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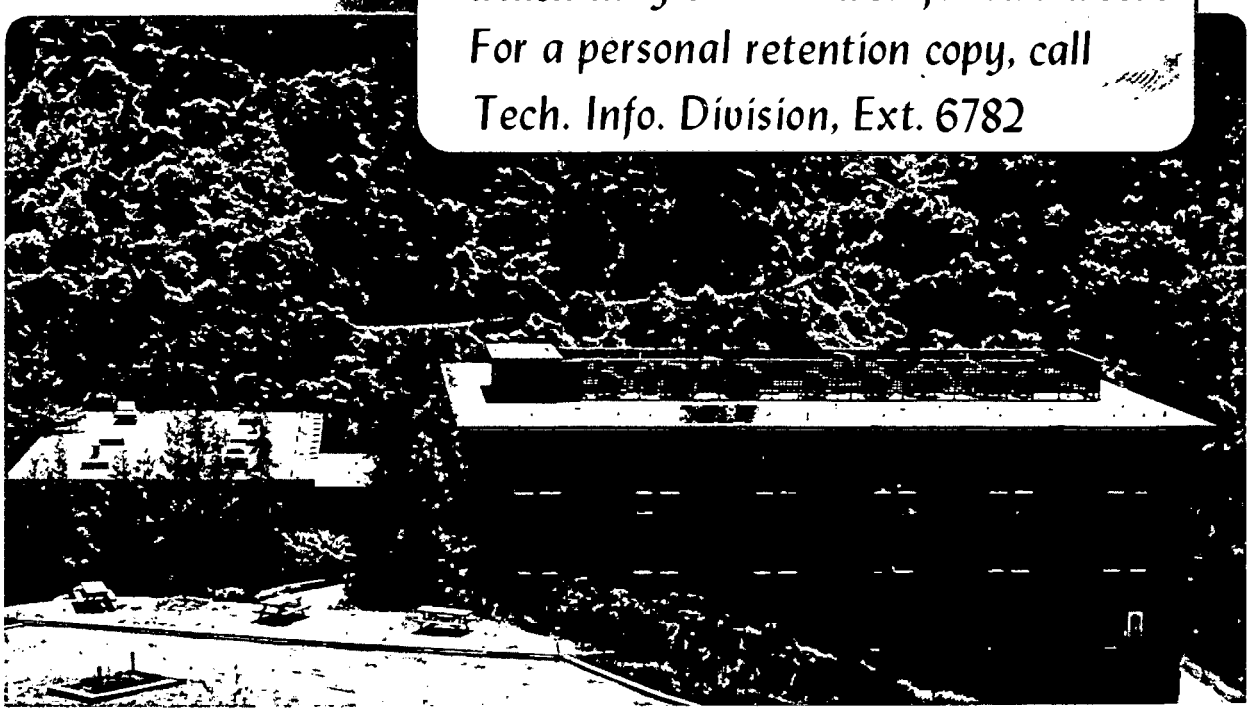

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EFFECT OF EXTENDED SURFACE PLASMONS ON SURFACE ENHANCED RAMAN SCATTERING

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ABSTRACT

Surface enhanced Raman scattering of pyridine adsorbed to weakly roughened silver films is studied using a well-characterized extended surface plasmon excitation. We show that the additional increase in the Raman signal associated with the extended surface plasmon is fully accounted for by the enhancement in the average macroscopic field.

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Surface enhanced Raman scattering (SERS) has recently stimulated a tremendous amount of experimental and theoretical research.[1,2] It is now believed by most researchers that the local field enhancement arising from surface plasmon excitation on rough metal structures is largely responsible for the observation.[3-6] In the literature, however, there is sometimes confusion about enhancement due to localized[3-6] and extended[7] surface plasmon excitation. Localized surface plasmons exist on metal structures with dimensions small compared to a wavelength. Extended surface plasmons occur on macroscopic surfaces with dimensions larger than a wavelength. Both can give rise to enhanced fields and enhanced Raman signals.[5,8] But on a very rough metal surface, it is the former that is mainly responsible for SERS. In this paper, we report an experiment which clearly separates the contribution of extended surface plasmons to SERS from that of localized surface plasmons and metal-molecule interaction.

On a small metal structure, the local field can be generally written as $E_{loc}(\omega) = L(\omega)E(\omega)$, where $L(\omega)$ is the local field correction factor and $E(\omega)$ is the macroscopic field. For a metal sphere with a dielectric constant $\varepsilon_m(\omega)$ immersed in a dielectric medium with a dielectric constant $\varepsilon(\omega)$, we have[4] $L(\omega) \propto (\varepsilon_m - \varepsilon)/(\varepsilon_m + 2\varepsilon)$. At the local surface plasmon resonance, $Re[\varepsilon_m + 2\varepsilon] = 0$, and $L(\omega)$ is resonantly enhanced. For a metal structure of more general shape, $L(\omega) \propto 1/f(\varepsilon_m)$ which is resonantly enhanced when $Re[f(\varepsilon_m)] = 0$. The Raman signal from an adsorbed molecule on a metal structure is given by[4]

$$S \propto L^2(\omega_s)L^2(\omega_\ell)\sigma_R E^2(\omega_\ell)$$

cont'd

$$= \sigma_{eff} E^2(\omega_\ell) \tag{1}$$

where ω_ℓ and ω_s are the laser and Stokes frequencies respectively. We note that the effective Raman cross-section can be enhanced through the resonant enhancement of $L(\omega_\ell)$ and $L(\omega_s)$ and also through the enhancement of σ_R via metal-molecule interaction, although the latter is believed to account for an enhancement factor of less than 100. The enhancement of σ_{eff} over σ_R, $\sim 10^6$ for pyridine on rough Ag, is what is known as SERS. The Raman signal can also be enhanced by increasing the macroscopic field $E(\omega_\ell)$ through, for example, extended surface plasmon excitation.[7,8] This should be distinguished from SERS since it is not an intrinsic property of the system.

Our experiment was designed to show that the extended surface plasmon excitation leads to additional enhancement, instead of being just part of the enhancement in the usual SERS. An extended surface plasmon wave was propagated on an electrolytically cycled Ag surface. Then, from the measured wave propagation properties, the surface macroscopic field $E(\omega)$ could be calculated using a multilayer Fresnel coefficient,[7,9] and the effective Raman cross-section σ_{eff} of the adsorbed molecules could be estimated from the observed Raman signal in comparison with that obtained from the usual Raman excitation geometry. The experimental setup is shown in Fig. 1. The sample cell was made of teflon bounded on opposite sides by a glass window and by an F2 glass equilateral prism, on which a thin layer of Cr ($\sim$ 70 Å) followed by a layer of Ag ($\sim$ 400 Å) had been evaporated. The cell contained 0.1 M KCℓ and 0.05 M pyridine in doubly distilled water, continuously purged with N_2 gas. In addition to the Ag

film electrode, a platinum working electrode and a reference saturated calomel electrode (SCE) were submerged in the cell. After weak electrolytic cycling, pyridine molecules could be adsorbed on the roughened Ag film with a negative silver-SCE potential, V_{Ag-SCE}. The entire cell-prism assembly was mounted on a rotation table controlled by a stepping motor. Excitation of extended surface plasmons on the Ag-liquid interface using the Kretschmann attenuated total internal reflection (ATR) geometry could then be monitored by measuring the reflectivity from the prism side as a function of angle, and the intensity of the surface plasmon field could be calculated from the reflectivity curve.[7,9] We used a p-polarized Ar^+ laser beam at 5145 Å with a beam cross-section of 3 mm × 0.25 mm at the Ag-liquid interface for excitation. The extended surface plasmon field induced Raman scattering from the adsorbed pyridine molecules. The scattered light was collected through the glass window, approximately along the normal of the metal film, and was detected and analyzed by a spectrometer-photomultiplier-photon counting system. This signal was compared to that induced by an alternative beam, as illustrated in Fig. 1, which could be blocked or unblocked, and focused to the same spot on the Ag film from the liquid side so that negligible coupling to the extended surface plasmon occurred. We concentrated on the 1005 cm^{-1} mode of pyridine. If the extended surface plasmon did not contribute to SERS, then the ratio of the two Raman signals should be simply proportional to the intensity ratio of the extended surface plasmon to the beam excitation from the liquid side.

For a freshly evaporated metal film, the experimental reflectivity measured from the prism side as a function of the angle of incidence is

shown in Fig. 2a, together with the theoretical fit calculated from a three interface Fresnel coefficient, with dielectric constants $\varepsilon_p = 2.652$, $\varepsilon_{Cr} = -2.75 + i\,25.7$, $\varepsilon_{Ag} = -10.66 + i\,0.81$, and $\varepsilon_\ell = 1.814$, and film thicknesses $d_{Cr} = 70$ Å and $d_{Ag} = 402$ Å, where the subscripts p and ℓ refer to the prism and liquid respectively. The optimum extended surface plasmon excitation and the maximum field enhancement, $|E_{esp}/E_p|^2_{max} = 17$, at the metal-liquid interface occur near the reflectivity minimum, but slightly shifted, mostly as a result of the presence of the lossy Cr layer,[10] where the subscript esp refers to the extended surface plasmon. Before any electrolytic cycling, no Raman signal was observed with the extended surface plasmon excitation, and only a weak Raman signal arising from the pyridine (.05 M) in solution was observed with the conventional liquid-side excitation. Then, a single oxidation-reduction cycle was performed, with a total charge transfer of ~ 4.7 mCoul/cm^2 corresponding to an average removal and redeposition of ~ 20 layers of Ag. Following the electrolytic cycle, although the cosmetic appearance of the film was unchanged, the amount of elastically scattered light visibly increased, and the ATR reflectivity curve of the multilayer system appeared somewhat broader, as illustrated in Fig. 2b.[11] Also, over the subsequent period of 24 hours, there was no further broadening and very little change in the ATR curve. In fitting the reflectivity curve shown in Fig. 2b, the weakly roughened metal film was modeled by introducing a thin "rough" layer at the metal-liquid interface, with a thickness ~ 26 Å and a complex dielectric constant $\varepsilon = 1.52 + i\,1.12$, and by reducing the thickness of the Ag film to $d_{Ag} = 336$ Å. We believe that the deviation between the theoretical fit and the experimental curve, as well as the low value of

d_{Ag} results from 1) an oversimplified model of the roughened silver surface and/or 2) the assumption that both absorption and elastic scattering can be modeled by a non-zero angle-independent imaginary part of ε. Nevertheless, the value of $|E_{esp}/E_p|^2_{max} = 5.5$ is relatively insensitive to the particular parameters used to fit the ATR reflectivity curve, as long as the angular width and minimum reflectivity, corresponding to the damping of and the coupling to the extended surface plasmon approximately match the experimental values.[12]

Following the electrolytic cycle, both the conventional liquid-side excitation and the extended surface plasmon excitation gave rise to a large SERS signal, displaying the same dependence on V_{Ag-SCE}, in agreement with that reported by Jeanmaire and Van Duyne.[1] In addition, the ratio of the two SERS signals as a function of V_{Ag-SCE} was constant to within 4%, demonstrating that both techniques probed the same adsorbed molecules. Further confirmation that the SERS signals originated from the adsorbed molecules was provided by the following measurement. The Raman enhancement disappeared after the electrolytically cycled film was irradiated with five successive pulses of ~ 16 mJ/cm^2 Q-switched ruby laser pulses incident from the prism side at the angle for optimal extended surface plasmon excitation. The heat generated in the film by the irradiation presumably dislodged the adsorbed molecules. The desorption was irreversible, while the effect of the irradiation on the non-adsorbed molecules should have been reversible.

By comparing the Raman signal at $V_{Ag-SCE} = -0.6$ V before and after the weak electrolytic cycle using the conventional liquid-side excitation, we estimated that $\sigma_{SERS} \sim 10^4 \sigma_R$, assuming a uniform layer of adsorbed

molecules. This relatively weak enhancement, about two orders of magnitude smaller than that reported by Jeanmaire and Van Duyne[1] is a result of the weaker oxidation-reduction cycle. With stronger cycles of ~ 50 mCoul/cm^2 on bulk Ag samples, we also observed SERS enhancements of $\sim 10^6$.

To assess the contribution of the extended surface plasmon field enhancement, we monitored the Raman signal with the prism-side excitation as a function of the angle of incidence θ, or equivalently, of the intensity of the extended surface plasmon. The ratio of this Raman signal to that measured from the liquid-side excitation is given by $|E_{esp}/E_p|^2 \times \sqrt{\varepsilon_\ell/\varepsilon_p}$, assuming the same incident laser fluences in the prism and the liquid and the same excitation areas on the film, and is plotted versus θ in Fig. 3. The experimental data had an overall uncertainty of 50%, resulting mostly from the uncertainty in the overlap of the excitation areas. The theoretical curve in Fig. 3, using $|E_{esp}/E_p|^2(\theta)$ calculated from the measured reflectivity curve in Fig. 2b, shows good agreement with the experimental data, in the position, width, and absolute magnitude, within the experimental uncertainty. The small shift of $\sim 0.5°$ between the theoretical and experimental curves is most likely the result of our oversimplified model of the rough silver film. The good agreement in the maximum value of $|E_{esp}/E_p|^2$ between the theory and experiment unambiguously demonstrates that the increase of the Raman signal associated with the extended surface plasmon excitation supplements the existing SERS signal and can be completely understood by the enhancement of the average macroscopic field at the metal-liquid interface. This result makes it improper to invoke a SERS mechanism involving an extended surface plasmon.

Additional cycles of 4.7 mCoul/cm^2 in our experiment broadened the extended surface plasmon dip in the reflectivity curve beyond recognition and hence reduced the value of $|E_{esp}/E_p|^2$. Yet, using the prism-side excitation, the SERS signal continued to increase in strength, presumably because of the increased surface roughness. This result again supports the picture that extended surface plasmons do not contribute to the usual SERS.

We now mention a number of other related observations in our experiment using extended surface plasmon excitation. First, a broad luminescent background[13] was always observed, with or without pyridine in the electrolytic solution. Its intensity increased with electrolytic cycling in agreement with the literature. Second, by rotating the input polarization from p to s, the Raman signal decreased by ~ 50 to 100 times, in general agreement with the decrease of the estimated exciting beam intensity at the silver-liquid interface. Third, with a p-polarized input, the polarization properties of the elastically scattered and Raman scattered light were measured before and after a single electrolytic cycle. Before cycling, the ratio of p to s polarized elastically scattered light was greater than 30 to 1. After cycling, it was still 4 to 1, in contrast to the Raman scattered light which was totally unpolarized. This indicates that multiple scattering arising from the surface roughness was not the cause of the Raman depolarization. Instead, the random orientation of the adsorbed molecule is most likely the explanation for the depolarization. Fourth, the enhanced Raman signal from the adsorbed molecules was also detected on the prism side, in the general direction expected for extended surface plasmon coupling at the Stokes frequency.[14] Finally, in a separate experiment using the same weakly cycled silver film as used for the

SERS measurements of Fig. 3, we observed 5×10^2 enhancement in the second harmonic signal[6] from the rough silver-air interface, instead of 10^4 from a strongly cycled rough Ag surface, in comparison to that from a smooth silver-air interface. This relatively weak surface enhanced second harmonic signal is consistent with the relatively weak 10^4 SERS enhancement, and is presumably a result of the weak electrolytic cycle creating a relatively less rough Ag surface.

In conclusion, we have shown that surface enhanced Raman scattering can be studied by a well-characterized extended surface plasmon excitation on an electrochemically processed silver film. The additional increase in the Raman signal associated with the extended surface plasmon is fully accounted for by the enhancement in the average macroscopic field at the metal-liquid interface.

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10. The presence of the Cr layer, which was necessary for the adherence of the metal film to the prism, also reduced the maximum value of $|E_{esp}/E_p|^2$ by approximately a factor of two.

11. We note that Pettinger et al. of Ref. 8 have used extended surface plasmon excitation to study the same material system. However, in that paper, the authors stated that the optical properties of their silver film substantially deteriorated during the electrolytic cycle. Furthermore, no experimental ATR curves were presented, and no attempt was made to quantify the contribution of the extended surface plasmon field enhancement to the overall Raman signal.

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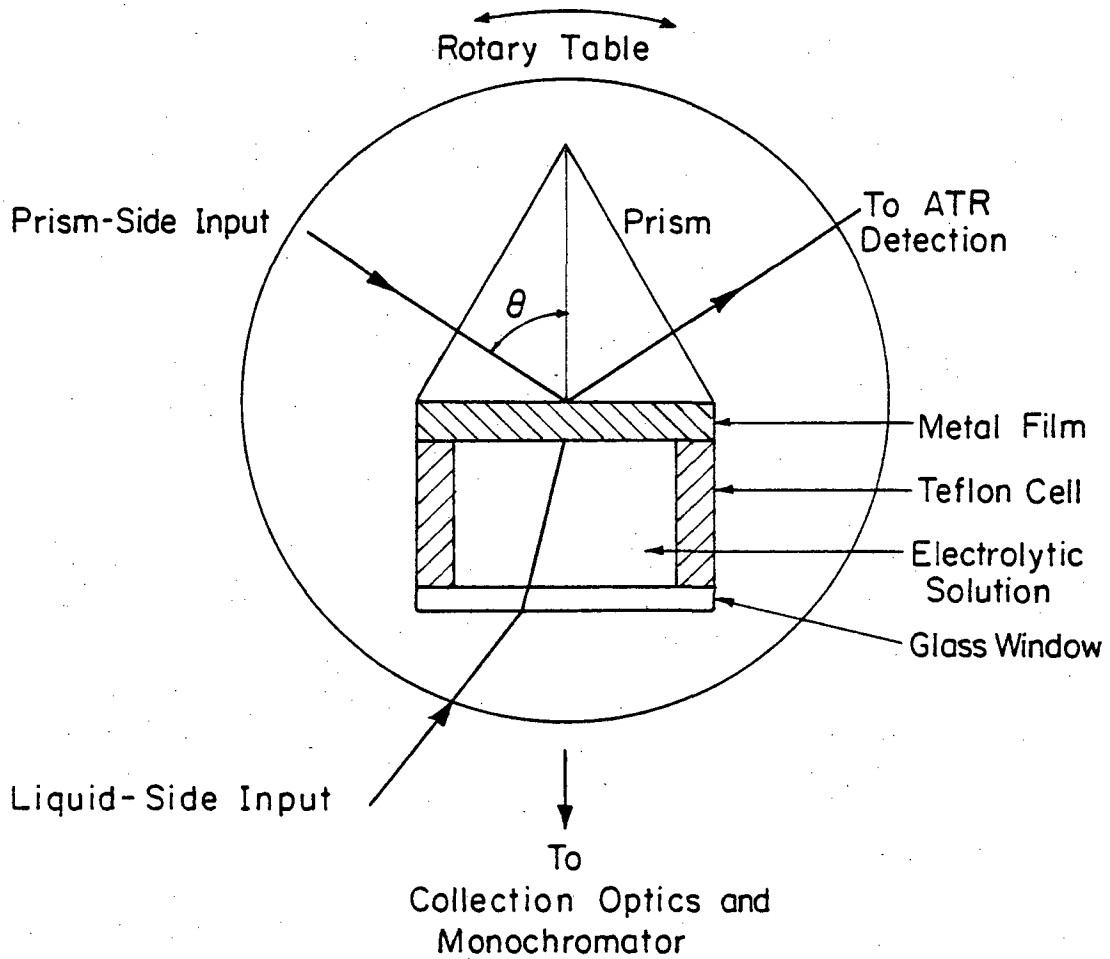
Figure Captions

Fig. 1 Schematic of the experimental setup. The angle of incidence, θ, is defined at the prism-metal film interface.

Fig. 2 Reflectivity (absolute) of the prism-metal film-liquid assembly, a) before and b) after a weak electrolytic cycle, versus θ. The solid curve is the experimental data and the dots show the theoretical fit to the data.

Fig. 3 Experimentally measured ratio of SERS signals of prism-side to liquid-side excitation (dots), and calculated $|E_{esp}/E_p|^2$ (solid curve) versus θ.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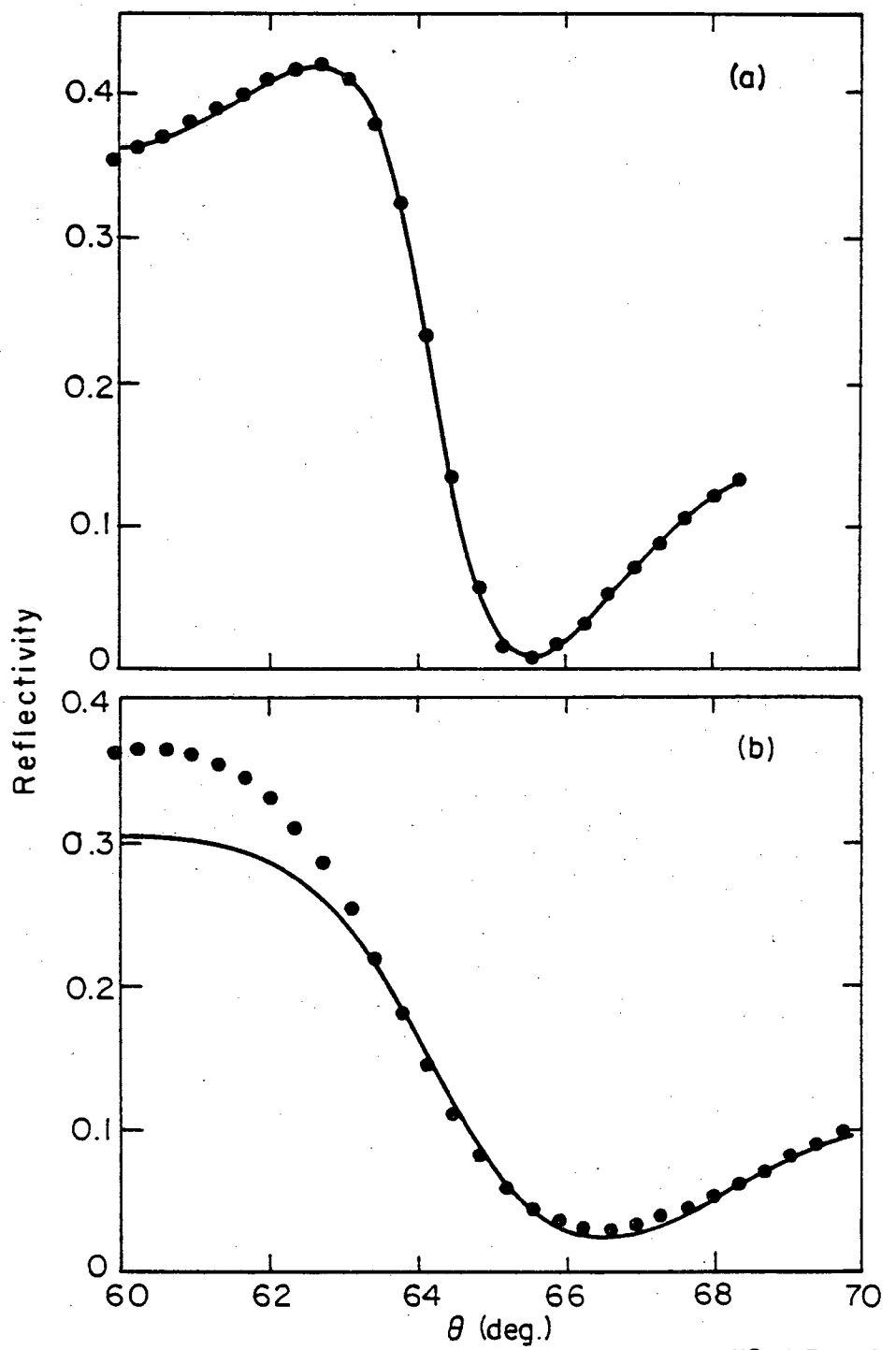

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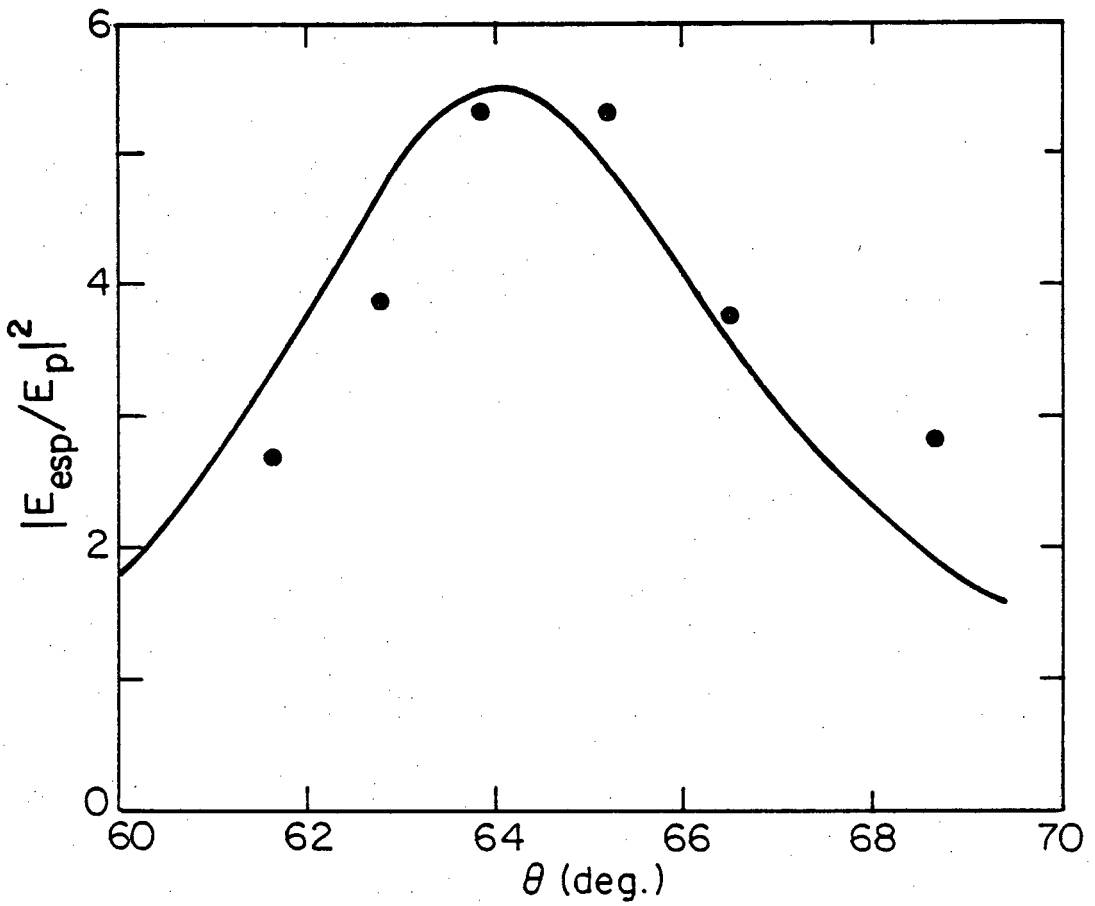

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