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

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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.

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Surface enhancement of the second harmonic (SH), generated with reflection of light from a rough silver surface, was first observed by Chen *et al.*[1,2] 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 ε_M, ε_{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.[2,3] When the pumping radiation is in resonance with the local surface plasmons, $\mathrm{Re}[\varepsilon_M(\omega) + \eta\varepsilon_{av}(\omega)] = 0$ and the local field factor $L(\omega) \sim \mathrm{Im}[\varepsilon_M \times(\omega) + \eta\varepsilon_{av}]^{-1}$ increases in a resonant manner.

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

$$P(2\omega) = L(2\omega)L^2(\omega)\chi^{(2)}_{\mathrm{eff}}(2\omega; \omega, \omega)E^2(\omega),$$

where $\chi^{(2)}_{\mathrm{eff}}$ 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 ε_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-

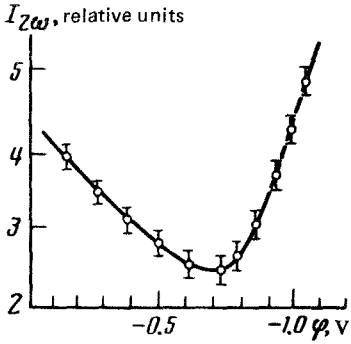

FIG. 1. Dependence of the giant SH intensity on the voltage drop φ across the silver-electrolyte interface.

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 $q = 100$ mC/cm^2. Investigation of the silver surface with an electron microscope showed the presence of roughness with characteristic size ~ 1000 Å. 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 $E_0 \sim 10^6$–10^7 V/cm[4] across the metal-electrolyte interface.[4]

We observed the generation of giant SH with reflection of a single mode YAG:Nd^{3+} laser pulse with wavelength $\lambda = 1060$ nm, pulse duration 15 ns, and energy density ~ 5 mJ/cm^2. The SH radiation with $\lambda = 530$ 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 φ in the Helmholtz layer at the silver-electrolyte interface (the potential φ 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 φ_l, called the zero-charge potential. For silver in a KCl solution, we have $\varphi_l = -0.76$ V.[5] The value of the potential $\varphi_{\min}$, at which a minimum is observed in the intensity of the giant SH, agrees well with the quantity φ_l. As $\Delta\varphi = |\varphi - \varphi_l|$ is increased, the field E_0 in the Helmholtz layer increases, reaching magnitudes of $\sim 10^7$ 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,[6] but the asymmetry of the curve $I_{2\omega}(\varphi)$ relative to φ_l could be related to the contribution of the Helmholtz layer, which has a different structure for $\varphi < \varphi_l$ and $\varphi > \varphi_l$. 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 φ_l 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 nonliner-optical method for measuring the zero-charge potential of the metal is proposed.

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