this examination of micrographs that there are no great differences between the films formed on the SiO and on the graphite directly, and that there is nothing in the morphology of the films to explain the differences in their SERS performance.

To measure the variation of SERS on these samples, we deposited a monolayer of adsorbed molecules of *para*-nitrobenzoic acid (*p*-NBA), whose SERS spectrum is well characterized, and whose deposition from an ethanol solution follows a standard recipe.¹⁶

We took Raman spectra of *p*-NBA molecules on these samples using laser light sources of various wavelengths. We had to take care to avoid problems caused by changes in the Raman spectra induced by continued irradiation at high laser powers.¹⁷ We therefore satisfied ourselves with limited incident power: 5 mW in a line focus on the films which included the SiO spacer, and 50 mW in a line focus on the films directly on graphite. At these powers, the spectra were stable and unchanging. Furthermore, we concentrated especially on the intensity of the *p*-NBA line at 1355 cm⁻¹, which was relatively unchanged by the laser irradiation. The spectra were recorded with a conventional scanning double spectrometer followed by a photomultiplier and photon counting electronics.

We measured the intensity of Raman scattering as a function of position on the samples described above. In Fig. 2 we show our results for two samples, prepared on cool graphite substrates.

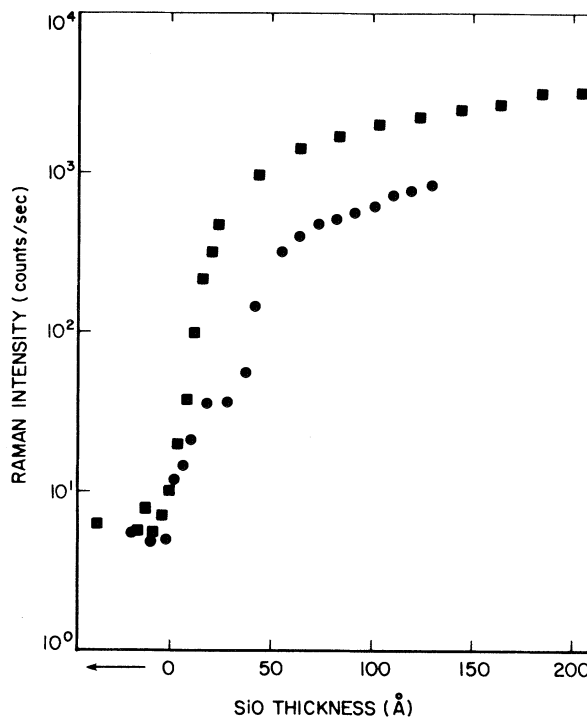


FIG. 2. Intensity of the Raman scattering from the 1355 cm⁻¹ line of *p*-NBA as a function of the SiO-spacer thickness. The intensities are normalized to a 5-mW incident laser power, though for points below about 10² counts/sec, 50 mW was used. The wavelength of the excitation was 5145 Å.

The two do not give identical results, but are in qualitative agreement: The salient conclusion is that the Raman scattering is suppressed when the silver-island films are near or in contact with the graphite substrate. The suppression ratio varies, but is in the range of 300–500. Since we are not sure that our SiO wedges are continuous, but may contain pinholes and inhomogeneities, we will not dwell on the way in which the intensity varies with position. Were the films perfect and regular, the measurements would give a way of estimating the spatial range near the silver islands, but even so this range is not identical to that measured for SERS,¹⁸ and there are factors other than field strength which may affect enhancement. Since from the electron micrographs we concluded that the differences between island films on graphite and on SiO were minor, but might include a factor of 2 less coverage on the graphite, we arrive at an estimate of the effect of the nearby presence of the lossy dielectric: SERS is suppressed by a factor of several hundred, but probably not more than 500. This is the central finding of this work.

In additional experiments, we studied the excitation spectra for the Raman effect on these samples—in this case for the silver-island films deposited on heated substrates. Figure 3 shows these spectra. The connected dots represent the excitation spectrum for *p*-NBA on silver islands with a thick SiO film, and our curve resembles those previously published for similar structures by Weitz, Garoff, and Gramila.¹⁹ The unconnected crosses are from *p*-NBA on silver islands deposited on bare graphite, with no SiO spacer. There is no remnant of the resonant peak, and we take this as additional evidence that the lossy dielectric close to the particles has suppressed the resonances by damping. The resonance peak is not just shifted,¹¹ it is removed. If for some reason the graphite did not damp the resonances, we would expect, in fact, a sharper resonance, because of the reduced density of islands and a consequent reduction in interactions between islands.

The electromagnetic enhancement in the Raman cross section of a molecule near a small metallic ellipsoid is $F = |f(\omega_i)|^2 |f(\omega_s)|^2$ where, with use of the results of Gersten and Nitzan,²⁰ $f(\omega)$ can be written as

$$f(\omega) = (1 - \Gamma)^{-1} [1 - A_{LR} A_R(\omega)]^2, \quad (1)$$

with

$$A_R(\omega) = \frac{\epsilon_s - \epsilon(\omega)}{\epsilon(\omega) + a_R \epsilon_s}. \quad (2)$$

The laser and scattered frequencies are ω_i and ω_s , ϵ and ϵ_s are the dielectric constants of the ellipsoid and surrounding medium, a_R is a geometrical factor determined by the eccentricity and orientation of the ellipsoid, and Γ is related to the image part of the enhancement as discussed by Gersten and Nitzan.²⁰ The two factors A_{LR} and A_R are the “lightning-rod” and resonant parts of the electromagnetic enhancement, respectively. Both A_{LR} and A_R depend upon the shape of the particle while only A_{LR} contains the position of the molecule. The effect of the graphite can be modeled by adding an extra imaginary part to the denominator of Eq. (2). For the damping that we must introduce to reproduce the Raman excitation spectra of silver islands on bare graphite, shown in Fig. 3, the remaining resonant enhancement is less than a factor of 3. Including this factor, we find that the contribution to SERS of undamped plasma resonances in a silver island film is a factor less than 1000.

The plasma-resonance model of SERS has been

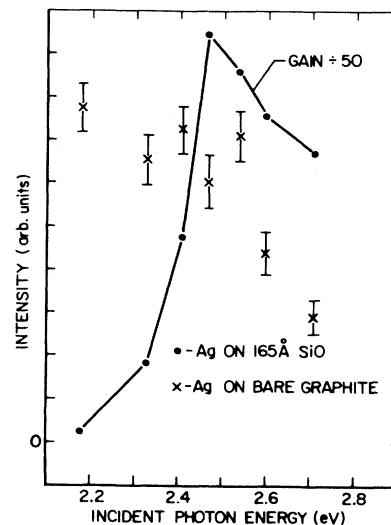


FIG. 3. Excitation spectra for the 1355-cm^{-1} Raman line of *p*-NBA. The connected dots are for Ag islands deposited on a thick SiO-spacer layer. The crosses are for islands on bare graphite. The Ag islands were deposited with the substrate held at 150°C .

attractive because those metals with small imaginary dielectric constants, the noble metals, were strong in exhibiting SERS. Additionally, simple model calculations for idealized structures⁵⁻⁷ gave the right order of magnitude of enhancement, leading some to conclude that that was the whole story. Here we have shown, quantitatively, that the plasma resonance is not alone, but contributes only an enhancement factor of the order of 300–1000. Thus other mechanisms give a Raman enhancement of the order of 1000.

In addition to Ag islands on graphite, enhanced Raman signals have been previously observed from other nonresonant structures. Liao and Stern²¹ have found Raman scattering from *p*-NBA on aluminum microstructures, which they attribute to nonresonant electromagnetic enhancement augmented by a lightning-rod effect in their elongated particles. Potts, Merlin, and Partin²² reported Raman signals for molecules on roughened PbTe and suggested a similar interpretation. Probably other mechanisms are acting in concert, notably chemisorption and charge transfer,²³ but we cannot take space to discuss them in detail here. Suffice it to say that there can be a factor of several hundred to several thousand enhancement left over after the resonant effects are removed, and this should help to motivate the search for SERS in the interesting catalytic

metals such as nickel and platinum, where no strong plasma resonance can be expected.

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