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Surface Coherent Anti-Stokes Raman Spectroscopy

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We demonstrate here that nonlinear mixing of four surface-plasmon waves can be used to probe the Raman resonances of liquids. The results are in good agreement with theoretical prediction. The technique should be useful for surface studies.

The propagation of surface electromagnetic waves on solids and their applications have recently attracted considerable attention.[1] They have been used to study adsorbed molecules[2] and overlayers on surfaces,[3] to probe phase transitions,[4] etc. In most cases, linear optics is employed in the excitation and detection of the surface waves. Observations of nonlinear optical processes involving surface electromagnetic (EM) waves have been rather rare. Simon, Benner, and Rako[5] have used the linearly excited surface-plasmon wave on metal films to generate a bulk second-harmonic wave. DeMartini *et al.*[6] have used the mixing of two bulk waves to generate a surface EM wave, and have used the mixing of a bulk wave and a surface wave as a means to detect the surface wave. Since high-intensity surface EM waves can be readily excited, one would expect that pure surface nonlinear optical effects (i.e., all input and output optical waves are surface waves) should also be easily observable. In this paper, we present the first results of such an experiment on the mixing of four surface-plasmon waves.[7]

The process we have been studying is the surface coherent anti-Stokes Raman spectroscopy (CARS). Two surface-plasmon waves at ω_1 and ω_2 propagate on the plane boundary surface between a metal and a dielectric medium with wave vectors, $(\vec{k}_1)_{\parallel}$ and $(\vec{k}_2)_{\parallel}$, respectively, parallel to the surface. These waves interact on the surface via the third-order nonlinearity in the medium to produce a third-order nonlinear polarization at $\omega_a = 2\omega_1 - \omega_2$ which in turn generates a surface anti-Stokes plasmon wave at ω_a. This anti-Stokes generation will be phase matched if $(\vec{k}_a)_{\parallel} = 2(\vec{k}_1)_{\parallel} - (\vec{k}_2)_{\parallel}$, and will be resonantly enhanced if $\omega_1 - \omega_2$ approaches the resonant frequency of some excitation in the medium. Therefore, just like bulk CARS, the surface CARS can also be used as a spectroscopic technique to study the resonances in a medium.

The theory of surface CARS is a straightforward extension of the theory on nonlinear generation and detection of surface polaritons developed earlier.[8] Suppose the Kretschmann geometry[9] [Fig. 1(a)] is used for excitation of the surface plasmons. The dispersion relation of the surface

plasmons is then given by

$$D(k_{\parallel}=K_{\parallel},\omega)=0, \tag{1a}$$

$$D(k_{\parallel},\omega)=(\epsilon_l k_{mz}-\epsilon_m k_{lz})(\epsilon_m k_{gz}+\epsilon_g k_{mz})+\exp(2ik_{mz}d)(\epsilon_l k_{mz}+\epsilon_m k_{lz})(\epsilon_m k_{gz}-\epsilon_g k_{mz}), \tag{1b}$$

where the subscripts l, m, and g refer to liquid, metal, and glass, respectively [see Fig. 1(a)], d is the thickness of the metal film, ϵ's are the dielectric constants, k_z's are the z components of the wave vectors, $k_{mz}\equiv i\alpha_m=[\omega^2\epsilon_m/c^2-k_{\parallel}^2]^{1/2}$ and $k_{lz}\equiv -i\alpha_l=[\omega^2\epsilon_l/c^2-k_{\parallel}^2]^{1/2}$, and $K_{\parallel}=K_{\parallel}'+iK_{\parallel}''$ is the complex wave vector of the surface plasmon. An incoming TM wave $\vec{E}_{gi}=\vec{\mathcal{E}}_{gi}\exp(i\vec{k}_{gi}\cdot\vec{r}-i\omega_i t)$ from the glass side, with $k_{\parallel}\sim K_{\parallel}'$ can linearly excite a surface plasmon wave described by a field $\vec{E}_{li}=\vec{\mathcal{E}}_{li}\exp[i(\vec{k}_i)_{\parallel}\cdot\vec{\rho}+\alpha_{li}z-i\omega_i t]$ in the liquid medium with $\vec{\rho}$ in the x-y plane. Because of its physical confinement to the boundary, the surface wave can have an intensity significantly higher than the incoming bulk wave. The field amplitudes are related by

$$|\mathcal{E}_{li}|=|4\epsilon_l^{1/2}\epsilon_g^{1/2}\epsilon_m\alpha_{mi}k_{gzi}\exp(-\alpha_{mi}d)/D(k_{i\parallel},\omega_i)\|\mathcal{E}_{gi}|. \tag{2}$$

The anti-Stokes generation is governed by Maxwell's equations with the nonlinear polarization $\vec{P}_a^{(3)}(\omega_a=2\omega_1-\omega_2)=\vec{\chi}^3:\vec{E}_{1l}(\omega_1)\vec{E}_{1l}(\omega_1)\vec{E}_{2l}^{*}(\omega_2)$ and the proper boundary conditions at the interfaces.[8] Here, we shall assume that only the nonlinear susceptibility $\chi^{(3)}$ of the liquid contributes to the anti-Stokes generation. The surface anti-Stokes wave is then generated at the liquid-metal interface and coupled out through the glass side. The solution, when the (small) TE component of $\vec{P}_a{}^{(3)}$ is neglected, yields a coherent anti-Stokes TM waves in the glass $\vec{E}_a(\omega_a,k_a)$ with $k_a{}^2=\epsilon_g\omega_a{}^2/c^2$, $(\vec{k}_a)_{\parallel}=2(\vec{k}_1)_{\parallel}-(\vec{k}_2)_{\parallel}$, and intensity

$$|E_a|^2=|8\pi\epsilon_m k_g\alpha_m\exp(-\alpha_m d)H/D(k_{a\parallel},\omega_a)|^2, \tag{3a}$$

$$H=(-i\alpha_{al}P_{a\parallel}{}^{(3)}+k_{a\parallel}P_{az}{}^{(3)})/(2\alpha_{1l}+\alpha_{2l}+\alpha_{al}). \tag{3b}$$

In Eq. (3) all ϵ's are taken at ω_a.

The anti-Stokes power output from the glass side is then given by

$$\mathcal{P}(\omega_a)=(\epsilon_g^{1/2}c/2\pi)\int|E_a|^2dA, \tag{4}$$

where surface integration is over the beam cross-sectional area.

From Eqs. (3) and (4) we notice that the anti-Stokes output should be strongly enhanced if (1) the incoming waves $\vec{E}_1$ and $\vec{E}_2$ excite the surface plasmon resonances, i.e., $k_{i\parallel}=K_{i\parallel}'$ $(i=1,2)$; (2) the surface anti-Stokes generation is phase matched [Fig. 1(b)], i.e., $k_{a\parallel}=K_{a\parallel}'$; and (3) $\omega_1-\omega_2$ approaches the resonance excitation frequency of the liquid medium so that $\vec{\chi}^{(3)}$ is resonantly enhanced.

Our experimental arrangement is shown in Fig. 1(c). A Q-switched ruby laser at 6943 Å with a linewidth ≤ 0.5 cm^{-1} delivered 30-nsec and 500-mJ pulses at a repetition rate of 10 pulses/min. Part of the beam was used as the ω_1 pump beam and the rest was used to pump a dye laser (NK199 in acetone) oscillator and amplifier system to yield a tunable ω_2 beam at ~7456 Å with a linewidth ≤ 1 cm^{-1} and an energy of 20 mJ/pulse. The two beams were then directed from the prism side onto the sample, which is a glass-prism–

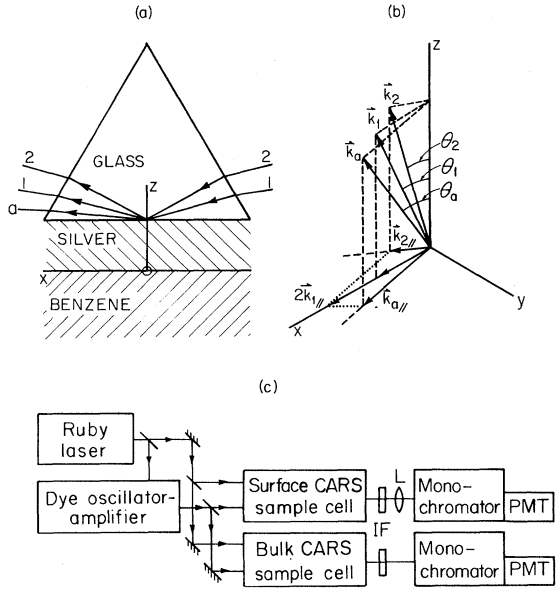

FIG. 1. (a) Prism-metal-liquid assembly. Beam 1 propagates in the x-z plane; beam 2 and the output do not. (b) Wave vectors in the glass prism; components in the x-y plane are phase matched. (c) Diagram of the apparatus. IF is an interference filter and L is a lens.

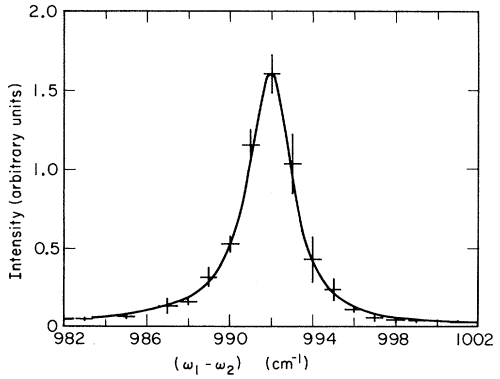

FIG. 2. Signal vs $\omega_1 - \omega_2$ near resonance.

silver-film–benzene combination [Fig. 1(a)] sitting on a rotatable table. In order to avoid excessive heating and burning of the metal film, only 2.5 mJ/cm^2 from the ω_1 beam and 25 mJ/cm^2 from the ω_2 beam were used in the experiment. The anti-Stokes output from the prism was then collected by the detection system consisting of an interference filter, a monochromator, and an RCA 7265 photomultiplier. For the purpose of signal normalization and monitoring of the Raman resonance, a bulk CARS experiment on benzene was also set up in parallel. The surface plasmon resonances at ω_1 and ω_2 were monitored and their characteristics determined by independent attenuated total reflectance (ATR) measurements using the above-mentioned lasers.

Our experimental results on surface CARS are presented in Figs. 2–4 in comparison with theoretical curves derived from Eq. (3). Figure 2 shows the variation of the anti-Stokes signal as $\omega_1 - \omega_2$ moves through the 992-cm^{-1} vibrational resonance in $\chi^{(3)}$ of benzene; in this case, the input beams were properly directed so that both ω_1 and ω_2 surface plasmons were optimally excited and the phase-matching condition for surface CARS was satisfied. The theoretical curve describing this resonance peak was calculated by using a resonance linewidth determined from the parallel bulk CARS measurement. The nonresonant contribution to $\chi^{(3)}$ must be included in the calculation in order to obtain a good fit to the experimental data in the wings.[10] Aside from an amplitude normalization constant, no other adjustable parameter was used in the calculation of all the theoretical curves. Each datum point in the figures was the result of an average over ten shots. The error bars on the data points presumably arise from laser mode fluctuations.

When both ω_1 and ω_2 beams were fixed in space and in frequency, but the prism-sample assembly was rotated about the $\hat{y}$ axis, the surface CARS signal varied as a result of changing $(\vec{k}_1)_{\parallel}$ and $(\vec{k}_2)_{\parallel}$; first, the resonance excitation conditions of the surface plasmons at ω_1 and ω_2 were changed, and then, the phase mismatch in surface CARS was also varied. The results are shown in Fig. 3. Again, the theoretical curve derived from Eq. (3) gives a good fit to the experimental data. Here, the peak is dominated by the effect due to resonance excitation of the surface plasmons at ω_1 and ω_2. The effect of phase mismatch is of secondary importance in reducing slightly the width of the peak. In the present case, the phase-matching peak is expected to be extremely broad because the effective interaction length of surface CARS is limited by the attenuation length $1/$

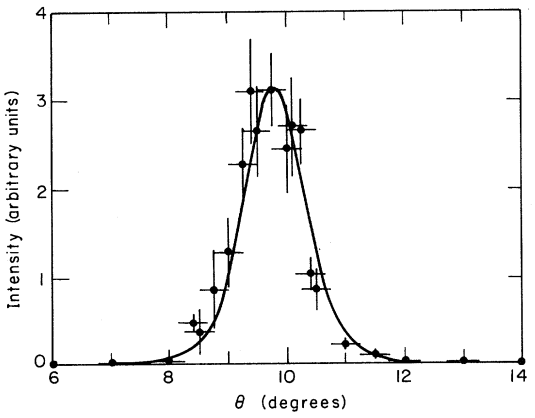

FIG. 3. Signal vs the angular position of the prism assembly about the $\hat{y}$ axis. θ is the angle between the direction of beam 1 incident on the prism and the prism normal.

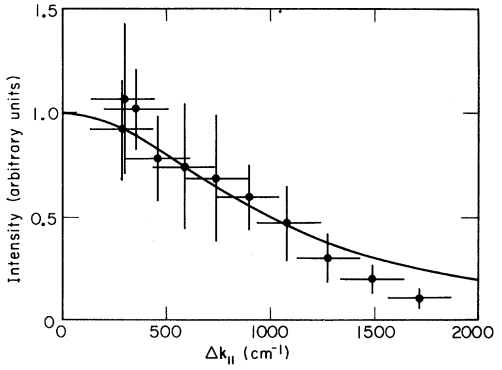

FIG. 4. Signal vs the phase mismatch $\Delta k_{\parallel}$.

$K_{\parallel}''$ of the surface plasmons. In Fig. 4 we show the results on the surface CARS signal versus $\Delta k_{\parallel} = |2(\vec{k}_1)_{\parallel} - (\vec{k}_2)_{\parallel} - (\vec{K}_a)_{\parallel}|$. In the experiment, $\Delta k_{\parallel}$ was varied by changing the direction of $(\vec{k}_2)_{\parallel}$ through variation of $\hat{k}_2$ while keeping the surface plasmons at ω_1 and ω_2 still optimally excited. Here, relatively large uncertainty in the experimental results came from the fact that for each change of $\Delta k_{\parallel}$, the beams had to be readjusted to optimize the beam overlap on the silver film. The theoretical curve is essentially a Lorentzian in $\Delta k_{\parallel}$, arising from the $|D(k_{a\parallel}, \omega_a)|^{-2}$ term in Eq. (3), and agrees fairly well with the experimental results.

The polarization of the anti-Stokes signal was found to be TM as expected, and the signal disappeared with the ω_1 beam was made TE. With phase matching and with surface plasmons at both ω_1 and ω_2 optimally excited, our theory predicts a maximum surface CARS output power of $\mathcal{P}(\omega_a) = 1.1\times10^{-34}\mathcal{P}^2(\omega_1)\mathcal{P}(\omega_2)/W^4$ ergs/sec at the resonance peak of $\chi^{(3)}$, where W is the incoming beam waist. With $\mathcal{P}(\omega_1) = 0.5$ mJ and $\mathcal{P}(\omega_2) = 5$ mJ in a 30-nsec pulse width, we should obtain an anti-Stokes output of 2.5×10^5 photons/pulse. From the actually observed signal from the photomultiplier, we estimated an output of $\sim2\times10^5$ photons/pulse in good agreement with the prediction. The power dependence of the anti-Stokes output on $\mathcal{P}(\omega_1)$ and $\mathcal{P}(\omega_2)$ was also experimentally verified over an order of magnitude in signal strength. When either the ω_1 or ω_2 beam was blocked, no signal at ω_a was detected after more than ten shots, indicating that the signal-to-background ratio in our experiment was greater than 10^3. Bulk CARS generation in the glass prism could contribute to the background, but in our case, it was six orders of magnitude smaller than the surface CARS because of phase mismatch.

In comparison with the bulk CARS, the surface CARS has some advantages and rather unique applications. Because the effective interaction length in surface CARS is only $1/K_{\parallel}'' \sim 10$ μm, the technique can be used to probe $\chi^{(3)}$ for materials with strong absorption and fluorescence. Also, since only a thin layer ($\sim\lambda/6\pi$) of dielectric medium at the interface effectively contributes to the surface CARS signal, the technique can be used to study thin films, overlayers, and perhaps even adsorbed molecules. The sensitivity of the technique with nanosecond laser pulses is limited by the maximum laser fluence incident on the film during the laser pulse. However, because the signal is proportional to $\mathcal{P}^2(\omega_1)\mathcal{P}(\omega_2)$, the sensitivity can be greatly improved by use of picosecond pulses. Consider, for example, a 10-psec pulse with 10-μJ/pulse focused to a diameter of 400 μm. Then, for the benzene-silver-glass system, we expect to find an anti-Stokes signal of 1×10^{11} photons/pulse. This suggests that we should be able to detect a submonolayer of benzene molecules on silver. The technique has a surface-specific nature and may find potential important applications in surface science.

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