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COHERENT RAMAN SPECTROSCOPY VIA SURFACE PLASMONS

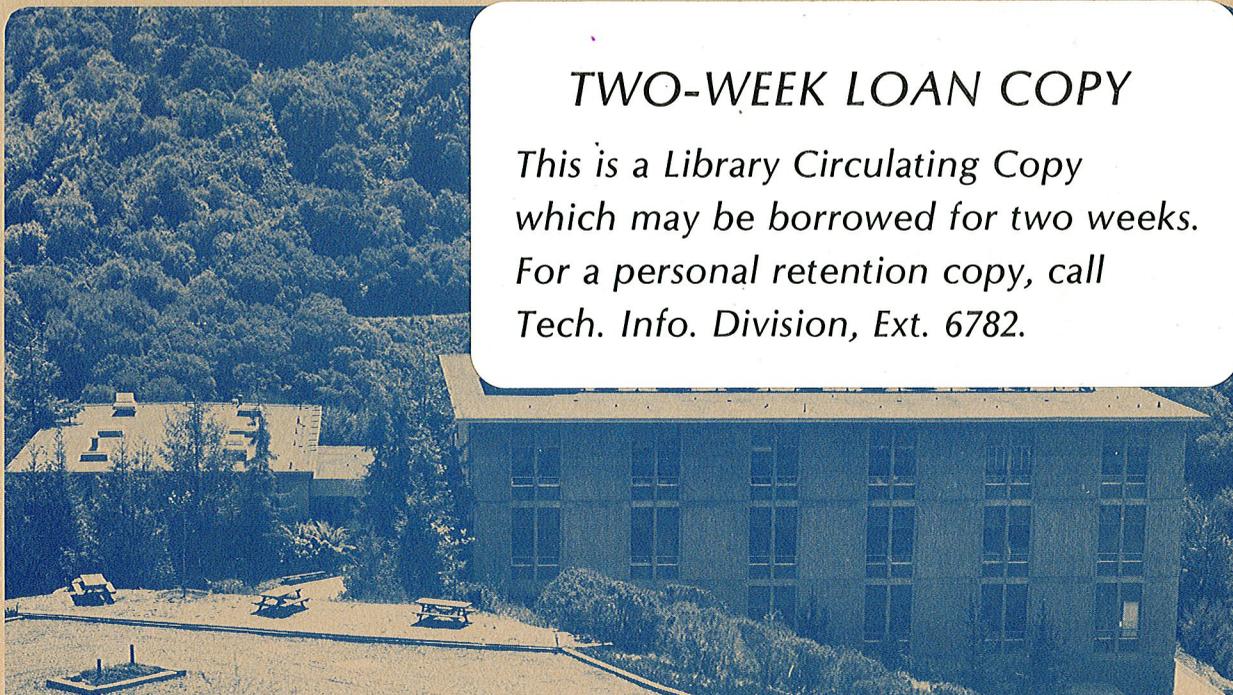
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COHERENT RAMAN SPECTROSCOPY VIA SURFACE PLASMONS

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ABSTRACT - Coherent antiStokes Raman scattering resulting from mixing of surface plasmons is investigated. The technique is shown to be sensitive and surface-specific.

We describe in this paper how coherent Raman spectroscopy can be performed via surface plasmons, and how it can be used to study surface-specific problems. Surface plasmons are surface electromagnetic waves confined to the interface between a metal and a dielectric.¹ They propagate along the interface with their amplitudes dropping off exponentially within a wavelength on either side of the interface. Thus, in exciting the surface plasmons, the incoming laser power gets squeezed into a layer of thickness less than a wavelength. Consequently, the beam intensity is greatly enhanced, and the surface plasmon propagation characteristics are extremely sensitive to the interface structure. Small perturbation on the interface can be readily detected. Surface plasmons can therefore be used for accurate measurements of refractive indices of a dielectric,² for probing of phase transitions,² and for study of overlayers and molecular adsorption on metal surfaces.^{3,4}

The very high intensities of surface plasmons achievable by laser excitation suggest the possibility of observing nonlinear interaction by surface plasmons. Nonlinear optical effects in bulk media have been well explored in the past two decades, but their surface counterparts have not yet received adequate attention. Actually, nonlinear optical effects involving surface plasmons are easily observable. Second harmonic generation by surface-plasmons has been measured,⁵ and coherent antiStokes Raman spectroscopy resulting from nonlinear mixing of four surface plasmon waves has been demonstrated.⁶ Here, we discuss the latter case in more detail.

The theory of nonlinear interaction of surface plasmons has been developed elsewhere. We present here only a brief outline. First, through nonlinearity of mainly the dielectric medium, a nonlinear polarization $P^{NL}(\omega)$ is induced in the interface region by the interacting surface plasmons. Then, $P^{NL}(\omega)$ acts as a source for the generation of a coherent output at ω . If the wavevector component k_{\parallel} of $P^{NL}(\omega)$ along the interface matches the wavevector k_{\parallel} of the surface plasmon at ω , it will result in a phase-matched coherent excitation of the surface plasmon. The output field has a magnitude

$$|E_{out}(\omega)| = |C_{\parallel} P_{\parallel}^{NL} + C_{\perp} P_{\perp}^{NL}| / [(\vec{k}_{\parallel} - \vec{k}_{\parallel})^2 + \gamma^2]^{1/2}$$

where C_{\parallel} and C_{\perp} are coefficients and γ the damping constant of the surface plasmon. A detailed calculation would show that if $|P^{NL}|$ is of the order of 10^{-5} esu in a 10-nsec pulse, the output can be readily detected.

We now consider the special case of coherent antiStokes Raman scattering (CARS) by surface plasmons using the Kretschmann geometry shown in Fig. 1. The surface plasmons at ω_1 , $k_{1,\parallel}$ and ω_2 ,

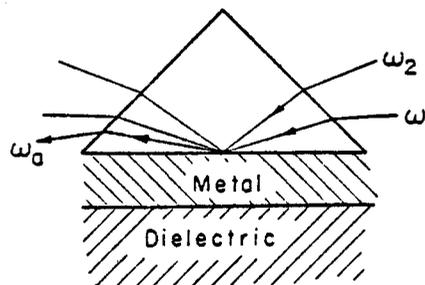


Fig. 1

$\vec{k}_{2,\parallel}$ are linearly excited by incoming laser beams through the glass prism. Under optimum conditions, the excitation efficiency is nearly 100%. From the consideration of conservation of total power flow, the surface plasmon intensity should be about $\alpha/2\gamma$ times larger than the incoming laser intensity, where α^{-1} is the penetration depth of the field into the dielectric medium. Typically, for silver-dielectric interfaces, $\alpha \sim 10^5 \text{ cm}^{-1}$, $\gamma \sim 10^3 \text{ cm}^{-1}$, and hence $\alpha/\gamma \sim 50$. If the incoming laser beam intensities are 1.2 MW/cm^2 , the linearly excited surface plasmon intensities are 60 MW/cm^2 , corresponding to a field strength of 10^3 esu. We then find in the dielectric medium with $\chi^{(3)}(\omega_a = 2\omega_1 - \omega_2) \geq 10^{-13}$ esu around a Raman resonance at $\omega_2 - \omega_1 = \omega_{\text{vibration}}$, a nonlinear polarization $|P^{NL}(\omega_a)| = |\chi^{(3)} E^*(\omega_1) E^*(\omega_2)| \sim 10^{-4}$ or larger. According to our previous estimate, the coherent antiStokes output generated by $P^{NL}(\omega_a)$ is expected to be several orders of magnitude above the detection limit.

The above discussion suggests that the surface CARS (and in fact, other nonlinear mixing ef-

facts of surface plasmons) can be easily observed. We have tested out the idea by using benzene as the dielectric medium and silver as the metal film in Fig. 1. The ω_1 beam was provided by a Q-switched ruby laser and the ω_2 beam by a tunable ruby-laser-pumped dye laser oscillator-amplifier system. The generated surface plasmon at $\omega_a = 2\omega_1 - \omega_2$ was coupled out through the prism as a highly directional coherent beam, and was detected by a photomultiplier with proper filtering in front of it. As a third-order nonlinear optical effect, the signal should increase with the pump laser intensities $I_1(\omega_1)$ and $I_2(\omega_2)$ as $I_1^2(\omega_1)I_2(\omega_2)TA$, where T and A are the pulse duration and the beam cross-section at the interface respectively. Thus, one would like to focus the laser beams onto the interface tightly in order to obtain the maximum I_1 and I_2 possible. As usual, however, the laser intensities are always limited by optical damage of materials. In our case, the laser beam would burn off the metal film at a power flux higher than 50 mJ/cm^2 . Thus, we limited the laser flux in our experiment to less than 30 mJ/cm^2 .

As we discussed earlier, the output should be proportional to $|\chi^{(3)}(\omega_a = 2\omega_1 - \omega_2)|^2$ which shows a Raman resonant enhancement at $\omega_1 - \omega_2 = \omega_{\text{vib}}$. In our experiment, benzene has a well-known Raman mode at 992 cm^{-1} . By scanning $\omega_1 - \omega_2$ around 992 cm^{-1} through variation of ω_2 , we indeed observed a resonant curve of surface CARS as shown in Fig. 2. The results were in very

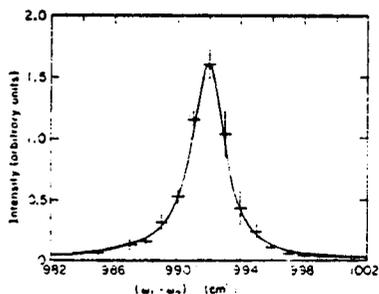


Fig. 2

good agreement with the theoretical prediction. At the resonant peak, the phase-matched coherent antiStokes output was detected to be about 2×10^5 photons per pulse when the input beams were $I_1(\omega_1) = 80 \text{ KW/cm}^2$, $I_2(\omega_2) = 300 \text{ KW/cm}^2$, $T = 30 \text{ nsec}$, and $A = 0.2 \text{ cm}^2$. A theoretical estimate predicted an output of 2.5×10^5 photons/pulse.

That the observed CARS signal indeed came from mixing of surface plasmons was verified by a number of experimental checks. First, in order to excite a surface plasmon, the incoming laser beam must be transverse magnetic. If either ω_1 or ω_2 beam becomes transverse electric, the surface CARS signal should decrease drastically. This was actually what we observed. Then, the observed signal also decreased drastically when the prism assembly was rotated away from the optimum angular position for surface plasmon excitation. Finally, the output signal was also transverse magnetic, suggesting that it origin-

ated from a surface plasmon. This was further confirmed by the phase-matching curve for four-surface-plasmon mixing shown in Fig. 3.

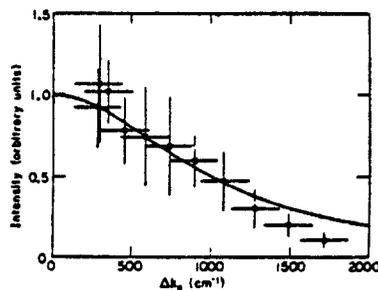


Fig. 3

The maximum signal-to-noise ratio in our experiment was around 10^3 and could probably be improved to 10^4 . With $I_1T + I_2T$ limited to 30 mJ/cm^2 , if we choose $I_1 = 670 \text{ KW/cm}^2$ and $I_2 = 330 \text{ KW/cm}^2$, the signal could increase by a factor of 30. Now, it appears that the threshold for optical damage is more a power flux threshold than an intensity threshold. The signal should therefore increase even further if shorter pulses with the same power flux are used. For example, with $T = 30 \text{ psec}$, $A = 0.2 \text{ cm}^2$, $I_1 = 670 \text{ MW/cm}^2$ and $I_2 = 330 \text{ MW/cm}^2$, the output being proportional to $I_1^2 I_2 T A$ can be as large as 7.5×10^{12} photons/pulse. The same signal can be obtained with 3-psec input pulses of $20 \text{ }\mu\text{J/pulse}$ at ω_1 and $10 \text{ }\mu\text{J/pulse}$ at ω_2 focused to a spot of $2 \times 10^{-3} \text{ cm}^2$. The latter case is not difficult to achieve with the present-day picosecond technology. Now that the surface plasmon intensities decay exponentially away from the interface, the nonlinear polarization induced in the benzene medium is significant only in a layer of about $\lambda/2\pi \sim 1000 \text{ \AA}$, neighboring the interface. In other words, the surface CARS signal is mainly generated by the induced nonlinear polarization in ~ 100 layers of benzene molecules. Then, since the output is proportional to $|\text{PNL}(\omega_a)|^2 \propto N^2$, where N is the density of molecules, the above estimate shows that even submonolayers of molecules adsorbed on the metal surface should be detectable in surface CARS with sufficiently short input laser pulses.

Our discussion here suggests that surface four-wave mixing can be a potentially useful technique to study thin films and adsorbed molecules on surfaces. With picosecond pulses, the dynamical properties of surface overlayers or adsorbed molecules can also be investigated. In addition, since the attenuation length of surface plasmons is $\sim 10 \text{ }\mu\text{m}$, and the metal film acts an effective filter for the coherent output, the technique should be useful for studying materials with strong absorption, strong scattering, or/and strong fluorescence.

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Figure Captions

- Fig. 1 Prism assembly for surface plasmon excitation and mixing in the Kretschmann geometry.
- Fig. 2 Surface CARS signal as a function of $\omega_1 - \omega_2$ around the 992-cm^{-1} vibrational mode of benzene. The crosses are the data points and the solid line is the theoretical curve.
- Fig. 3 Surface CARS signal as a function of phase mismatch Δk_{\parallel} along the interface. The crosses are the data points and the solid line is the theoretical curve.