

# Electric-field-induced reflection in silver accompanying generation of the giant second harmonic

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(Submitted 6 May 1983)

*Pis'ma Zh. Eksp. Teor. Fiz.* **37**, No. 12, 592-594 (20 June 1983)

The dependence of the intensity of the surface-enhanced second harmonic on the magnitude of the constant electric field [not observed by T. F. Heinz *et al.*, *Chem. Phys. Lett.* **83**, 1 (1981)] is observed.

PACS numbers: 78.20.Jq

Surface enhancement of the second harmonic (SH), generated with reflection of light from a rough silver surface, was first observed by Chen *et al.*<sup>1,2</sup> This phenomenon is closely related to giant Raman scattering of light (GRS) and is caused by the increase in the local field  $E_l(\omega) = L(\omega) E(\omega)$  accompanying resonant excitation of surface plasmons in a metal with incident radiation  $E(\omega)$ , where  $L(\omega)$  is the local field factor. For a rough metal surface, the local field factor has the form

$$L(\omega) = [\epsilon_M(\omega) - \epsilon_{av}(\omega)][\epsilon_M(\omega) + \eta\epsilon_{av}(\omega)]^{-1},$$

where  $\epsilon_M$ ,  $\epsilon_{av}$  are the complex dielectric constants of the metal and of the surrounding medium, and  $\eta \sim 10$  is a coefficient that depends on the geometry of the surface inhomogeneities.<sup>2,3</sup> When the pumping radiation is in resonance with the local surface plasmons,  $\text{Re}[\epsilon_M(\omega) + \eta\epsilon_{av}(\omega)] = 0$  and the local field factor  $L(\omega) \sim \text{Im}[\epsilon_M \times (\omega) + \eta\epsilon_{av}]^{-1}$  increases in a resonant manner.

The polarization of the surface layer of the metal, including the local field factor, is determined by the expression

$$P(2\omega) = L(2\omega)L^2(\omega)\chi_{\text{eff}}^{(2)}(2\omega; \omega, \omega)E^2(\omega),$$

where  $\chi_{\text{eff}}^{(2)}$  is the effective quadratic susceptibility of the metal (including the quadrupolar susceptibility for media with an inversion center). At resonance  $L(\omega) \sim 10$  and the intensity of SH with reflection from a rough metal surface  $L_{2\omega}$  increases by four orders of magnitude compared to SH generated on a smooth surface. Such surface enhancement of  $I_{2\omega}$ , by analogy with GRS, can be called generation of giant SH.

A constant electric field  $E_0$ , applied to the surface, changes  $\epsilon_M$  due to the contribution of cubic susceptibility  $\chi^{(3)}(\omega; \omega, 0, 0)E_0^2$  and thereby changes the magnitude of the local field factor. The quadratic susceptibility of the metal also changes when a constant electric field is applied due to the contribution of  $\chi^{(3)}(2\omega; \omega, \omega, 0)E_0$ . Both factors must change the intensity of the giant SH with the application of  $E_0$ . This dependence of  $I_{2\omega}$  on the electric field could be caused by electric-field-induced reflection accompanying generation of the giant SH. However, the dependence  $I_{2\omega}(E_0)$  was not observed in Ref. 1.

We investigated electric-field-induced reflection accompanying generation of gi-

20th  
anniversary of coming out  
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on surface nonlinear optics

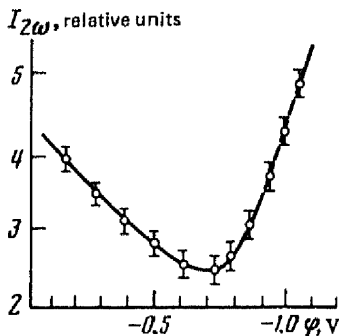


FIG. 1. Dependence of the giant SH intensity on the voltage drop  $\varphi$  across the silver-electrolyte interface.

ant SH from the surface of silver. The controlled roughness was deposited on the metal surface by anodic etching in an electrolytic solution of KCl with a concentration of 0.1 mole/liter. The charge density, transferred over one anode cycle, for which the gain in the SH intensity reached saturation  $\sim 10^4$ , was  $q = 100 \text{ mC/cm}^2$ . Investigation of the silver surface with an electron microscope showed the presence of roughness with characteristic size  $\sim 1000 \text{ \AA}$ . The constant electric field was applied to the surface of the metal by applying a voltage across the electrolyte between the silver and the auxiliary platinum electrode. With this method, it was possible to achieve fields  $E_0 \sim 10^6\text{--}10^7 \text{ V/cm}$  across the metal-electrolyte interface.<sup>4</sup>

We observed the generation of giant SH with reflection of a single mode YAG:Nd<sup>3+</sup> laser pulse with wavelength  $\lambda = 1060 \text{ nm}$ , pulse duration 15 ns, and energy density  $\sim 5 \text{ mJ/cm}^2$ . The SH radiation with  $\lambda = 530 \text{ nm}$ , collected at the input slit of a DFS-24 monochromator, was recorded by a strobe amplitude-digital converter.

Figure 1 shows the dependence of  $I_{2\omega}$  on the voltage drop  $\varphi$  in the Helmholtz layer at the silver-electrolyte interface (the potential  $\varphi$  was measured relative to a chlorine-silver comparison electrode). It is well known that a constant electric field  $E_0$  in the Helmholtz layer vanishes at some value of the potential  $\varphi_1$ , called the zero-charge potential. For silver in a KCl solution, we have  $\varphi_1 = -0.76 \text{ V}$ .<sup>5</sup> The value of the potential  $\varphi_{\text{min}}$ , at which a minimum is observed in the intensity of the giant SH, agrees well with the quantity  $\varphi_1$ . As  $\Delta\varphi = |\varphi - \varphi_1|$  is increased, the field  $E_0$  in the Helmholtz layer increases, reaching magnitudes of  $\sim 10^7 \text{ V/cm}$  at  $\Delta\varphi \sim 1$ , which is what leads to the increase in  $I_{2\omega}$ .

The ionic layer in the electrical double-layer at the metal-electrolyte interface can contribute to  $I_{2\omega}$ , together with the surface layer of the metal. The dependence of  $I_{2\omega}$  on the field  $E_0$  is apparently determined primarily by the contribution of the metal due to the large values of  $\chi^{(3)}$  for silver,<sup>6</sup> but the asymmetry of the curve  $I_{2\omega}(\varphi)$  relative to  $\varphi_1$  could be related to the contribution of the Helmholtz layer, which has a different structure for  $\varphi < \varphi_1$  and  $\varphi > \varphi_1$ . The interference of nonlinear contributions of the component parts of the electrical double layer could shift the position of the minimum in  $I_{2\omega}(\varphi)$ , which must be taken into account when measuring  $\varphi_1$  by the method of giant SH generation.

Thus we have observed for the first time electric-field-induced reflection accompanying generation of surface-enhanced SH. Based on this phenomenon, a nonlinear-optical method for measuring the zero-charge potential of the metal is proposed.

In conclusion, we thank L. V. Keldysh for formulating the problem and for useful discussions.

<sup>1</sup>T. F. Heinz, C. K. Chen, D. Ricard, and Y. R. Shen, *Chem. Phys Lett.* **83**, 1 (1981).

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<sup>3</sup>F. J. Adrian, *Chem. Phys Lett.* **78**, 45 (1981).

<sup>4</sup>A. B. Bucman and N. M. Bashara, *Phys. Ref.* **174**, 719 (1968).

<sup>5</sup>A. V. Shlepkov and E. S. Sevast'yanov, *Elektrokhimiya* **14**, 287 (1978).

<sup>6</sup>M. D. Levenson and N. Bloembergen, *Phys. Rev. B* **10**, 4447 (1974).

Translated by M. E. Alferieff

Edited by S. J. Amoretty