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Raman scattering mediated by surface-plasmon polariton resonance

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We have measured the enhanced Raman scattering by a liquid (methyl alcohol) in contact with an evaporated film of silver (~400 Å) deposited on the flat surface of a hemispherical prism. The exciting laser light (5145 Å) was incident on the film through the prism and the scattered light from the liquid was collected also through the prism. The Raman-scattering intensity is a sharp function of both the incident and the scattered angles. The observed angular dependence of the Raman intensity can be fitted remarkably well by assuming that the enhanced scattering process is mediated by surface-plasmon polaritons at the silver-liquid interface. The observed scattering intensity is consistent with the predicted enhancement factor of 4×10^4.

In a three-layered geometry with a thin metal film sandwiched between two dielectrics, the normal modes of surface electromagnetic waves (SEW) are two branches of surface-plasmon polaritons (SPP).[1] Here we are interested in a geometry involving a glass (BK-7) prism, a silver flim (~400 Å), and a liquid (methyl alcohol), the so-called Kretchmann configuration shown in Fig. 1. Let us designate the three media, glass, silver, and alcohol, by medium 1, 2, and 3, respectively, and their dielectric constants by ϵ_1, ϵ_2, and ϵ_3. The dielectric constants for BK-7 glass and methyl alcohol are essentially frequency independent and positive in the range of interest. The dielectric constant of silver ϵ_2 is frequency dependent, complex, and its real part is negative. Figure 2 illustrates only the upper branch of SPP whose dispersion curve is given by[1]

$$\left(1+\frac{\alpha_1\epsilon_2}{\alpha_2\epsilon_1}\right)\left(1+\frac{\alpha_2\epsilon_3}{\alpha_3\epsilon_2}\right)+e^{-2\alpha_2 d}\left(1-\frac{\alpha_1\epsilon_2}{\alpha_2\epsilon_1}\right)\left(1-\frac{\alpha_2\epsilon_3}{\alpha_3\epsilon_2}\right)=0 \ , \tag{1}$$

where

$$\alpha_i=(k_{\parallel}^2-\epsilon_i\omega^2/c^2)^{1/2} \ . \tag{2}$$

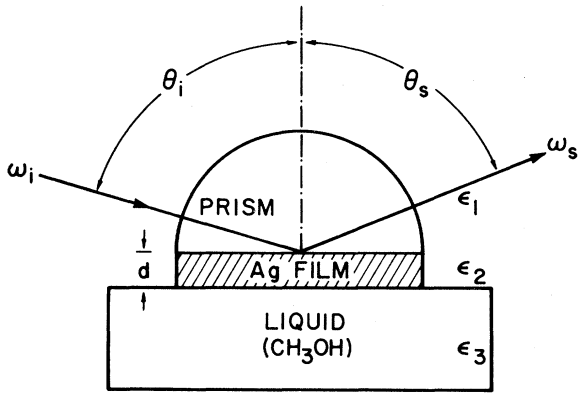

FIG. 1. Kretchmann geometry used in this experiment.

$k_{\parallel}$ is the wave vector of SPP along the interfaces and d is the thickness of the metal film. Since the dielectric constant of the BK-7 glass ($\epsilon_1=2.30$) is greater than the dielectric constant of methyl alcohol ($\epsilon_3=1.76$), the upper branch is mostly localized at the silver-alcohol interface and is leaky into the prism on the left-hand side of the light line for the prism, $\omega=ck_{\parallel}/\sqrt{\epsilon_1}$.

In this situation an incident beam of light from the prism side at frequency ω_i can be injected into the upper SPP branch. The maximum injection efficiency is obtained when the angle of incidence θ_{i0} satisfies the condition

$$k_{\parallel i}=\frac{\sqrt{\epsilon_1}\omega_i}{c}\sin\theta_{i0} \ , \tag{3}$$

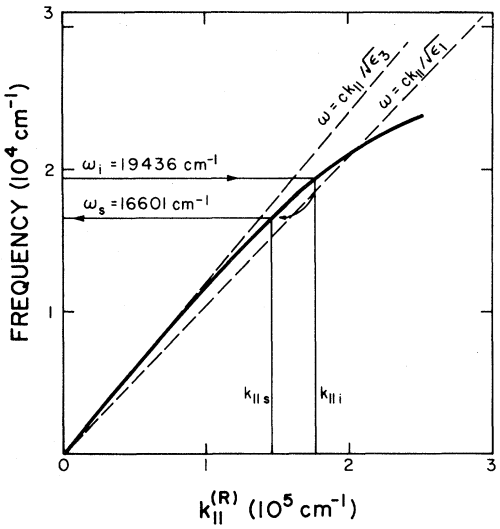

FIG. 2. Dispersion curve of the upper SPP branch. The two broken lines are the light lines for BK-7 glass and methyl alcohol. The arrows indicate the Raman-scattering process. $k_{\parallel}^{(R)}$ is the real part of the wave vector $k_{\parallel}$ parallel to the interfaces.

where $k_{\|i}$ is the value of $k_{\|}$ at ω_i on the dispersion curve of the upper branch as indicated in Fig. 2. When Eq. (3) is satisfied, the injection efficiency can exceed 95%; i.e., most of the energy of the incident volume electromagnetic wave (VEW) is converted into that of an SEW in the form of SPP in this case. The electromagnetic field of the upper branch of SPP extends into the liquid, diminishing exponentially away from the metal-liquid interface. This evanescent field in the liquid is scattered by molecular vibrations of the liquid, and the light from the scattered SPP is emitted through the prism at a scattering angle θ_{s0} defined by

$$k_{\|s}=\frac{\sqrt{\epsilon_1}\omega_s}{c}\sin\theta_{s0} \ , \tag{4}$$

where the scattered frequency ω_s is determined by the vibrational frequency of the liquid molecules Ω_0, according to $\omega_s=\omega_i-\Omega_0$; and $k_{\|s}$ is the wave vector of the scattered SPP at ω_s. This scattering process is indicated in Fig. 2 by a curved arrow.

The theory of this light scattering process was originally formulated by Chen, Chen, and Burstein,[2] and a similar theory was presented more recently by Sakoda, Ohtaka, and Hanamura.[3] A related experiment to the present one was reported by Pettinger, Tadjeddine, and Kolb[4] who injected the incident light at θ_{i0} from the prism side and measured the scattered light on the liquid side. According to both theories the enhancement factor is much greater if the scattered light is measured on the prism side. A CARS (coherent anti-Stokes Raman spectroscopy) experiment using SPP in a similar Kretchmann geometry was reported by Chen, de Castro, Shen, and DeMartini.[5] The two experiments cited above, as well as the present experiment, measure basically the same effect of the enhanced electromagnetic fields near the surface of a metal due to resonant excitation of SPP. In this regard the work by Tsang, Kirtley, and Theis[6] should also be noted. They injected VEW into SPP and induced the emission of VEW by the scattered SPP by means of a grating created on the surface of a metal.

In the experiment reported here, we have measured the Raman intensity of the 2835-cm^{-1} vibrational line of methyl alcohol as a function of the incident angle θ_i and the scattered angle θ_s. According to Eq. (1), the wave vector of the injected SPP at the 5145-Å line of an argon ion laser, $\omega_i=19436\ cm^{-1}$, is $k_{\|i}=1.78\times10^5\ cm^{-1}$, and the wave vector of the scattered SPP at $\omega_s=16601\ cm^{-1}$ is $k_{\|s}=1.47\times10^5\ cm^{-1}$. Using Eqs. (3) and (4), we find the optimum injection angle $\theta_{i0}=72.6°$ and the optimum scattering angle $\theta_{s0}=68.0°$. In calculating the dispersion curve of Eq. (1), we have used the actual values of $\epsilon_2=\epsilon_2(\omega)$ for silver measured by Johnson and Christy[7] and the silver film thickness, $d=400$ Å.

The silver film was evaporated on the flat surface of a semispherical prism made of BK-7 glass ($n=1.518$) at the rate of ~100 Å/min in a vacuum evaporator at $\sim10^{-6}$ Torr. The film thickness was monitored by a quartz oscillator thickness gauge. Raman-scattering experiments were carried out at room temperature using the 5145-Å (19436-cm^{-1}) line of an argon-ion laser as the exciting source. The power level was approximately 50 mW CW. The scattered light was collected through an angle defining aperture of a rectangular shape ($1.5\times4.0\ mm^2$) at 10 cm from the bottom surface of the prism. The Raman intensity of the 2835-cm^{-1} line of methanol was measured as a function of the incident angle θ_i and the scattered angle θ_s. The Raman spectra obtained for a fixed incident angle at $\theta_i=\theta_{i0}$ are shown in Fig. 3 for different scattering angles. We see that the maximum intensity is obtained when $\theta_s=\theta_{s0}$. The measured values of θ_{i0} and θ_{s0} were $\theta_{i0}=73.0°\pm1°$ and $\theta_{s0}=68.0°\pm0.5°$. These values agree with the predicted values of 72.6° and 68.0°, respectively, within the uncertainties of the angular measurements. Similar spectra to those in Fig. 3 were measured for a fixed scattering angle at $\theta_s=\theta_{s0}$ and for different incident angles θ_i. The intensity data obtained from the scans with a fixed value of

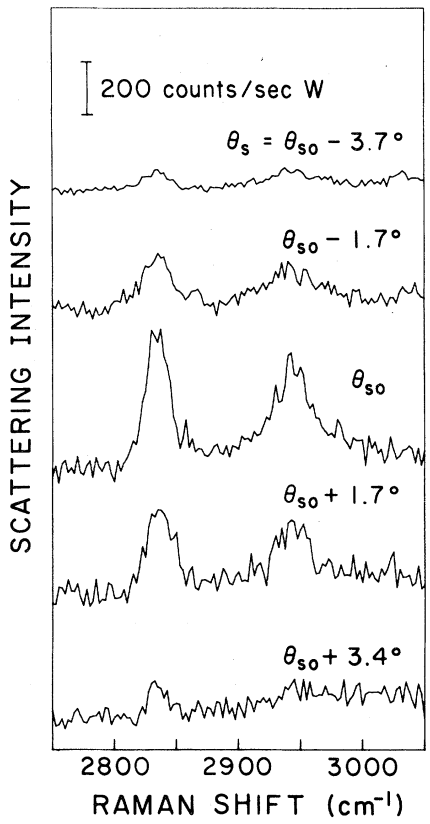

FIG. 3. Sample Raman spectra of methyl alcohol for a fixed incidence angle $\theta_i=73.5°$ and for different scattering angles θ_s. We use the peak height of the 2835-cm^{-1} line.

$\theta_i = \theta_{i0}$ and $\theta_s = \theta_{s0}$ as a function of θ_s and θ_i, respectively, are plotted in a normalized scale in Fig. 4. For both cases the intensities are normalized at the maximum value. In order to facilitate comparisons with theoretical predictions, we have displaced the data points by $-0.4°$ for θ_i. We note that the spread for the incident angle θ_i is considerably greater than the spread in the scattered angle θ_s, and that the broadening observed for θ_i is noticeably asymmetric.

The solid curves are the calculated angular intensity distributions at $\omega_s = 16\,601$ cm^{-1} and $\omega_i = 19\,436$ cm^{-1}. We used the equation

$$|E(\theta)|^2 = A \cot^2\theta \left|\frac{\alpha_1}{\alpha_3}\right|^2 \frac{\exp[-2(\mathrm{Im}\alpha_2)z_0]}{|D(k_{\|},\omega)|^2} , \quad (5)$$

where A is a normalization constant; θ is the incident or scattered angle; $D(k_{\|},\omega)$ is the left-hand side of the dispersion relation, Eq. (1); and z_0 is the distance from the silver-liquid interface to the scattering molecule which was set arbitrarily at 2500 Å for the curves shown in Fig. 4. (The shapes of the normalized theoretical curves do not depend on the specific value of z_0.) Equation (5) was derived by applying the Green's functions, reported by Laks and Mills[8] and by Mills and Maradudin,[9] to the present geometry. $|E(\theta)|^2$ in Eq. (5) is identical to $|\Gamma^{P_0}_{cb\xi\nu}|^2$ and $|G^{P_0}_{bc\alpha\beta}|^2$ given by Chen *et al.*[2] and to $|\vec{\Pi}_3|^2$ given by Sakoda *et al.*[3] in its angle dependent features. We note that the angle dependence of Eq. (5) is contained explicitly in $\cot\theta$ and implicitly in $k_{\|}$ through the relation

$$k_{\|} = \frac{\sqrt{\epsilon_1}\omega}{c}\sin\theta . \quad (6)$$

Equation (5) can be interpreted in two ways. When we fix the incident angle, making the incident field intensity at the scattering molecule constant, $|E(\theta_s)|^2$ represents the angular dependence of the scattered light intensity in the prism. On the other hand, when we fix the scattering angle, we can interpret $|E(\theta_i)|^2$ to represent the incident angle dependence of the light intensity at the scattering molecule. In both cases $|E(\theta)|^2$ is proportional to the measured Raman intensity through the prism.

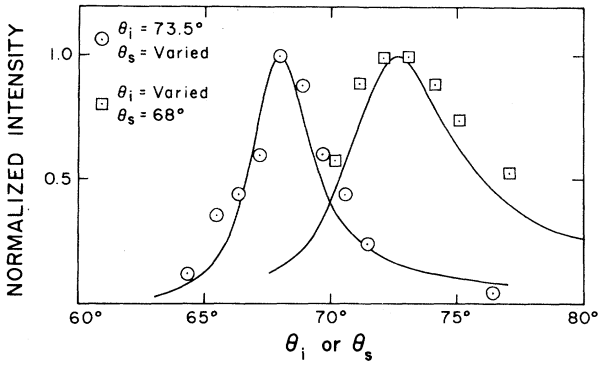

FIG. 4. Incident or scattered angle vs normalized intensity. The squares are for a fixed scattered angle and varied incident angles, and the circles are for a fixed incident angle and varied scattered angles. The solid curves are calculated from Eq. (5) and normalized to one at the maximum value.

The two theoretical curves in Fig. 4 were calculated, using the interpolated values of n and κ for silver obtained by Johnson and Christy.[7] We see that the data points for both θ_i and θ_s agree quite well with the theory. The agreement is quite remarkable, since there is no adjustable parameter other than the absolute scattering intensity. It is interesting to note that the data points show a slightly broader angle profile than the theory. We believe that this extra broadening arises from extrinsic electron scattering mechanisms in the silver film such as the scattering from surfaces. The electron mean free path in silver calculated from the optical data of Johnson and Christy[7] is approximately equal to the film thickness. Thus we expect surface scattering to be appreciable.

The widths of the angular profile reflect the magnitude of the imaginary part $k_{\|}^{(I)}$ of the wave vector $k_{\|}$. Since the SPP in the region of interest is leaky into the prism side, $k_{\|}^{(I)}$ contains the contributions from the intrinsic radiative loss of the modes and from the dissipative loss in silver due to $\mathrm{Im}\epsilon_2$. When we calculate $k_{\|}^{(I)}$ with and without the dissipative loss ($\mathrm{Im}\epsilon_2 \neq 0$ and $\mathrm{Im}\epsilon_2 = 0$), we find that the two energy-loss mechanisms contribute about equal amounts to $k_{\|}^{(I)}$ for $d = 400$ Å. When the dispersion curve of SPP approaches the light line of the prism, $k_{\|}^{(I)}$ increases rapidly. This is the reason why the angular profile at $\omega_i = 19\,436$ cm^{-1} shows the asymmetry with a greater width on the high angle side than on the low angle side.

Since the coupling between VEW and SPP is allowed only for p-polarized light, we expect no enhancement for s-polarized incident or scattered light. We confirmed this by rotating the polarization of the incident and scattered light. No Raman signal could be measured when either the incident or the scattered light is s polarized.

In order to estimate the absolute enhancement factor for the optimum incident and scattered angles, we measured the Raman intensity of the 2835-cm^{-1} line of the methyl alcohol in an optical cell using the right-angle scattering geometry. For this measurement the laser path length in the sample was $l \cong 0.5$cm, and the solid angle of collection was $\Delta\Omega \cong 3\times10^{-2}$ sr. The input optics other than the solid angle of collection was kept identical to the setup used in making the measurements using the Kretchmann geometry. The scattered peak intensity was 2.6×10^2 cps/50 mW. When the light is scattered by using the Kretchmann geometry, the effective thickness of the layer of alcohol that is sampled is on the order of $l \cong 1/2\alpha_3 \sim 7\times10^{-6}$ cm, and the solid angle

of collection was $\Delta\Omega \cong 6 \times 10^{-4}$ sr. The peak counting rate was 25 cps/50 mW. If we convert this counting rate to that of the right-angle scattering geometry using the ratio of $I(\Delta\Omega)$, the estimated counting rate is $\sim 9.5 \times 10^6$ cps/50 mW for the right-angle scattering geometry. This value is approximately 4×10^4 times greater than the actual measured value of the scattering intensity from the liquid cell. Thus the estimated enhancement factor is $\sim 4 \times 10^4$. This estimate agrees exactly with the predicted enhancement factor given by Sakoda *et al.*[3] Since the method used above in estimating the enhancement factor is quite crude, the exactness of the agreement is fortuitous, but we can safely conclude that the observed enhancement factor is consistent with the theoretical prediction.

To conclude, we have measured the angular dependence of the resonance Raman scattering mediated by surface plasmons in a Kretchmann geometry. The observed angular dependence of the Raman-scattering intensity agrees very well with the predictions of the recent theories and the rough estimate of the enhancement factor agrees with the theoretically predicted value.

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