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SURFACE NONLINEAR OPTICS

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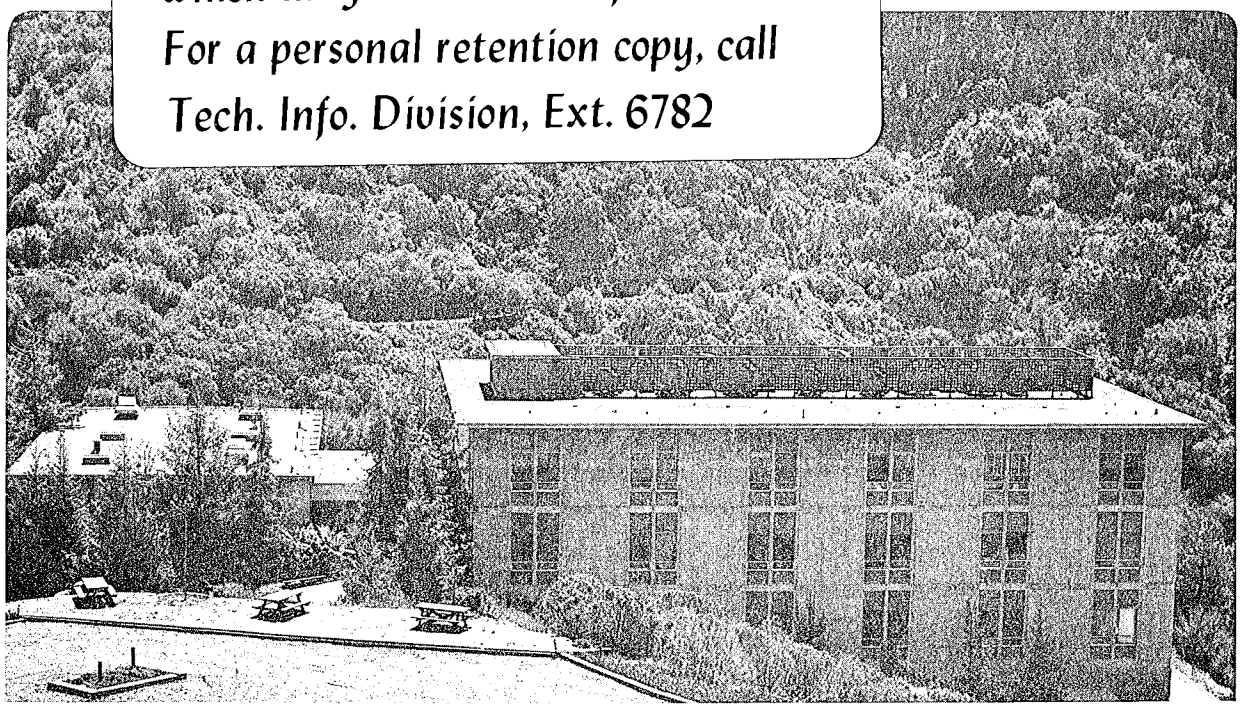

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SURFRACE NONLINEAR OPTICS

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Surface electromagnetic waves are waves propagating along the interface of two media. Their existence was predicted by SOMMERFIELD in 1909 [1]. In recent years, they have found interesting applications in the study of overlayers and molecular adsorption on surfaces [2], in probing of phase transitions [3], and in measurements of refractive indices [4]. In our laboratory, we have been interested in the nonlinear interaction of surface electromagnetic waves. The motivation is two fold. First, while nonlinear optics in the bulk is a well developed field, surface nonlinear optics is still in its infant stage. Second, we would like to look into the possibility of using surface nonlinear optics for material studies. In this paper, we describe the preliminary results of our recent venture in this area.

Surface Plasmons

Surface plasmons (SP) are surface electromagnetic waves confined to the interface between a metal and a dielectric. Their propagation characteristics are governed by the dispersion relation

$$K_{\parallel} = K'_{\parallel} + iK''_{\parallel} = \frac{\omega}{c}\left[\frac{\epsilon_D\epsilon_M}{\epsilon_D + \epsilon_M}\right]^{1/2}, \tag{1}$$

which can be readily derived from the boundary conditions at the interface. Here, ϵ_D and ϵ_M are the dielectric constants of the dielectric and the metal respectively, and $K_{\parallel}$ is the wavevector along the interface with $K_{\parallel}^2 > \omega^2\epsilon_D/c^2$, when $\epsilon_M < 0$, $\epsilon_D > 0$, and $|\epsilon_M| > \epsilon_D$. The wave is transverse magnetic and has the form

$$\begin{aligned}\vec{E} &= (\mathcal{E}_{\parallel}\hat{\rho} + \mathcal{E}_z^D\hat{z})e^{iK_{\parallel}\rho - \alpha_D z} \quad \text{for } z > 0 \\ &= (\mathcal{E}_{\parallel}\hat{\rho} + \mathcal{E}_z^M\hat{z})e^{iK_{\parallel}\rho + \alpha_M z} \quad \text{for } z < 0,\end{aligned} \tag{2}$$

where $z = 0$ is the interface between the dielectric medium in the upper half plane and the metal in the lower half plane. On either side of the interface, the wave amplitude drops off exponentially. Thus, in exciting the surface plasmon, the incoming laser power is squeezed into a layer of less than a wavelength thick ($\alpha_D^{-1} = \lambda|\epsilon_D + \epsilon_M|^{1/2}/2\pi|\epsilon_M|$, $\alpha_M^{-1} = \lambda|\epsilon_D + \epsilon_M|^{1/2}/2\pi|\epsilon_M|$). The beam intensity is then greatly enhanced and the surface plasmon propagation characeristics appear to be rather sensitive to the interface structure.

Since small perturbation on the interface can be easily detected, surface plasmons can be used as a sensitive surface-specific probe. The enhanced beam intensity also facilitates the study of nonlinear optical effects on surfaces.

There are various methods one can use to excite a SP, either linearly or nonlinearly. The one most commonly used is the Kretschmann method, shown schematically in Fig. 1(a) [5]. The SP is excited when the angle of incidence of the exciting laser beam through the prism is properly adjusted so that its wavevector component along the surface is equal to $K_{\|}(\omega)$. This is seen by a corresponding reflectivity drop of the beam reflection from the prism. An example is shown in Fig. 1(b). In the experiments described below, the Kretschmann method is always used for SP excitation.

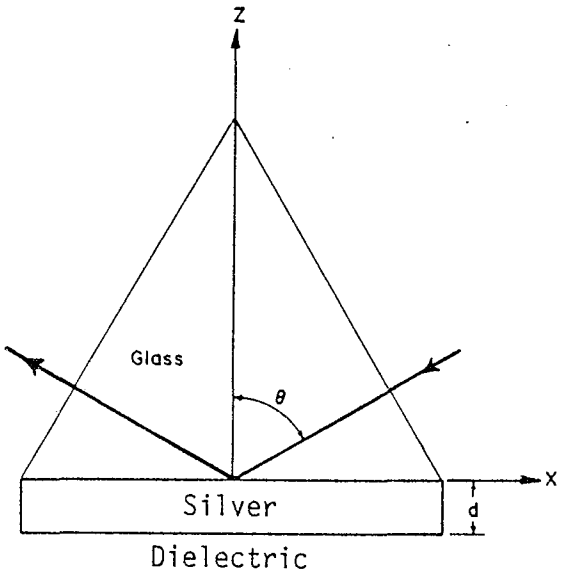

Fig.1(a) Kretschmann geometry for exciting surface plasmons

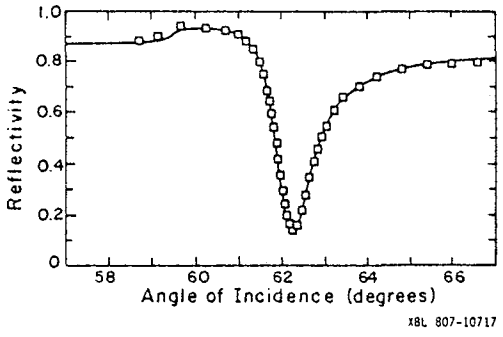

Fig.1(b) Reflectivity versus the angle of incidence θ showing the sharp dip resulting from surface plasmon excitation. The solid curve is a theoretical curve that fits the experimental data points

Theory of Nonlinear Interaction of Surface Plasmons

We now describe briefly the theory of wave mixing of surface plasmons [6]. The output is governed by the wave equation

$$[\nabla \times (\nabla x) - \omega^2 \in / c^2]\vec{E}(\omega) = (4\pi\omega^2/c^2)\vec{P}^{(n)}(\omega)$$

$$\nabla \cdot (\in \vec{E} + 4\pi\vec{P}^{(n)}) = 0, \qquad (3)$$

where the source of mixing is the nonlinear polarization

$$\vec{P}^{(n)}(\omega) = \overleftrightarrow{\chi}^{(n)}(\omega = \omega_1 + \text{---} + \omega_n):\vec{E}_1(\omega_1)\text{---}\vec{E}_n(\omega_n)$$
$$\propto \exp(i\vec{k}_s \cdot \vec{r} - i\omega t), \tag{4}$$

with $\vec{k}_s = \vec{k}_1 + \text{---} + \vec{k}_n$. In our case, the fields $\vec{E}_1(\omega_1)$, ---, $\vec{E}_n(\omega_n)$ are assumed to be all SP. Equation (3) can be solved straightforwardly with the proper boundary conditions. Because of the limited space, we will not reproduce the results here. It is easy to see, however, that the output field is linearly proportional to $P_{\parallel}^{(n)}(\omega)$ and $P_z^{(n)}(\omega)$. For $k_s > \omega\in_D^{1/2}/c$, the output can only appear as a coherent beam on the prism side with the beam direction determined by $\vec{k}_{s\parallel}$, although surface roughness may couple part of the output out through the dielectric side. If $k_{s\parallel} = K'_{s\parallel} > \omega\in_D^{1/2}/c$, then $\vec{P}^{(n)}(\omega)$ drives the SP at ω resonantly. In other words, the SP at ω is now generated from optical mixing of the pump SP under the phase matching condition. For $k_s < \omega\in_D^{1/2}/c$, the output appears as coherent beams on both the dielectric and the prism sides with their directions determined by $\vec{k}_{s\parallel}$.

Physically, the output arises from the collection of dipole radiation from a thin layer of oscillating dipoles induced by the mixing of pump SP at the interface. Thus, in the visible region, only a few hundred atomic or molecular layers effectively contribute to the nonlinear mixing. The output signal reduces by a factor of $10^4 - 10^5$ if only a monolayer of materials is present.

Harmonic Generation by Surface Plasmons

The simplest nonlinear optical process is the optical second harmonic generation. Second harmonic generation by SP is in fact readily observable even at the air-metal interface as first demonstrated by SIMON and coworkers [7]. In this case, metal is the nonlinear medium. Its second-order nonlinearity is, however, small because of the existence of inversion symmetry. The induced second-order nonlinear polarization arises from electric-quadrupole and magnetic-dipole contribution and can be written in the form [8]

$$\vec{P}^{(2)}(2\omega) = \alpha(\vec{E} \cdot \nabla)\vec{E} + \beta(\nabla \cdot \vec{E})\vec{E} + \gamma\vec{E} \times \vec{B}. \tag{5}$$

The first two terms are the electric-quadrupole terms. They are only nonvanishing within the Thomas-Fermi screening length (i.e., one or two atomic layers) near the surface. The last term is the magnetic-dipole term and is nonvanishing throughout the bulk. In practice, however, the total magnetic-dipole contribution is often negligible in comparison with the electric quadrupole contribution. This is because the nonlinearity from a single atomic layer without inversion symmetry is already appreciably larger than the nonlinearity from the magnetic-dipole contribution of a hundred atomic layers penetrated by the incoming pump field.

From the wavevector matching condition, it is easily seen that two counter-propagating fundamental SP should generate a bulk second harmonic output propagating along the surface normal [9]. The corresponding nonlinear polarization obtained from (5) has however a vanishing component parallel to the surface. Consequently, no second harmonic generation along the surface normal should be observed. We have verified experimentally that this is indeed the case. By varying the angle between the two fundamental SP, we should be able to determine the coefficients α, β, and γ in (5) separately. Such work

is presently still in progress. Harmonic generation by SP is actually a viable method for studying optical nonlinearity of metals.

The second harmonic generation can be greatly enhanced if in the above case, air is replaced by a nonlinear dielectric medium, for example, quartz or KDP [7]. The process is now dominated by the nonlinearity of the nonlinear dielectric. Symmetry of the medium generally allows the existence of a nonlinear polarization component parallel to the surface even for counter-propagating SP. Thus, second harmonic generation along the surface normal becomes easily observable [9]. That there is a one-to-one correspondence between the propagation direction of the second harmonic beam in the three-dimensional space and the interaction geometry of the two SP in the two-dimensional plane may find applications in information processing.

We have also observed third harmonic generation by SP at the interface between metal and some organic liquid. The nonlinearity of the liquid appears to dominate, as is evidenced by the reduction of the third harmonic signal beyond our detectability when the liquid is replaced by air. If the SP dispersion curve $\omega(K_{||})$ concaves downward, then $2K'_{||}(\omega) < K'_{||}(2\omega)$ and it is impossible to have phase-matched generation of a harmonic SP by fundamental SP. Anomalous dispersion of the dielectric may be used to achieve phase matching.

Surface CARS

Coherent antiStokes Raman scattering (CARS) has recently become a useful spectroscopic technique [10]. The nonlinear polarization governing the antiStokes output is

$$\vec{P}^{(3)}(\omega) = \overleftrightarrow{\chi}^{(3)}(\omega = 2\omega_1 - \omega_2) : \vec{E}(\omega_1)\vec{E}(\omega_1)\vec{E}^*(\omega_2)$$

with the nonlinear susceptibility

$$\overleftrightarrow{\chi}^{(3)} = \overleftrightarrow{\chi}^{(3)}_{NR} + \frac{A}{[(\omega_1 - \omega_2) - \omega_v] + i\Gamma} .$$

As $(\omega_1 - \omega_2)$ approaches the vibrational frequency ω_v of the nonlinear medium, $\overleftrightarrow{\chi}^{(3)}$ is resonantly enhanced, and so is the antiStokes output. CARS can therefore be used for probing Raman resonances. Clearly, the same process can be extended to the surfaces using SP. Actually, with surface SP as pump waves, the magnitude of $\vec{P}^{(3)}(\omega)$ can be greatly enhanced. So the antiStokes output is still quite appreciable even though, as we discussed earlier, $\vec{P}^{(3)}(\omega)$ is limited to a very thin layer near the interface.

We have demonstrated the feasibility of surface CARS using the setup shown in Fig.2 [11]. The SP at ω_1 and ω_2 are efficiently excited by the input beams through the prism. In this case, phase-matched generation of anti-Stokes SP is possible by properly adjusting the relative angle between the pump SP in the surface plane. Then, the resonant spectrum of the antiStokes output can be obtained by scanning $(\omega_1 - \omega_2)$. An example of pyridine on silver is presented in Fig.3, where the experimental results are in good agreement with the theoretical prediction. For an input of 2.8 mJ/cm^2 at ω_1 and 32 mJ/cm^2 at ω_2 with a pulsewidth of 30 ns and a beam cross-section of 0.25 cm^2, the measured signal at the resonance 991 cm^{-1} peak is 1.5×10^4 photons/pulse, while the theoretical prediction is 3.3×10^4 photons/pulse. Other characteristic features of the observed antiStokes output also agree well with the surface CARS prediction.

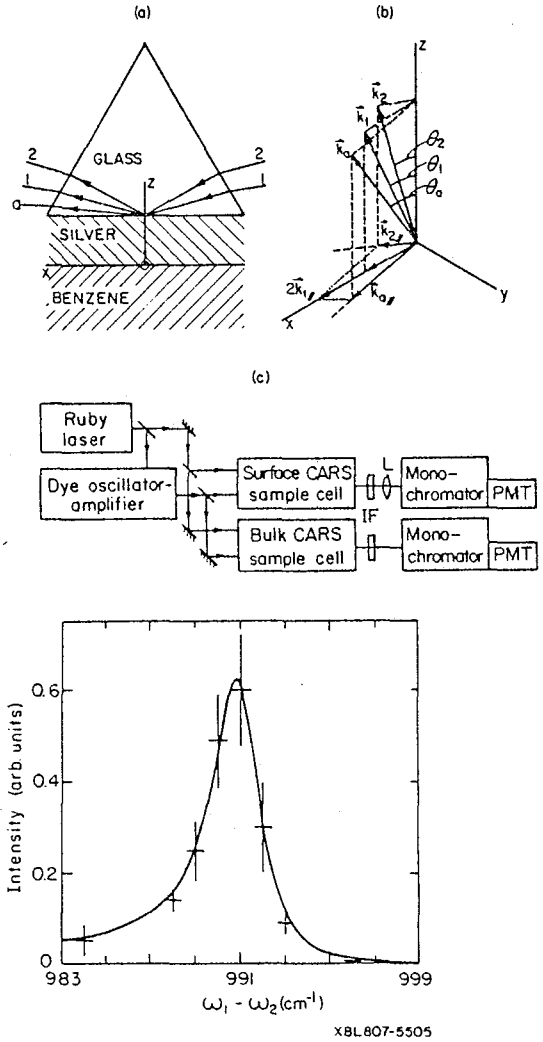

Fig.2 (a) Prism-metal-liquid assembly for surface CARS measurement. Beam 1 is in the x-z plane, but beam 2 and the output are not. (b) Wavevectors in the glass prism with components in the x-y plane phase-matched. (c) Diagram of the apparatus: IF is an interference filter and L is a lens

Fig.3 AntiStokes signal versus $\omega_1-\omega_2$ around the 991 cm^{-1} Raman resonance of pyridine

Surface plasmons actually have rather short attenuation lengths ℓ because of the large loss in the metal. Typically, $\ell = 1/K_{\parallel}'' \sim 10$ μm on silver in the visible. This means that the interaction length in surface CARS is only of the order of 10 μm. Then, even if the dielectric medium is strongly absorbing, the antiStokes is not expected to be appreciably reduced by the absorption. We have tested this out with a 1 : 2 acetone-benzene mixture on silver. When 1.1 mM of oxazine 725 is dissolved in the solution so that it has an absorption coefficient of $\alpha \sim 400$ cm^{-1} at the antiStokes frequency, the antiStokes output remains essentially unchanged.

In summary, the surface CARS has the characteristics of large induced nonlinear polarization, small field penetration depth into the medium at the surface, short nonlinear interaction length, a highly directional coherent output, and the possibility of an effective reduction of luminescence background. It can therefore be used to study materials with strong absorption and luminescence, thin films, molecular overlayers, and adsorbed molecules, and other surface specific problems. The surface CARS output increases with the input laser intensities as $I^2(\omega_1)I(\omega_2)$. Its ultimate sensitivity is limited by optical damage on the surface. Since the damage usually has a fluence threshold rather than an intensity threshold, the ultimate sensitivity of surface CARS can be greatly improved by using picose-

cond pump pulses. From our experimental results with Q-switched pulses, we can estimate an output of $\sim 10^{11}$ photons/pulse for benzene on silver from an input of 10 μJ/pulse with a pulsewidth of 10 ps and a focal spot of 0.15 mm^2. As we mentioned earlier, the signal will reduce by a factor of $10^4 - 10^5$ if there is only a monolayer of benzene molecules on silver. Thus, with picosecond pulses, surface CARS should have the sensitivity of detecting submonolayer of adsorbed molecules.

Enhanced Second Harmonic Generation on a Rough Metal Surface

Recently, surface enhanced Raman scattering has attracted a great deal of attention [12]. The effective Raman cross-section of some adsorbed molecules on a roughened silver surface seems to have increased by $10^5 - 10^6$ in comparison to that of the same molecules in solution. Various mechanisms have been suggested to explain the enhancement: some are purely electromagnetic in origin while others rely on the quantum-mechanical interaction between molecules and metal. A recent controlled experiment of ROWE et al. [13] indicates that local field enhancement in local regions of the rough surface is mainly responsible for the Raman enhancement. According to the simple theoretical model [14], the local field enhancement decays away in a distance of few molecular layers from the surface.

If the local field picture is correct, then the interaction of molecules with metal is only of secondary importance. Furthermore, the enhancement phenomenon should be fairly general. It should show up in all nonlinear optical effects involving metal surfaces. In this respect, second harmonic reflection from metal surfaces in air is most interesting because, as we mentioned earlier, only one or two atomic layers at the surface are supposed to contribute to the second harmonic generation, and the local field effect is particularly strong in the surface atomic layers.

We have carried out a preliminary study of second harmonic reflection on rough silver surfaces. We prepare the rough surfaces by cycling in electrolytic solution followed by dry cleaning with nitrogen gas. In comparison with a smooth surface, the roughened surface shows an enhancement of $> 10^3$ in the second harmonic output. Unlike the smooth surface, the second harmonic output from a rough surface is strongly diffused by scattering from surface roughness. Although theoretically the local field enhancement in second harmonic reflection may not be the same as that in the Raman case, our results do indicate that the local field effect is at least partially responsible for the surface Raman enhancement.

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