

Photoactivation of the giant second harmonic; surface-enhanced Raman scattering

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Photoactivation of the giant second harmonic has been observed. An interchangeability is demonstrated for surface-enhanced Raman scattering.

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The generation of a giant second harmonic and the surface-enhanced Raman scattering of light are surface nonlinear-optics effects in which the intensity of the reflected second harmonic and the Raman-scattering cross section increase dramatically (by four to six orders of magnitude) for molecules adsorbed on a rough metal surface.^{1,2} This intensification of nonlinear-optics processes is apparently general in nature and is related to an increase in the local field of the pump wave at the surface because of the excitation of surface plasmons in the metal.¹

A photoactivation of the surface-enhanced Raman effect has been observed^{3,4} for pyridine molecules (C_5H_5N) adsorbed on silver. The intensity of the Raman-scattering lines increased by a factor of three to six after the silver surface was illuminated during anodic etching required to create a surface roughness. If the intensification of the giant second harmonic and the surface-enhanced Raman effect have common mechanisms, involving a resonant increase in the local field, then a similar effect should be observed during the generation of the giant second harmonic.

In this letter we report a study of the photoactivation of the giant second harmonic in harmonic generation at the surface of silver in an electrolytic solution of KCl at a concentration of 0.1M with an admixture of 0.05M of pyridine. To create a rough surface, we carried out anodic etching with a charge density $q = 100$ mC/cm², during which the metal was illuminated with a cw laser beam with a power density $W \sim 50$ – 100 mW/cm² over the range of wavelengths λ from 441.6 nm to 632.8 nm. Generation

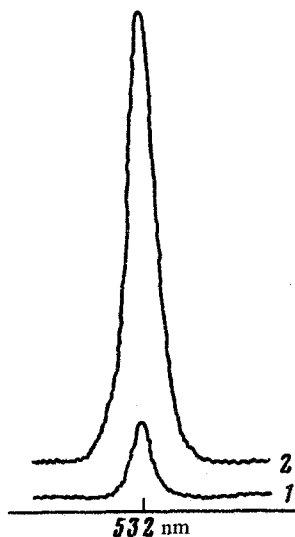


FIG. 1. Intensity of the giant second harmonic vs the intensity of the surface illumination during anodic etching. 1—The signal representing the giant second harmonic during the creation of a surface roughness in darkness; 2—during illumination of the silver with light at $\lambda = 632.8$ nm with $W = 100$ mW/cm².

of the giant second harmonic was observed during the reflection of the beam at $\lambda = 1060$ nm from a *Q*-switched single-mode YAG:Nd³⁺ laser at a power density ~ 0.1 MW/cm². The system used to detect the giant second harmonic with $\lambda = 530$ nm was similar to that of Ref. 5.

Figure 1 shows spectrograms of the giant second harmonic for experiments in which two methods were used to create the surface roughness. In one case the anodic etching was carried out in darkness (curve 1), while in the other it was carried out in a laser beam (curve 2). Comparison of the second-harmonic intensities $I_{2\omega}$ reveals that the surface enhancement of the second harmonic due to the photoactivation is by a factor of five to seven in comparison with the enhancement in darkness. Illumination of the metal surface during the anodic etching causes an increase in $I_{2\omega}$ with illumination anywhere over the λ range specified.

Photoactivation of the surface-enhanced Raman effect was studied under the same conditions as for the photoactivation of the giant second harmonic. The surface-enhanced Raman-effect spectrum of pyridine was excited by the beam from a He-Ne laser with $\lambda = 632.8$ nm and with a power of 40 MW. The system used to measure the Raman-effect signal I_R consisted of a DFS-24 double monochromator, a cooled FEU-79 photomultiplier, and a photon-counting system.

Figure 2a is a plot of $I_R(W)$, the intensity of the surface-enhanced Raman line of the vibration $\nu = 1010$ cm⁻¹ of the pyridine molecule, vs the power density of the illumination during the creation of the surface roughness. We see that there is a threshold for the effect: Photoactivation sets in at $W \gtrsim 10$ mW/cm². Then comes a region of a linear increase in the Raman surface enhancement, followed by a saturation

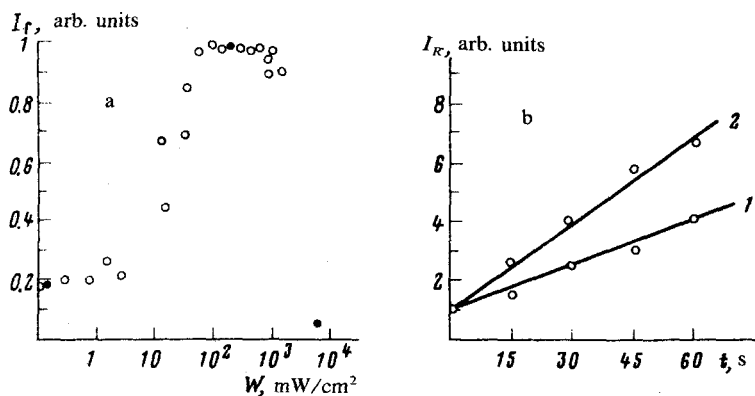


FIG. 2. a: Intensity of the surface-enhanced Raman scattering vs the illumination power density. ○—Surface-enhanced Raman-effect line of pyridine with $\nu = 1010 \text{ cm}^{-1}$ (illumination at $\lambda = 632.8 \text{ nm}$); ●—surface-enhanced Raman-effect line of uracil with $\nu = 1642 \text{ cm}^{-1}$ (illumination at $\lambda = 488 \text{ nm}$). b: Intensity of the surface-enhanced Raman scattering vs the illumination time ($\lambda = 632.8 \text{ nm}$) for the surface-enhanced Raman-effect line of pyridine with $\nu = 1010 \text{ cm}^{-1}$. 1— $W = 25 \text{ mW}/\text{cm}^2$; 2— $W = 50 \text{ mW}/\text{cm}^2$.

region. At $W \gtrsim 5 \times 10^3 \text{ mW}/\text{cm}^2$ we see a deactivation of the surface-enhanced Raman effect: The scattering intensity falls below the level of the signal during the creation of the surface roughness in darkness. The frequency dependence of the photoactivation of the surface-enhanced Raman effect is analogous to that for the activation of the giant second harmonic. Illuminating the surface with infrared light at $\lambda = 1060 \text{ nm}$ did not cause photoactivation of the surface-enhanced Raman effect.

We recorded the time dependence of I_R during anodic etching for two values of the illumination power density in the linear region of the $I_R(W)$ curve (Fig. 2b). The linear nature of $I_R(W)$ and the relationship between the slope of the line and the illumination power density show that the photoactivation of the surface-enhanced Raman effect is determined by the exposure $H = Wt$, where W and t are on an equal footing; i.e., an interchangeability law applied.

The photoactivation of the surface-enhanced Raman effect is not selective in terms of the adsorbed molecules; it is observed not only for pyridine but also for uridine and uracil molecules.

Examination of the silver surface in a scanning electron microscope revealed no significant changes in the morphology (with a roughness with a characteristic dimension of $500\text{--}100 \text{ \AA}$) of a surface photoactivated at $W \sim 50 \text{ mW}/\text{cm}^2$ from that of a surface on which a roughness was created in darkness. Changes in the surface morphology were observed in Ref. 6 at values of W three orders of magnitude higher than the linear region on the photoactivation curve (Fig. 2a). The light apparently has a deactivating effect on the large-scale ($\sim 1000\text{-}\text{\AA}$) inhomogeneity, and the photoactivation is related to the submicroscopic ($< 100\text{-}\text{\AA}$) structure of the surfaces of the roughness ellipsoids themselves. This structure may be determined by the lifetime of local surface plasmons and thus by the sharpness of the resonance in the local field.

In summary, these experiments have demonstrated for the first time a photoactivation of the giant second harmonic. An interchangeability law has been established for the photoactivation of the surface-enhanced Raman effect. It has also been found that there are two thresholds in the effect, at low and high illumination intensities.

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