

Excitation spectra of surface-enhanced Raman scattering on silver-island films

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Both the spectral dependence and the magnitude of the excitation spectra of surface-enhanced Raman scattering are found to be quantitatively related to the absorption spectra for silver-island films. This relationship is maintained even when the local electromagnetic enhancement at the islands is varied by coating the film with a layer of absorbing dye molecules. The results illustrate a simple experimental way to determine independently the role of the electronic plasma resonances in the enhancement process on these films and shed new insights into the details of the electromagnetic interactions responsible for surface-enhanced Raman scattering.

The observation of surface-enhanced Raman scattering (SERS) has stimulated numerous investigations of the optical properties of rough metal surfaces and their adsorbates.¹ SERS has been observed from a variety of different interfaces, and several mechanisms have been proposed to account for the origin of the enhancement. However, the origin is still controversial,² and it appears that more than one mechanism may be involved in the overall enhancement, with the relative contribution of each depending on the particular interfacial system. Nevertheless, one mechanism that appears to make a major contribution in all environments is the strong electromagnetic interaction among the optical fields, the adsorbed molecules, and the electronic plasma resonances localized on the roughness features of the surface.³ A detailed understanding of these electromagnetic effects is essential to distinguish and study the contribution of other enhancement processes as well as to make SERS into a useful form of surface spectroscopy.

Silver-island films are an excellent surface for the investigation of the electromagnetic effects. Both theoretical⁴ and experimental⁵ evidence suggests that the plasma resonances on individual islands play an important role in causing SERS. Their role is confirmed by the agreement obtained between the theoretical prediction for SERS from an isolated ellipsoid and the observed SERS from a periodic array of uniform silver ellipsoids.⁶ However, on island films and other more random surfaces, electromagnetic interactions among the silver particles and with the substrate, as well as the distribution of sizes and shapes of the silver particles, are vitally important in determining the nature and role of the plasma resonances. For these more complicated surfaces, an independent characterization of the plasma resonances, which accounts for all these effects, can be obtained experimentally from the absorption spectrum. This fact has been used to obtain qualitative agreement between the SERS intensity and the mean-field absorption of the film at a single wavelength as the thickness of the film is increased.⁵ In this

Letter we show that both the spectral dependence and the magnitude of the SERS excitation spectrum of silver-island films can be related to the absorption spectrum in a simple yet quantitative way. The local fields external to the islands, which cause the SERS, are shown to have a different spectral dependence from the internal fields, which cause the absorption. However, the absorption and excitation spectra can be related by inclusion of the appropriate electromagnetic boundary conditions, and the resulting agreement provides new insights into the detailed electromagnetic behavior and the spectral widths of the plasma resonances involved in SERS. Furthermore, when the local electromagnetic environment of the same films is changed by coating them with a thin layer of strongly absorbing molecules, these changes are reflected in a similar fashion both by the absorption of the film and by the resonant SERS excitation spectra of the adsorbate. Our results confirm the dominant contribution of the electromagnetic effects in the optical enhancement on these films and suggest simple ways to measure and maximize the contribution of the plasma resonances to the enhancement when island-film substrates are used in applying SERS as a surface spectroscopy.

A dipping technique⁸ is used to coat the island films with approximately a monolayer of adsorbate. For a nonabsorbing molecule, we use *p*-nitrobenzoic acid, which is adsorbed as nitrobenzoate as determined from the absence of the band in the 1700-cm⁻¹ region of the observed SERS spectrum.⁹ For the absorbing molecule, we use rhodamine 6G (R6G). A backscattering geometry normal to the surface of the substrate is used. By maintaining the laser excitation intensity below ~1W/cm², and by spinning the substrate, we reduce laser-induced decay of the SERS signal to less than 5% during our measurement time. The SERS signals are normalized to the Raman scattering (RS) from cyclohexane to account for any spectral dependence of the detection system and to remove the ω^4 behavior in the excitation spectra. The absorption is determined by measuring the normal-incidence transmission, the

specular reflection, and the diffuse scattering with a spectrophotometer.

The excitation spectrum of the 1600 cm^{-1} band of nitrobenzoate is shown with the absorption spectrum of a typical 50-Å mass-thickness island film in Fig. 1. Both exhibit a pronounced resonance because of the excitation of the electronic plasma resonances but are peaked at different wavelengths. We can use the theoretical models for SERS applied to island films⁴ to relate the excitation and absorption spectra quantitatively. The excitation of the electronic plasma resonances on the film results in an increase in the electric fields inside the islands, causing the peak in the absorption. Thus the fractional absorption of the film can be expressed as

$$A(\omega) = qd\epsilon_2 \frac{\omega}{c} \frac{|E_{\text{in}}|^2}{|E_0|^2}, \quad (1)$$

where q is the volume fraction of silver in the film, d is an effective thickness of the film, $\epsilon(\omega) = \epsilon_1 + i\epsilon_2$ is the dielectric constant of bulk silver, and E_0 is the incident field strength. Since the actual field strength in any given island, E_{in} , depends on its exact shape as well as on the effects of the fields induced in neighboring islands and in the substrate, we use $|E_{\text{in}}|^2$ in Eq. (1) to represent an effective average field intensity inside the islands of the film.

In the spirit of the electromagnetic models,²⁻⁶ the SERS intensity at each molecule can be expressed as the product of the local field-intensity enhancements at the excitation and emission frequencies, ω_L and ω_S , respectively. Thus we define a local internal field-intensity enhancement factor $f^2(\omega) = |E_{\text{in}}|^2/|E_0|^2$, in which case the external field-enhancement factors at surface-adsorbed molecules are determined by the electromagnetic boundary conditions and are f^2 for the component of the field tangential to the surface and $|e|^2 f^2$ for the component normal to the surface. To sum the strongly position-dependent product of enhancements at ω_L and ω_S for all the molecules on the surface, the local field intensities are expressed in terms of $|E_{\text{in}}|^2$ and the appropriate boundary conditions. However, since $|\epsilon(\omega_L)|^2|\epsilon(\omega_S)|^2 \simeq 10^4$, we neglect the contribution of fields tangential to the surface. The product of the measured absorption at ω_L and ω_S is then used to approximate the relative SERS intensity,

$$I_{\text{SERS}} \approx \frac{c^2}{q^2 d^2} \frac{|\epsilon(\omega_L)|^2 A(\omega_L) |\epsilon(\omega_S)|^2 A(\omega_S)}{\epsilon_2(\omega_L) \omega_L \epsilon_2(\omega_S) \omega_S}. \quad (2)$$

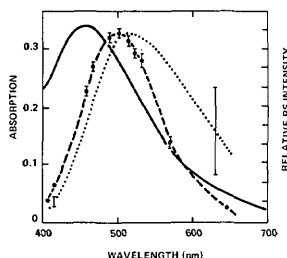


Fig. 1. Nitrobenzoate on silver-island film. Measured absorption (solid line) and excitation (dashed line) spectra and predicted excitation spectrum (dotted line).

The prediction of expression (2) is shown in Fig. 1, in which the values of ϵ reported for bulk silver films¹⁰ are used and the peak of the calculated intensity is normalized to the peak of the measured relative intensity. The error bars reflect the accuracy of the measurements of A , which becomes relatively poor at long wavelengths when the magnitude of A is small. By using high-resolution electron micrographs to estimate the surface area of the silver islands, and taking a monolayer coverage¹¹ of 6×10^{14} molecules/ cm^2 on the silver, the peak enhancement of the signal over nitrobenzoate in solution is measured to be $\sim 10^5$ /molecule. This compares favorably with the value of 2×10^6 calculated using experimentally determined values for all the quantities in expression (2). The agreement with both the spectral behavior and the magnitude of the data is remarkably good considering the simplicity of the model and demonstrates the power of characterizing the optical properties of the film to obtain a quantitative measure of the effects of the plasma resonances on the SERS.

The wavelength shift between the peaks in the absorption and the relative SERS intensity reflects the fact that the absorption is caused by the fields inside the silver islands, whereas the SERS is caused by the local fields at the molecules, outside the islands. The discontinuity at the surface in the normal components of the field results in the $|\epsilon(\omega_L)|^2|\epsilon(\omega_S)|^2$ term in expression (2), which rises rapidly as the wavelength increases and causes the SERS to peak at a longer wavelength than the absorption. This result clearly indicates the necessity of considering the local fields at the molecules themselves and illustrates a shortcoming of any mean-field approach that considers an average field throughout the whole film.

The use of $A(\omega_L)A(\omega_S)$ in expression (2) approximates the spatial average of the product of the local external field-intensity enhancements by the product of the spatial averages. This approximation is valid only if the spectral dependence of $|E_{\text{in}}|^2$ is the same in each island of the film. If there were a significant variation from island to island, the SERS at any excitation frequency would originate from some subset of the islands on the film. The absorption at that frequency would also be dominated by that subset of islands, permitting the use of $A(\omega_L)$ in expression (2). However, the enhancement at the Raman frequency would be determined by the same subset of islands, whereas the absorption at ω_S would reflect the contribution of a different subset, making the use of $A(\omega_S)$ in expression (2) incorrect. In fact, the relatively good agreement obtained with expression (2) suggests that the approximation made in using $A(\omega_L)A(\omega_S)$ is valid. Therefore, the electronic plasma resonances on the individual islands must have approximately the same spectral dependence, and their width must be comparable with the measured width of the absorption of the entire film. Although this is perhaps surprising since in reality there is a distribution of sizes and shapes of islands, the observed broadening can be caused by two effects. Impurity- or disorder-induced scattering of the conduction electrons reduces their mean free path, causing an increased ϵ_2 .¹² In addition, the electrodynamic interactions between the islands and the sub-

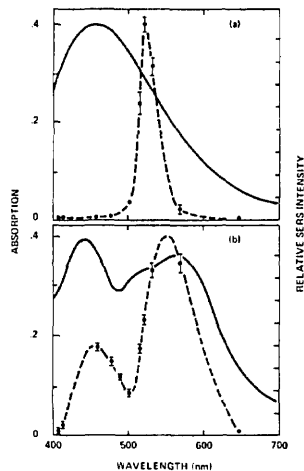


Fig. 2. Absorption (solid line) and excitation (dashed line) spectra for R6G-coated silver-island films. (a) Thin coating and (b) thicker coating.

strate result in an effective broadening and delocalization of the resonance.¹³ In comparison, we note that this spectral homogeneity probably does not exist for the resonance of the individual particles in a colloid, in which much larger interparticle separations result in significantly less broadening because of interactions. Thus the use of the experimentally measured $A(\omega_S)$ in expression (2) would not give good agreement with the measured excitation profiles of colloids.¹⁴

Modifying the local electromagnetic environment around the silver islands will change the behavior of the plasma resonances and therefore alter both the absorption and the SERS excitation profiles. An elegant way of making a continuous alteration of the local electromagnetic environment of the same island films is to coat the films with increasing thicknesses of strongly absorbing dye molecules.¹³ The resonant SERS from the dye molecules themselves can be used for the excitation spectra measurements. For a thin coating of dye, the coverage is so dilute that the electromagnetic environment is barely perturbed and the absorption spectrum is the same as that for an uncoated film, as shown in Fig. 2(a). The excitation spectrum of the 1650-cm^{-1} band of R6G is also shown in Fig. 2(a) and exhibits a resonance similar to that of the nitrobenzoate. However, it is considerably narrower because of the convolution of the molecular resonance RS of the dye molecules themselves with the electromagnetic resonance. When the thickness of the dye layer is increased, the absorption spectrum is radically altered because of the modification of the electromagnetic response of the coated islands, as shown in Fig. 2(b). The SERS excitation spectrum reflects this directly, developing a double peak to match the absorption, further confirming the intimate connection between the electromagnetic origin of optical adsorption and SERS on these films, even in the case of an adsorbate that exhibits resonance Raman scattering.

A similar, although more qualitative, relation between the absorption and SERS excitation spectra can also be obtained for the dye-coated films.¹⁵ It is complicated

by the contribution of the molecular-resonance RS and the significant dispersion in the dielectric function of the coating, and the details will not be presented here. We note, however, that the results indicate that the peak at longer wavelengths in Fig. 2(b) has a significant contribution from the molecular resonance, unlike the shorter-wavelength peak, which is due predominantly to the increased field strength. This accounts for the increased relative height of the long-wavelength peak. Furthermore, despite the existence of aggregates of dye molecules, an equivalent thickness of R6G on glass does not exhibit either sufficient breadth or splitting in its absorption spectrum to account for our observation.

Island films are relatively easy to fabricate and to characterize optically, and therefore they may find considerable use in the application of SERS as a spectroscopic technique. The relationship between the absorption and excitation profiles should prove useful in determining the optimum excitation frequency and in separating the electromagnetic contribution to the total SERS intensity in the search for other possible enhancement mechanisms. Furthermore, these results demonstrate that the field just outside the surface, which causes the SERS, can be considerably larger than the field inside the silver, which causes the absorption. Thus, if the resonance can be pushed still further to the red by controlling the island morphology, even larger external fields will be obtained. This further intensification of the fields may be particularly useful for the study of phenomena strongly dependent on the magnitude of the local electric field, such as multiphoton photochemical effects or nonlinear optical effects.

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