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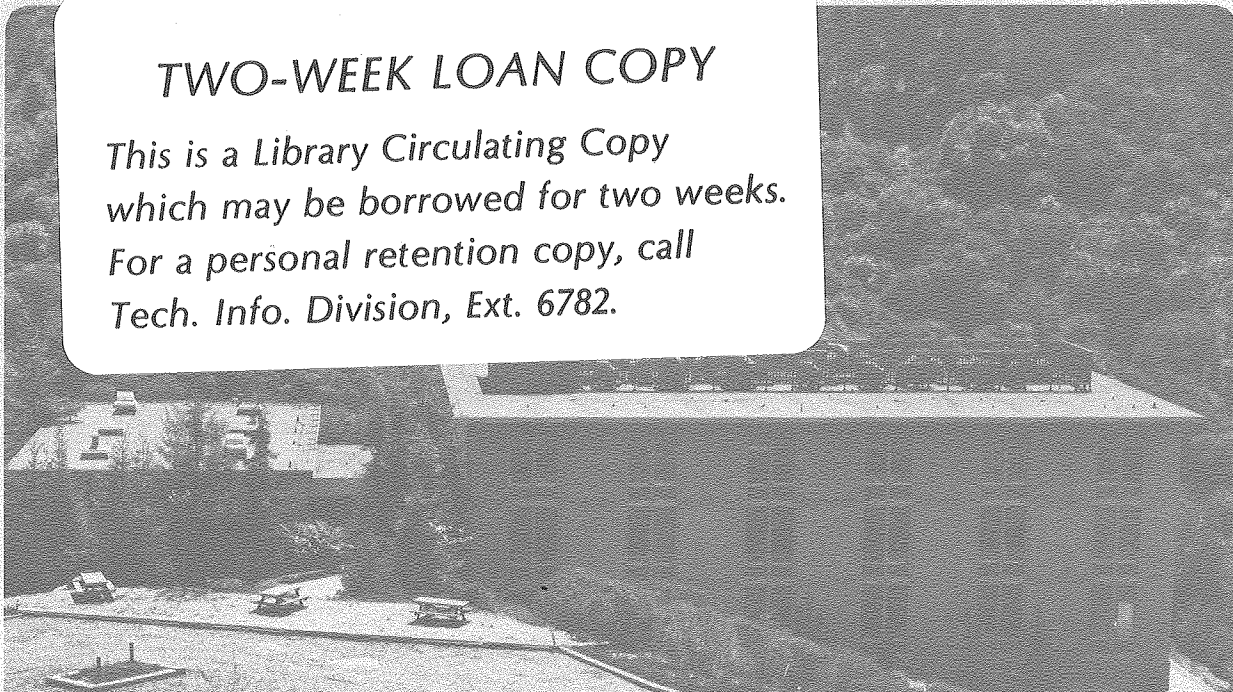
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SURFACE ENHANCED SECOND HARMONIC GENERATION

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ABSTRACT

Second harmonic generation at a silver-air interface was enhanced due to surface roughness by a factor of  $10^4$ . The local field enhancement is believed to be responsible for the effect. An unusually broad luminescence background extending far beyond the antiStokes side of the second harmonic was also observed.

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Surface enhanced Raman scattering (SERS) has recently caused a great deal of excitement.<sup>1</sup> It was found experimentally that the effective Raman cross-sections of some molecules on a roughened silver surface can be  $10^5 - 10^6$  times larger than those of the same molecules in solution.<sup>2</sup> Various mechanisms have been suggested to explain the enhancement. Some involve molecular interaction between the molecules and the metal (known as the chemical effect).<sup>1,3</sup> Others rely on the electromagnetic interaction between molecules and metal (the electromagnetic effect).<sup>1,4</sup> The chemical effect is often the main issue of discussion on SERS, and is evidenced by the observation that only selective molecules on metal surfaces exhibit Raman enhancement.<sup>2</sup> However, there is difficulty in understanding how an allowed Raman transition of the molecules can have its strength increased by  $10^6$  through metal-molecule interaction but have its corresponding Raman shift nearly unchanged. The electromagnetic effect, on the other hand, can lead to an enhancement of  $\sim 10^4$ , as demonstrated by the recent experiment of Rowe et al.<sup>5</sup> with controlled surface preparation under ultrahigh vacuum. The local field created by local surface plasmon excitation on the rough surface structure is presumably responsible for the enhancement.<sup>4,6</sup> Most likely, however, it is the combined force of the chemical effect and the electromagnetic effect that gives rise to the total enhancement of  $\sim 10^6$ . In this respect, we note that in the usual experiments, the minimum observable enhancement factor is  $\sim 10^4$  as limited by the sensitivity of the detection system, and the chemical effect may be of critical importance in bringing the total enhancement to a detectable level.

One would like to separate the chemical effect from the electromag-

netic effect. This is, unfortunately, not easy with the molecules adsorbed on the metal surface. We realize, however, that if the local field enhancement picture is correct then the surface enhanced phenomenon should be rather general. Harstein et al.<sup>7</sup> have recently reported an observed enhancement of  $\sim 20$  for infrared absorption of molecular monolayers on metal surfaces. The enhancement should also be present for all nonlinear optical processes. If the metal surface alone has a detectable nonlinearity, then the enhancement of the nonlinear optical effect should be observable on a metal-air interface without the presence of adsorbed molecules. This eliminates the complication of the chemical effect that may change the nonlinear optical coefficient and contribute to the enhancement as in the Raman and infrared cases. Second harmonic (SH) reflection from metal surfaces in air is most interesting.<sup>8</sup> The nonlinearity originates from the first one or two layers of metal atoms at the surface, and according to the theory,<sup>5</sup> the local field enhancement is expected to be strongest in these layers. We report here our recent measurements on second harmonic reflection ( $2\omega$  at  $0.53 \mu\text{m}$ ) from smooth and rough surfaces of evaporated films and bulk samples of silver, copper, and gold.<sup>9</sup> Large enhancements due to surface roughness were actually observed.

Second harmonic reflection results from the nonlinear polarization  $\vec{P}(2\omega)$  induced by the laser on the metal surface,<sup>8</sup>

$$\vec{P}^{(2)}(2\omega) = \alpha(\nabla \cdot \vec{E})\vec{E} + \beta(\vec{E} \cdot \nabla)\vec{E} + \gamma\vec{E} \times (\nabla \times \vec{E}) \quad (1)$$

where  $\alpha$ ,  $\beta$ , and  $\gamma$  are coefficients characteristic of the metal.

Because of the large dielectric constant of a metal, the  $\alpha$  and  $\beta$  terms

dominate in  $\vec{P}^{(2)}(2\omega)$ , and are mainly due to contribution from the first one or two layers of metal atoms at the surface. For a rough surface, however,  $\vec{P}^{(2)}(2\omega)$  varies over the surface. The local  $\vec{P}^{(2)}(2\omega)$  should experience a local field correction. Following the usual simple derivation in nonlinear optics, if  $\vec{E}_{loc}(\omega) = L(\omega)\vec{E}(\omega)$ , we can write

$$\vec{P}_L^{(2)}(2\omega) \cong \alpha_{eff}(\nabla \cdot \vec{E})\vec{E} + \beta_{eff}(\vec{E} \cdot \nabla)\vec{E} \quad (2)$$

with  $\alpha_{eff} = L^2(\omega)L(2\omega)\alpha$  and  $\beta_{eff} = L^2(\omega)L(2\omega)\beta$ . McCall et al.<sup>6</sup> showed that for a spheroid,

$$L(\omega) \propto \frac{1}{[\epsilon(\omega) + 2]} \quad (3)$$

where  $\epsilon(\omega)$  is the dielectric constant of the metal. At the surface plasmon resonance,  $\text{Re}[\epsilon(\omega) + 2] = 0$  and  $L(\omega)$  becomes resonantly enhanced with the enhancement inversely proportional to  $\text{Im}(\epsilon)$ . For a different geometrical shape of small metal aggregates,  $\epsilon(\omega) + 2$  should be replaced by another function  $f(\epsilon)$ , and the surface plasmon resonance is excited when  $\text{Re}[f(\epsilon)] = 0$ .

The second harmonic signal from reflection is proportional to  $\int |\vec{P}_L^{(2)}(2\omega)|^2 dA$ , where the integration is over the surface irradiated by the incoming laser beam. The second harmonic generation should be dominated by  $\vec{P}_L^{(2)}(2\omega)$  in regions with the near maximum local field correction. Let  $x$  be the fractional area of such regions. Then, the local field enhancement of second harmonic generation from a rough surface over that from a smooth surface should be given approximately by

$$\eta = |L^2(\omega)L(2\omega)|_{\max}^2 x. \quad (4)$$

Our experimental setup is shown in Fig. 1. A Q-switched Nd:YAG laser with 10 pulses/sec was used to provide the pump beam at 1.06  $\mu\text{m}$  at a 45° angle of incidence. To avoid damage of the sample surface, the 10 ns pump pulse energy was limited to  $\sim 7$  mJ in a 5-mm diameter spot on the sample. Two types of samples were mainly used in the experiment: smooth evaporated films,  $\sim 1000$  Å thick, and bulk samples roughened by electrolytic cycling. In preparing a rough sample surface, the electrolytic process was performed in 0.1 M KCl in water, and with  $\sim 65$  mC/cm<sup>2</sup> of charge transportation occurring in each cycle. As a calibration, we checked that when 0.05 M of pyridine was also dissolved in the solution, the sample surface obtained after one or two such cycles produced a surface Raman enhancement of  $\sim 10^6$ . The roughened sample was taken out of the electrolytic solution (without pyridine), rinsed with distilled water, and finally dried by nitrogen gas before the measurement.

With the sample in the setup of Fig. 1, the reflected SH signals (verified to be originating from the Ag sample) were measured and analyzed. We believe that in our experiment, no adsorbed molecules would affect the signal for the following reasons. First, the adsorbed molecules, if present, would have been blown away by the first few laser shots, as this is a well known technique for cleaning a surface. Second, even if some adsorbed molecules were still present, their contribution to second harmonic generation would be negligible anyway.<sup>8</sup> With the 1.06  $\mu\text{m}$  TM input, the signal from the smooth film was a well collimated

beam in the specularly reflected direction, and was polarized in the TM mode.<sup>8</sup> The signal from the rough surface, however, was highly diffuse, nearly isotropic in angular distribution and independent of both input and output polarizations.

The spectra of the output signals were also analyzed, as shown in Fig. 2 for silver. The second harmonic generation was evidenced by the sharp peak at the second harmonic frequency. In addition, a broad spectral background, highly diffuse and extending from  $\sim 3500 \text{ \AA}$  to the infrared (limited to  $\sim 6000 \text{ \AA}$  by our detection system), also appeared. For the smooth film, the background was weak, but for the rough surface, it was exceptionally strong.

The second harmonic signal from the electrolytically roughened surface of bulk silver, integrated over the  $2\pi$  emission solid angle, was found to be  $1 \times 10^4$  times larger than the collimated SH from the smooth film. The exact value depended somewhat on the surface preparation, but with the same surface preparation procedure, the result was reproducible to within 20%. We note that here, unlike the Raman case, the signal was detectable even from the smooth film, and therefore the enhancement factor was obtained from a direct comparison of two signals, and should be quite accurate except for a possible error of  $\sim 50\%$  in the measured angular distribution of the diffuse signal from the rough surface. With less electrolytic cycling (less than  $65 \text{ mC/cm}^2$ ), both the second harmonic and the background output became weaker, indicating that roughness was essential for the observed background and signal enhancement.

The laser power dependency of the second harmonic signals from the smooth and rough surfaces was also measured. In all cases, the SH sig-



nal was quadratic in laser power, as shown in Fig. 3. For the electrolytically cycled bulk silver samples, the power dependency of the broadband background was found to be  $\sim I(\omega)^3$  on the antiStokes side and between  $I(\omega)^2$  and  $I(\omega)^3$  on the Stokes side, and the pulse shape closely resembled the pump laser pulse. However, for the electrolytically cycled silver films (charge transportation  $\lesssim 25 \text{ mC/cm}^2$ ), the power dependency of the broadband background was found to be  $\sim I(\omega)^6$  on the antiStokes side and  $\sim I(\omega)^3$  on the Stokes side. Furthermore, the temporal behavior of the rough film background showed a clear tail, several pulsewidths long. We do not understand this observed anomaly on the films. The result, however, makes us believe that the broadband background is of luminescence origin. Broadband luminescence from rough surfaces has also been observed with linear excitation in Raman studies.<sup>10</sup>

Similar results were obtained for gold, although both the second harmonic signal and the luminescence background from the rough surface was much weaker. The observed enhancement for second harmonic generation at the electrolytically cycled surface was  $\sim 10^3$ . For copper, the broadband luminescence from the rough surface was several times stronger than in silver, and masked off the narrow-band second harmonic signal. Consequently, we were only able to say that the surface enhancement for SH on copper, if any, was less than  $5 \times 10^3$ .

Electron micrographs of electrolytically cycled silver surfaces have indicated that the surface roughness consists of  $\sim 500 \text{ \AA}$  Ag particles separated by  $1500 - 3000 \text{ \AA}$ .<sup>5</sup> We can therefore reasonably assume in Eq. (4) the fractional area  $x$  where  $L(\omega)$  is nearly a maximum due to plasmon resonance to be  $\sim 5\%$ , and since  $2\omega$  is far away from  $\omega$  in our case,  $L(2\omega)$

$\sim 1$ . Using the observed enhancement of  $\eta = 10^4$  in Eq. (4), we obtain  $L(\omega) \approx 20$ . This value of local field correction is certainly very reasonable considering that on a smooth silver-air interface, the field enhancement due to surface plasmon excitation can already be as high as  $\sim 20$ . Copper and gold are expected to have smaller  $L(\omega)$  because of the larger values in their  $\text{Im}(\epsilon(\omega))$ . Measurement of the frequency dependence of enhanced second harmonic generation on rough surfaces is currently in progress. Of course, it would be better if the measurement can be carried out on well defined rough surface structure such as arrays of ellipsoids of the same size formed by lithographic techniques.<sup>11</sup>

In conclusion, we have demonstrated unambiguously via second harmonic reflection from metal surfaces that the local field on rough surface structure can lead to a large enhancement in the strength of a nonlinear optical process. Unlike the Raman case, the metal-molecule interaction does not play a role here. An unusually broad luminescence has also been observed from the rough metal surfaces. The mechanism leading to such luminescence is not yet understood.

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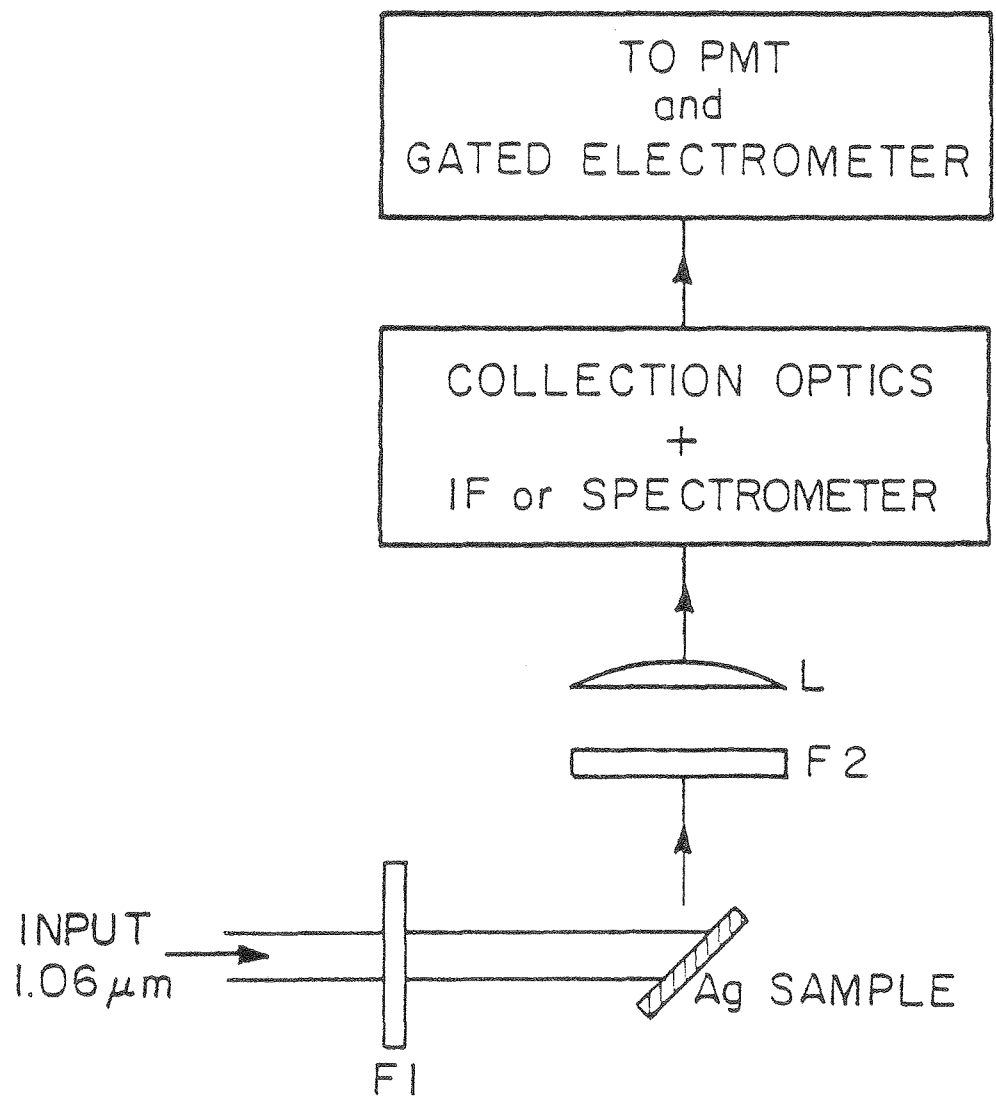
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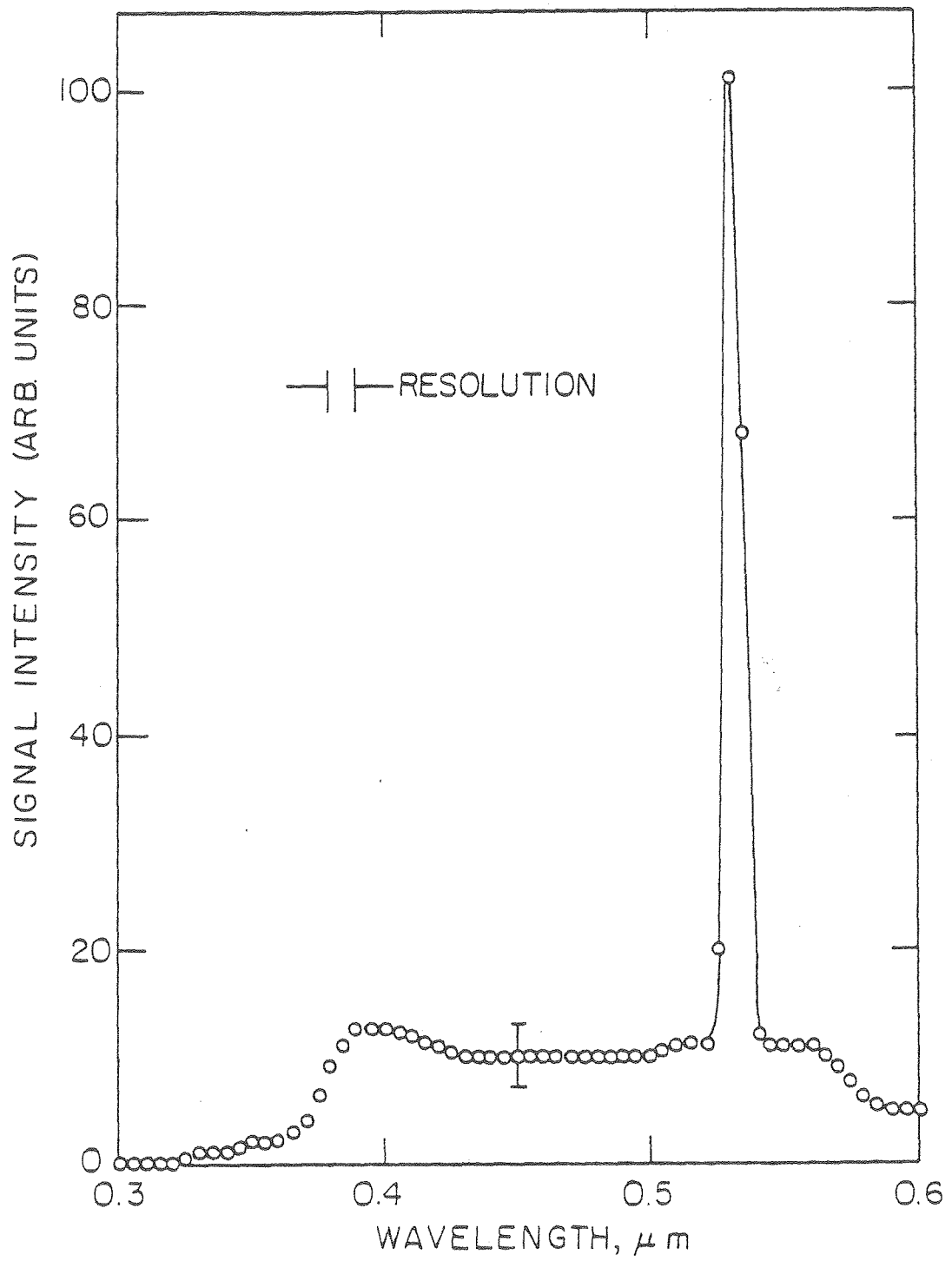
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## Figure Captions

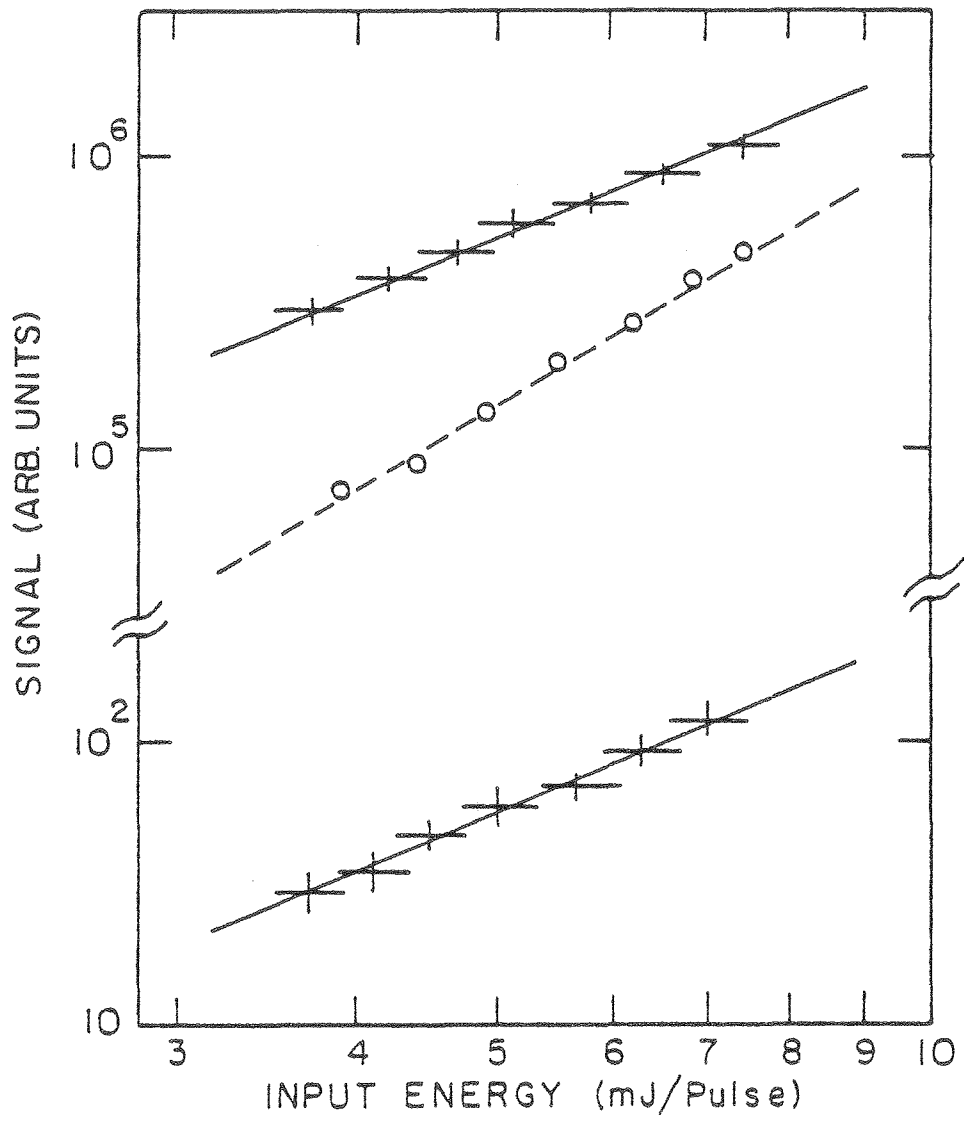
- Fig. 1 Experimental setup; F1 is a red cutoff color filter, F2 is an infrared blocking, visible passing color filter, IF is a narrow-band interference filter, center wavelength  $.53 \mu\text{m}$ , and L is a f/1 collection lens.
- Fig. 2 Spectral distribution of the nonlinear signal from a rough bulk silver sample.
- Fig. 3 Power dependencies of the nonlinear signal on silver; the upper and lower solid curves show the quadratic dependency of the diffuse SH signal from the rough bulk sample and of the collimated SH signal from the smooth film, respectively; the dashed curve shows the cubic dependency of the diffuse antiStokes signal from the rough bulk sample.



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