

# Photoactivation mechanism and Bunsen-Roscoe law in surface-enhanced Raman scattering and the giant second harmonic

O. A. Aktsipetrov, E. D. Mishina,<sup>1)</sup> T. V. Murzina, A. V. Petukhov,  
and A. L. Petukhova

*M. V. Lomonosov Moscow State University*

(Submitted 20 March 1987)

*Pis'ma Zh. Eksp. Teor. Fiz.* **45**, No. 9, 407-410 (10 May 1987)

The mechanism for the photoactivation of giant nonlinear-optics processes at a rough silver surface has been identified experimentally. The photoactivation of the giant second harmonic is shown to obey the Bunsen-Roscoe law.

The intensity of surface-enhanced Raman scattering (SERS) and that of the giant second harmonic can be increased by more than an order of magnitude by illuminating the surface of a metal during the imposition of a roughness by electrochemical (anodic) etching. This "photoactivation" was first observed for surface-enhanced Raman

scattering by Wetzel *et al.*<sup>1</sup>; for the giant second harmonic it was observed in Ref. 2. Reaching an understanding of the nature of photoactivation requires examining the mechanism for the enhancement of nonlinear-optics processes at surfaces.<sup>3</sup> The mechanism regarded as the primary one in surface-enhanced Raman scattering is a long-range electromagnetic mechanism by which the pump field  $E(\omega)$  increases upon the excitation of localized surface plasmons in the roughness granules. This effect intensifies the Raman scattering by four orders of magnitude for adsorbed molecules. In addition, there is short-range molecular-chemical mechanism which involves a change in the Raman-scattering polarizability of the molecules upon their adsorption. This mechanism provides an additional intensification of the Raman scattering by a factor  $\sim 10$ – $10^2$ . This mechanism consists of the formation at a surface, during its electrochemical etching, or organometallic complexes consisting of an adsorbed molecule and a metal adatom, which have a charge-transfer band in the visible range of their electron spectrum. Just which of these mechanisms is influenced by the illumination is not clear, however. The photoactivation of surface-enhanced Raman scattering can be explained in terms of either a change in the roughness (the electromagnetic mechanism for photoactivation)<sup>4</sup> or a change in the surface density of charge-transfer complexes,  $N_{CTC}$ , during the illumination (the molecular-chemical mechanism for photoactivation).<sup>5</sup> It is difficult to distinguish between these mechanisms in a study of the photoactivation of surface-enhanced Raman scattering (and this has been the topic of all studies on photoactivation), since the intensity of the surface-enhanced Raman scattering,

$$I_{RS} \sim N_{CTC} \alpha_{\text{eff}}^2 L^4(\omega) E^2(\omega)$$

always includes a combination of  $N_{CTC}$ , the effective Raman-scattering polarizability of the complexes,  $\alpha_{\text{eff}}$ , which incorporates the appearance of a charge-transfer band, and the local-field factor  $L(\omega)$ , which incorporates the excitation of surface plasmons.

Turning to the giant second harmonic, we find a different situation. The polarization of the surface layer at the frequency of the second harmonic is

$$P(2\omega) \sim (\chi_M^{(2)} + N_{CTC} \gamma_{\text{eff}}^{(2)}) L(2\omega) L^2(\omega) E^2(\omega),$$

where  $\chi_M^{(2)}$  is the nonlinear susceptibility of the metal, and  $\gamma_{\text{eff}}^{(2)}$  is the effective hyperpolarizability of the adsorbate molecules, with allowance for the charge-transfer band. The polarization  $P(2\omega)$  and thus the intensity of the second harmonic do not vanish at  $N_{CTC} = 0$ . This circumstance makes it possible to distinguish the effect of the illumination on the electromagnetic and molecular-chemical mechanisms.

We studied the mechanism for photoactivation in pure (0.9999) polycrystalline silver in an electrochemical cell with a 0.1M aqueous solution of KCL, to which pyridine ( $C_5H_5N$ ) could be added in a concentration of 0.05M. The giant second harmonic is excited by the light from an Nd:YAG laser with a wavelength  $\lambda_L = 1064$  nm. The surface-enhanced Raman scattering is excited by light from an argon laser with  $\lambda_L = 514.5$  nm. The region in which the second harmonic and the surface-enhanced Raman scattering are excited on the surface of the silver is illuminated dur-

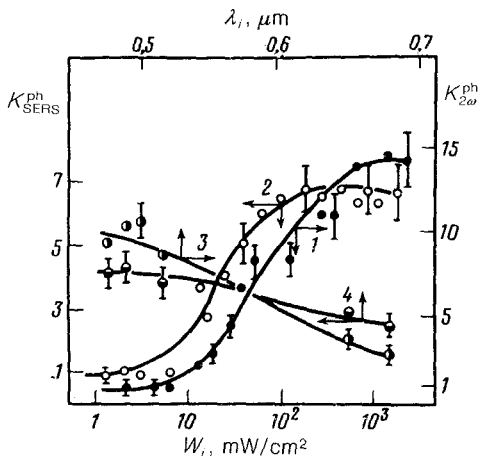


FIG. 1. 1,2—Photoactivation coefficients for the giant second harmonic and for surface-enhanced Raman scattering versus the power density of the illumination; 3,4—versus the wavelength of the illumination. 1,2— $\lambda_i = 488.0$  nm; 3,4— $W_i \sim 150$  mW/cm<sup>2</sup>.

ing anodic etching with the beam from an Ar<sup>+</sup>/Kr<sup>+</sup> laser with an adjustable power density  $W_i$  and a wavelength  $\lambda_i$ .

Figure 1 shows the photoactivation coefficients for the giant second harmonic,  $K_{2\omega}^{ph} = I_{2\omega}(W_i)/I_{2\omega}^0$ , and for the surface-enhanced Raman scattering,  $K_{RS}^{ph} = I_{RS}(W_i)/I_{RS}^0$ , versus the illumination parameters  $W_i$  and  $\lambda_i$ , where  $I_{2\omega}(W_i)$  and  $I_{RS}(W_i)$  are the photoactivated intensities of the second harmonic and the surface-enhanced Raman scattering, and  $I_{2\omega}^0$  and  $I_{RS}^0$  are the respective dark intensities. It is fair to say that, in general, there is quantitative similarity in these results, implying a common nature for the photoactivation of the giant second harmonic and the surface-enhanced Raman scattering.

We were able to vary  $N_{CTC}$  over a broad range in our experiments. The surface density of the adatoms is at maximum during the etching for  $\varphi = +0.15$  V; it falls off substantially when we leave the anodic cycle, at  $\varphi \leq 0$  V, dropping to essentially zero at  $\varphi \sim -0.7$  V. By adding pyridine to the electrode at various values of  $\varphi$ , we can vary  $N_{CTC}$  to the point that the molecular-chemical mechanism is completely eliminated. Figure 2 shows curves of  $K_{2\omega}^{ph}$  for the cases in which the pyridine is added *before* (curve 1) and *after* (curve 2) the anodic etching. The decrease in the photoactivation coefficient by a factor of eight to ten when the pyridine is added after the etching, at a time when the density of adatoms and thus  $N_{CTC}$  are small, indicates the importance of a complex-formation process for the photoactivation.

In a next experiment, photoactivated and dark cycles were carried out in a pure KCl solution, without pyridine. In this case we have  $N_{CTC} \cong 0$ , and the illumination can affect primarily the roughness. Measurements yield the value  $K_{2\omega}^{ph} = (1 \pm 0.2)$ ; no photoactivation occurs. To eliminate all adsorption effects at the silver-liquid interface and to isolate the part of the roughness change caused by the photoactivation, we withdrew the silver from the electrochemical cell after the anodic cycle (either photoactivated or dark). After a thorough washing of the surface, we studied the giant second harmonic in air. Again in these measurements we found  $K_{2\omega}^{ph} = (1 \pm 0.2)$ ,

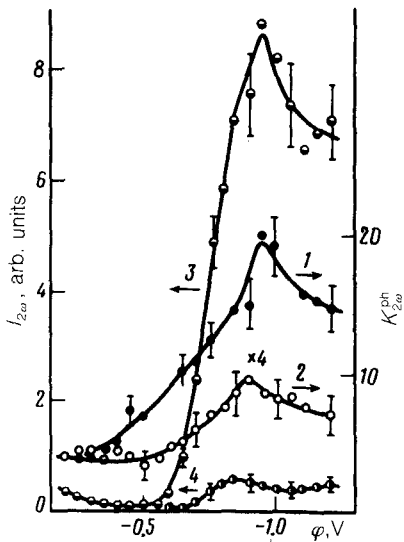


FIG. 2. Photoactivation coefficient of the giant second harmonic versus the potential, measured with respect to a saturated silver chloride reference electrode. 1—Pyridine is added before the etching; 2—after the etching, at  $\varphi = -0.2$  V (the scale for curve 2 is enlarged by a factor of 4). Curve 1 was found as the ratio of the intensities of the second harmonic in the cases of photoactivated (3) and dark (4) anodic cycles.

which ruled out an effect of the illumination on the imposition of the roughness. We wish to emphasize that the last two experiments, in which the organic adsorbate was not present on the surface, were not possible in the surface-enhanced Raman scattering.

In summary, we can conclude that the photoactivation occurs by a molecular-chemical mechanism: Illuminating the surface during the anodic cycle increases the surface density of charge-transfer complexes.

It has been shown that the photoactivation of the giant second harmonic obeys the Bunsen-Roscoe law in a certain interval of  $W_i$ . For values of  $W_i$  taken from the ascending part of curve 1 (Fig. 1) the coefficient  $K_{2\omega}^{ph}$  is proportional to the exposure  $H = W_i \cdot t$ ;  $W_i$  and the illumination time  $t$  enter in an interchangeable way (the Bunsen-Roscoe law has been demonstrated previously<sup>2</sup> for the photoactivation of surface-enhanced Raman scattering). It turns out that at saturation, where  $K_{2\omega}^{ph}$  is independent of  $W_i$ , we observe a linear increase in the photoactivation coefficient with the illumination time. This behavior may stem from diffusion near the surface of the electrolyte; it requires further study.

We wish to thank L. V. Keldysh for assistance in organizing the research and for useful discussions of the results.

<sup>1</sup>Moscow Institute of Radio Engineering, Electronics, and Automation.

<sup>1</sup>H. Wetzel, B. Pettinger, and U. Wenning, Chem. Phys. Lett. **75**, 173 (1980).

<sup>2</sup>O. A. Aktsipetrov and E. D. Mishina, Pis'ma Zh. Eksp. Teor. Fiz. **38**, 442 (1983) [JETP Lett. **38**, 535 (1983)].

<sup>3</sup>V. M. Agranovich (editor), Surface-Enhanced Raman Scattering (Russ. transl. Mir, Moscow, 1984).

<sup>4</sup>S. N. Macomber, T. E. Furtak, and T. M. Devine, Chem. Phys. Lett. **90**, 439 (1982).

<sup>5</sup>F. Barz, J. G. Gordon, M. R. Philpott, and M. J. Weaver, Chem. Phys. Lett. **91**, 291 (1982).

Translated by Dave Parsons