Frequency Shifts of an Electric-Dipole Resonance near a Conducting Surface

W. R. Holland and D. G. Hall

The Institute of Optics, University of Rochester, Rochester, New York 14627

The resonance frequency of an electric dipole placed near a conducting surface is shifted by the dipole-surface interaction. This Letter reports the observation and measurement of these shifts at optical frequencies for an experimental system that consists of a metal island film spaced a distance d from a continuous Ag film. The dependence of the shift in the frequency of the island resonance on d shows good agreement with that predicted by a classical theory of the dipole-surface interaction.

The interaction between electromagnetic radiation and an electric dipole is a fundamental process in physics. When the dipole is placed within a few wavelengths of a conducting surface, the major features of the interaction are changed from those observed for an isolated dipole. Experiments at optical frequencies have demonstrated (1) the strong dependence of the molecular fluorescent decay rate on the separation between a molecule and a metal surface,[1] (2) the transfer of energy between molecular dipoles and surface plasmons on the metal surface,[2-4] and (3) the ability of the dipole-surface interaction to enhance the strength of such processes as molecular Raman scattering[5] and molecular fluorescence.[6] In addition to these three effects, theoretical treatments of the problem also predict the existence of a shift in the dipole's resonance frequency.[7-12] This frequency shift is a universal feature of the dipole-surface interaction and, in simple terms, results from the coupling between the dipole and its own image in the metal surface. In spite of the fact that these frequency shifts should appear for both microscopic and macroscopic dipoles, there have been no reports of their observation, perhaps because their magnitudes are predicted to be quite small for the typical metal-molecule system as a result of the narrow linewidths associated with molecular resonances.[8]

This Letter reports the results of optical-frequency experiments on a dipole-metal system that exhibits resonance-frequency shifts that we attribute to the dipole-surface interaction. The observation of these shifts is significant because it confirms a previously untested feature of the theory, and because it reveals an important aspect of a class of sample geometries of widespread interest in the study of surface phenomena. Our sample geometry is shown in Fig. 1 and consists of a three-layer structure deposited on a glass substrate. First, a continuous silver film of thickness 50 nm was evap-

orated onto a glass substrate. After partial masking with a movable shutter, a lithium fluoride (LiF) spacer layer of thickness d was deposited over a portion of the silver surface. Further masking preceded the slow (0.5 Å/sec) deposition of either a silver or gold island film of mass thickness 3 nm (the mass thickness is the value determined by a quartz-crystal film-thickness monitor). The samples were prepared by thermal evaporation in an oil-free, cryogenically pumped ultrahigh vacuum system at pressures in the 10^{-8}-Torr range. Each three-layer structure was prepared without breaking vacuum, but all subsequent measurements were made in the ambient laboratory atmosphere. When gold islands were used, the sample was always baked at 300°C for 1 h in flowing nitrogen to sharpen the spectral resonance feature. Transmission measurements on witness samples showed that the silver (gold) island films display the familiar anomalous absorption at $\lambda_0 \cong 400$ nm ($\lambda_0 \cong 540$ nm) that is characteristic of localized plasma resonances.[13] This geometry was used in previous experiments directed toward an examination of the surface plasmon dispersion relation,[14] and Aravind and Metin suggested a similar geometry (small sphere above a planar interface) for use in surface-
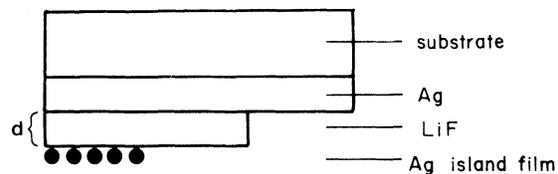
FIG. 1. Cross section of three-layer sample geometry used in the present experiment. The continuous silver film has a thickness of 50 nm. The thickness of the LiF spacer layer, d, was varied between 5 and 80 nm. The silver island film had a mass thickness of 3 nm.

enhanced spectroscopy.[11] The structure shown in Fig. 1 gave highly reproducible results; no discernible change in the properties of the island films was found over several deposition cycles with the same sample parameters.

The geometry shown in Fig. 1 is typical in form of that used to study the optical properties of molecules near surfaces. Our replacement of the molecular layer with an island film retains the qualitative features of the former, but alters the quantitative details considerably. The localized plasma resonances in the constituents of an island film are primarily dipole in nature,[15] but each island has a diameter in the range of a few hundred to a thousand angstroms and a dipole moment in the vicinity of $1000ea_0$ (e is the electronic charge and a_0 is the Bohr radius).[16] In addition, the island resonance is a broad resonance with a width of 10^{14}–10^{15} Hz, broadened by radiation damping[17] and by interactions among neighboring particles.[13] Finally, as is well known, the island resonances interact strongly with the radiation field and produce amplified local electric fields that can enhance a variety of optical processes.

To investigate the spectral characteristics of the structure shown in Fig. 1, we measured the near-normal reflectance (with light incident on the island side) of several samples with a Perkin-Elmer Model 330 scanning spectrophotometer. Two measure-

ments were made on each sample: (1) R_1, the near-normal reflectance of the substrate/Ag/LiF combination, and (2) R_2, the near-normal reflectance of the substrate/Ag/LiF/island combination. Figure 2 shows plots of R_2/R_1 versus the wavelength λ for three Ag-island structures, each with a different spacer-layer thickness d. The decrease in the ratio near $\lambda = 400$ nm is caused by the strong absorption of the island film. In the absence of a silver underlayer, the island resonance occurs at the wavelength $\lambda_0 \cong 400$ nm. Figure 2 shows that this resonance is shifted from λ_0, first to shorter wavelengths and then to longer wavelengths as d decreases. The fact that the absorption feature is deepest for an intermediate thickness $d \cong 25$ nm was reported in our previous paper. Figure 3 plots the measured wavelength shift $\Delta\lambda \equiv \lambda - \lambda_0$ versus the spacer thickness d for Ag-island samples which were annealed slightly to insure well formed islands with sharp spectral features.

Approximating the metal sphere as a point dipole oscillator driven by its own image field reflected from the surface, the effective polarizability of the dipole is given by

$$\alpha_{\text{eff}} \equiv \frac{\alpha_0}{1 - E_r\alpha_0/p}, \tag{1}$$

where α_0 is the polarizability with no surface present, p is the dipole moment, and E_r is the re-
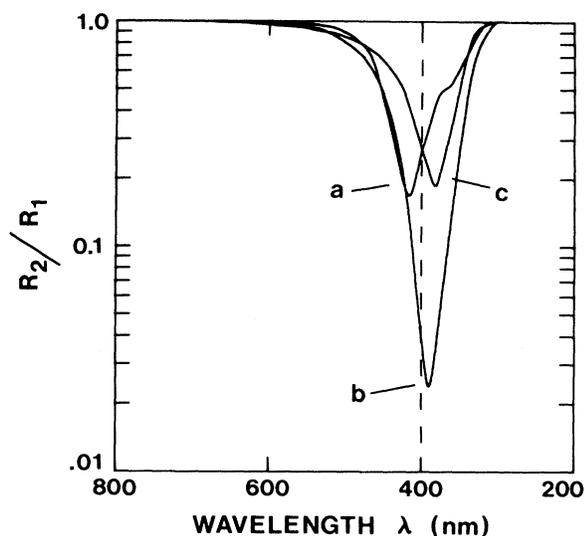
FIG. 2. Measured specular reflectance of silver-island samples R_2 (normalized by Ag-LiF reflectance R_1) as a function of wavelength for three different values of spacer-layer thickness d. The minima near $\lambda = 400$ nm correspond to absorption by the silver islands. Curve a, $d = 8$ nm; curve b, $d = 27$ nm; curve c, $d = 46$ nm.
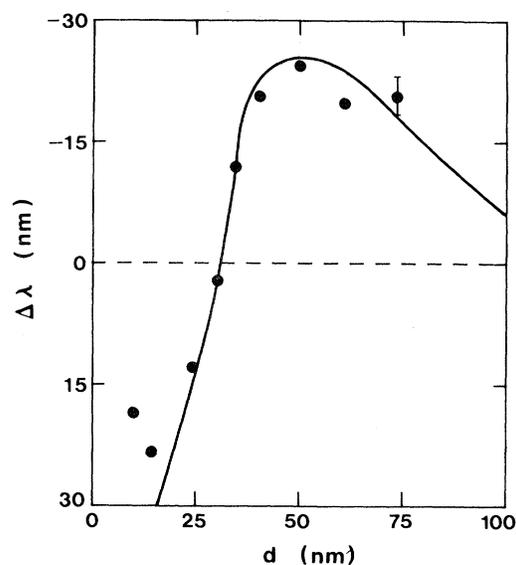
FIG. 3. Variation of observed silver-island resonance wavelength shift $\Delta\lambda \equiv \lambda - \lambda_0$ with spacer-layer thickness d. The solid curve is the wavelength shift predicted by classical theory.

flected field at the dipole location. We represent α_0 with a Lorentzian line shape centered at λ_0 and calculate E_r using procedures outlined by Chance, Prock, and Silbey.[7] Dielectric constants for silver are obtained from Johnson and Christy.[18] The solid curve in Fig. 3 is the predicted wavelength shift with the assumptions of a dipole moment of $\sim 1000ea_0$, a width of 10^{15} Hz, and an island radius of 570 Å.[19] We believe that the deviation for thicknesses less than 10 nm is due to the poor quality of the evaporated LiF layers in this range. The agreement between theory and experiment is quite good, both in terms of the overall shape of the curves and the existence of a zero crossing.

Because the Ag-island absorption resonance near $\lambda = 400$ nm falls very close to the asymptotic surface plasmon wavelength for silver at $\lambda = 350$ nm, we replaced the Ag islands with Au islands and thus a resonance further removed from the surface plasmon wavelength. This is important for two reasons. First, the theory of Chance, Prock and Silbey[8] predicts that the magnitude of the resonance-shift will decrease as one moves away from $\lambda = 350$ nm. Second, it is possible for the islands to act as surface roughness and couple the incident radiation to the surface plasmon; it is important to guarantee the existence of two separate mechanisms. The results for Au islands are shown in Fig. 4 for three values of $d \ll \lambda$. For the largest spacer thickness, we find a single feature due to the Au islands peaked near $\lambda = 540$ nm with the suggestion of a shoulder on the short-wavelength side. With decreasing d, the absorption maximum shifts to longer wavelengths and a second feature grows near $\lambda = 350$ nm. As expected, the wavelength shifts associated with the resonance near 540 nm are much smaller than those for the Ag-island case. For the smallest value of d, the Au-island resonance has been quenched appreciably by near-field absorption processes and the islands are now close enough to the metal to act as (short-wavelength) surface roughness and mediate coupling to the surface plasmon. These data provide conclusive evidence for the existence of two distinct absorption processes in our samples. In fact, returning briefly to Fig. 2, we see that a shoulder appears on the short-wavelength side of the absorption feature corresponding to the smallest value of d. This shoulder is most certainly due to surface-roughness–induced coupling to the surface plasmon, an effect that is also predicted by Eq. (1) for sufficiently small values of d.

In summary, the electric dipole resonances (localized plasma resonances) supported by the con-
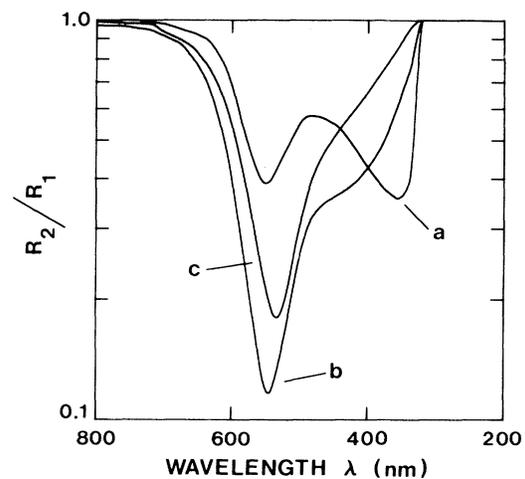
FIG. 4. Measured specular reflectance ratio R_2/R_1 (obtained as in Fig. 2 only with gold islands replacing the silver islands) as a function of wavelength for three values of spacer-layer thickness d. The minima near $\lambda = 540$ nm correspond to absorption by the gold islands. The minimum near $\lambda = 350$ nm which grows with decreasing d is associated with coupling to the surface plasmon via islands giving the effect of surface roughness. Curve a, $d = 21$ nm; curve b, $d = 41$ nm; curve c, $d = 51$ nm.

stituents of metal island films experience a frequency shift when placed in close proximity to a conducting surface. We have observed and measured these shifts as a function of the island-surface separation d and found that the results agree quite well with the predictions of a classical theory of the dipole-surface interaction. In the case of Ag islands near a silver surface, the bare-resonance wavelength $\lambda_0 \cong 400$ nm is shifted by as much as 20 nm as a result of the small wavelength difference (≈ 50 nm) between the island resonance and the surface plasmon ($\lambda_{sp} = 350$ nm). In the case of Au islands near a silver surface, the island resonance is separated from λ_{sp} by nearly 200 nm resulting in much smaller resonance shifts, as predicted by the theory of Chance, Prock, and Silbey.[8] We hope that these observations will stimulate theoretical treatments of the dipole frequency-shift problem that move beyond the point-dipole approximation.

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