

## Surface-Enhanced Second-Harmonic Generation

C. K. Chen, A. R. B. de Castro,<sup>(a)</sup> and Y. R. Shen

*Department of Physics, University of California, Berkeley, California 94720, and  
Materials and Molecular Research Division, Lawrence Berkeley Laboratory,  
Berkeley, California 94720*

(Received 6 October 1980)

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

PACS numbers: 78.45.+h, 78.20.-e, 78.30.-j

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 electromagnetic 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. Hartstein, Kirtley, and Tsang<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. In this respect, 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  $\vec{P}^{(2)}(2\omega)$  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 contributions 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  $\vec{E}_{\text{loc}}(\omega) = L(\omega)\vec{E}(\omega)$ , we can write

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

with  $\alpha_{\text{eff}} = L^2(\omega)L(2\omega)\alpha$  and  $\beta_{\text{eff}} = L^2(\omega)L(2\omega)\beta$ .

McCall, Platzman, and Wolff<sup>6</sup> showed that, for a spheroid with diameter  $d \ll \lambda$ ,

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

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

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

A Q-switched Nd:YAlG (neodymium-doped yttrium aluminum garnet) laser with 10 pulses/sec was used to provide the pump beam at  $1.06 \mu\text{m}$  at a  $45^\circ$  angle of incidence. To avoid damage of the sample surface, the 10-ns-pump-pulse energy was limited to  $\sim 7 \text{ mJ}$  in a 5-mm-diam spot on the sample. Two types of samples were mainly used in the experiment: smooth evaporated films,  $\sim 1000 \text{ \AA}$  thick; and bulk samples roughened by electrolytic cycling. In preparing a rough sample surface, the electrolytic process was performed in  $0.1M$  KCl in water, and with  $\sim 65 \text{ mC/cm}^2$  of charge transportation occurring in each cycle. As a calibration, we checked that when  $0.05M$  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.

The reflected SH signals (verified to be originating from the Ag sample) were measured and analyzed using color filters and an interference filter or monochromator to reject the  $1.06\text{-}\mu\text{m}$  light, and a photomultiplier, followed by a gated electrometer and a strip-chart recorder. With the  $1.06\text{-}\mu\text{m}$  TM input, the signal from the smooth film was a well-collimated beam in the specular-

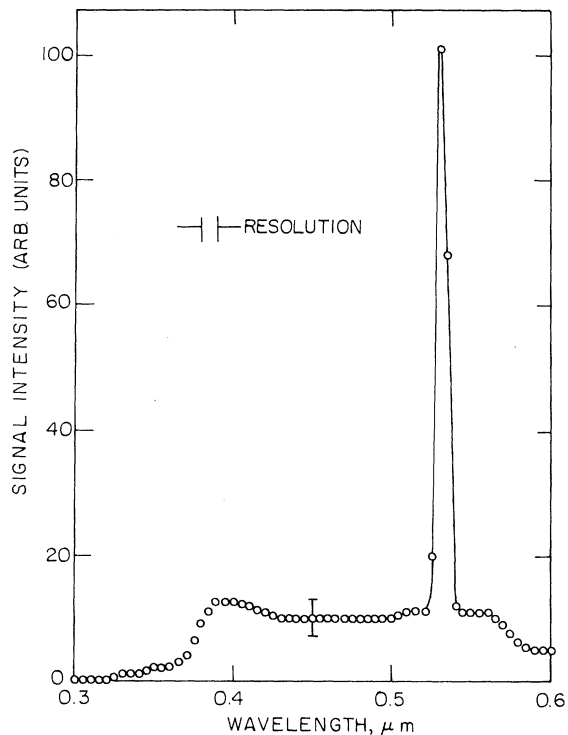


FIG. 1. Spectral distribution of the nonlinear signal from a rough bulk silver sample.

ly 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. 1 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  $2\pi$ -sr 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.

We believe that adsorbed molecules and hence the chemical effect played an insignificant role here in the observed enhancement. Electrolytic cycling roughened the metal surface, but did not leave a layer of adsorbed molecules on the surface. We actually confirmed our belief by monitoring the second-harmonic signal from the sample in the electrolytic solution during the cycle.<sup>10</sup>

The laser-power dependence of the second-harmonic signals from the smooth and rough surfaces was also measured. In all cases, the SH signal was quadratic in laser power, as shown in Fig. 2. For the electrolytically cycled bulk silver samples, the power-law dependence of the broadband background was found to be  $\sim [I(\omega)]^3$  on the anti-Stokes 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-law de-

pendence of the broadband background was found to be  $\sim [I(\omega)]^6$  on the anti-Stokes side and  $\sim [I(\omega)]^3$  on the Stokes side. Furthermore, the temporal behavior of the rough-film background showed a clear tail, several pulse widths 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>11</sup>

Similar results were obtained for gold, although both the second-harmonic signal and the luminescence background from the rough surface were 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  $\sim 500\text{-}\text{\AA}$  Ag particles separated by  $1500\text{-}3000 \text{ \AA}$ .<sup>5</sup> We can therefore reasonably assume in Eq. (4) that the fractional area  $x$  where  $L(\omega)$  is nearly a maximum because of plasmon resonance is  $\sim 5\%$ , and that structures in resonance at  $\omega$  will not also be in resonance at  $2\omega$ , so that  $L(2\omega) \sim 1$ . 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 could be carried out on well-defined rough surface structure such as arrays of ellipsoids of the same size formed by lithographic techniques.<sup>12</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

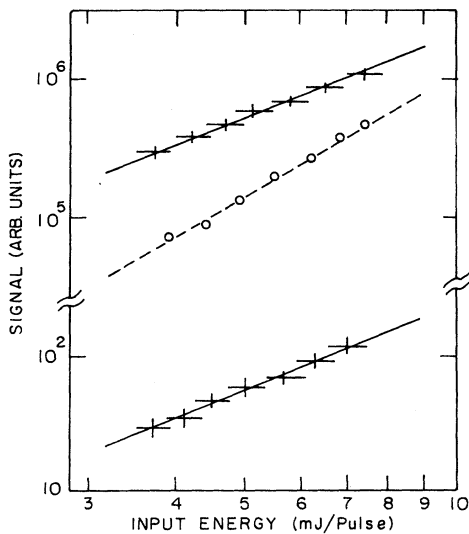


FIG. 2. Power-law dependences of the nonlinear signal on silver. The upper and lower solid curves show the quadratic dependence of the diffuse SH signal from the rough bulk sample and of the collimated SH signal from the smooth film, respectively; the dashed curve shows the cubic dependence of the diffuse anti-Stokes signal from the rough bulk sample.

luminescence has also been observed from the rough metal surfaces. The mechanism leading to such luminescence is not yet understood.

We thank Professor R. K. Chang for providing information about electrolytic cycling on Au and Cu. This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under Contract No. W-7405-ENG-48. One of us (A.R.B.d.C.) acknowledges support from Universidade Estadual de Campinas and Conselho Nacional de Pesquisas, Brazil.

<sup>(a)</sup>Permanent address: Instituto de Física, Universidade Estadual de Campinas, 13100 Campinas, São Paulo, Brazil.

<sup>1</sup>See, for example, the latest review by T. E. Furtak and J. Reyes, *Surf. Sci.* **93**, 351 (1980), and references therein.

<sup>2</sup>D. L. Jeanmaire and R. P. Van Duyne, *J. Electroanal. Chem.* **84**, 1 (1977); M. Fleischmann, P. J. Hendra, and A. J. McQuillan, *Chem. Phys. Lett.* **26**, 163 (1974).

<sup>3</sup>See, for example, A. Otto, J. Timper, J. Billman, and I. Pockrand, *Phys. Rev. Lett.* **45**, 46 (1980); J. I. Gersten, R. L. Birke, and J. R. Lombardi, *Phys. Rev. Lett.* **43**, 147 (1979); E. Burstein, Y. J. Chen, C. Y. Chen, S. Lundquist, and E. Tosatti, *Solid State Commun.* **29**, 567 (1979); S. S. Jha, J. R. Kirtley, and

J. C. Tsang, *Phys. Rev. B* **22**, 3973 (1980).

<sup>4</sup>See, for example, D. A. Weitz, T. J. Gramila, A. Z. Genack, and J. I. Gersten, *Phys. Rev. Lett.* **45**, 355 (1980); M. Moskovitz, *J. Chem. Phys.* **69**, 4159 (1978); G. L. Eesley and J. R. Smith, *Solid State Commun.* **31**, 815 (1979); S. S. Jha, J. R. Kirtley, and J. C. Tsang, *Phys. Rev. B* **22**, 3973 (1980).

<sup>5</sup>J. E. Rowe, C. V. Shank, D. A. Zwemer, and C. A. Murray, *Phys. Rev. Lett.* **44**, 1770 (1980).

<sup>6</sup>S. L. McCall, P. M. Platzman, and P. A. Wolff, *Phys. Lett.* **77A**, 331 (1980).

<sup>7</sup>A. Harstein, J. R. Kirtley, and J. C. Tsang, *Phys. Rev. Lett.* **45**, 201 (1980).

<sup>8</sup>N. Bloembergen, R. K. Chang, S. S. Jha, and C. H. Lee, *Phys. Rev.* **174**, 813 (1968).

<sup>9</sup>Y. R. Shen, C. K. Chen, and A. R. B. de Castro, in *Proceedings of the Eleventh International Quantum Electronics Conference*, Boston, June 1980 (to be published), paper N7, and in *Proceedings of the Sergio Porto Memorial Symposium on Lasers and Applications*, Rio de Janeiro, 29 June–3 July 1980 (to be published).

<sup>10</sup>C. K. Chen, T. Heinz, D. Ricard, and Y. R. Shen, to be published.

<sup>11</sup>R. L. Birke, J. R. Lombardi, and J. I. Gersten, *Phys. Rev. Lett.* **43**, 71 (1979); J. P. Heritage, J. G. Bergman, A. Pinczuk, and J. M. Worlock, *Chem. Phys. Lett.* **67**, 229 (1979).

<sup>12</sup>P. F. Liao, in *Proceedings of the U. S.-Japan Bilateral Seminar on Nonlinear Laser Spectroscopy*, 8–12 September 1980, Kauai, Hawaii (to be published).

## Search for Vortex Unbinding in Two-Dimensional Superconductors

Peter A. Bancel<sup>(a)</sup> and K. E. Gray

*Argonne National Laboratory, Argonne, Illinois 60439*

(Received 5 August 1980)

The Kosterlitz-Thouless theory applied to two-dimensional superconducting films suggests that vortex unbinding can explain their gradual resistive transitions. An experiment which directly probes the dynamics of unbinding is reported. The results indicate that, if vortex unbinding does occur in our superconducting films, the dynamic theory overestimates the relaxation time by almost two orders of magnitude.

PACS numbers: 74.40.+k, 64.60.Cn, 73.60.Ka

Phase transitions in two-dimensional (2D) systems are important because of their marginal dimensionality and have received considerable attention recently.<sup>1</sup> The Kosterlitz-Thouless (KT) prediction of a dislocation unbinding transition has been discussed in several systems including vortex unbinding in superconductors.<sup>2-4</sup> Experimentally, 2D superconducting systems are particularly interesting because of the ease with which one can make measurements.<sup>5-7</sup> Unfortunately, the subtle effects of the KT transition are difficult to distinguish unambiguously from effects

due to inhomogeneity, and since the very thin samples used are known to be inhomogeneous,<sup>7</sup> direct evidence of vortex unbinding is necessary.

The dynamics of vortex unbinding provides such a characteristic fingerprint. However, experimental results reported in this Letter show no evidence for vortex unbinding in samples whose homogeneity is unquestionably improved over that of others.<sup>6,7</sup> These negative results will be discussed within the context of theoretical models.

The KT theory applied to superconductors<sup>2-4</sup>