Photoactivation of giant Raman scattering and giant second harmonic

O. A. Aktsipetrov, E. D. Mishina, T. V. Murzina, A. V. Petukhov, and A. L. Petukhova

M. V. Lomonosov State University, Moscow

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A study was made of photoactivation of giant (surface-enhanced) Raman light scattering and of giant second harmonic generation. The common origin of the effects is demonstrated and a molecular-adsorption mechanism of photoactivation is established, a "memory" effect of photoactivation is reported, and it is shown that in a certain range of light intensities the photoactivation effect obeys the reciprocity (Bunsen-Roscoe) law. The photoactivation coefficient of giant second harmonic generation is maximal ($\sim 10^2$) after anodic etching of several surface monolayers of silver, which enhances greatly the sensitivity of the method of second harmonic generation to the presence of an adsorbate and makes it quasinondestructive because the changes in the initial topography of the investigated surface are small.

INTRODUCTION

Giant nonlinear optical processes on the surfaces of metals (usually called surface-enhanced processes in the Western literature) are attracting attention largely because of possible applications of these processes in the development of methods for the investigation and diagnostics of the surfaces of solids.[1–4] Therefore, the attainment of the highest surface-enhancement coefficients has become of fundamental importance and further investigations are needed of the enhancement mechanism and of the conditions under which the efficiency of such giant processes is maximal. Photoactivation of giant nonlinear optical processes is therefore undoubtedly of interest.

The photoactivation effect consists in a considerable (by an order of magnitude or more) increase in the intensity of giant Raman scattering (GRS) and generation of a giant second harmonic (SH) on illumination of the surface of a metal which is made rough by anodic etching. An increase in the intensity of GRS lines by a factor of 5–7 in the case of various molecules adsorbed on the surface of silver and copper is reported in Refs. 5–10. Photoactivation of a giant SH is reported in Ref. 7 and its study is described in Ref. 8. In spite of the fact that the photoactivation mechanism is not yet understood, this effect has been employed to increase considerably the sensitivity of GRS spectroscopy to the presence of an adsorbate.

The reasons for the influence of illumination of an anodically roughened surface on the enhancement coefficients of GRS and of a giant SH can be identified by considering the surface enhancement mechanisms. Two alternative approaches have been used to account for GRS: electromagnetic and molecular-adsorption. The electromagnetic mechanism of enhancement of GRS postulates an increase in the intensity of a local pump radiation field as a result of excitation of surface plasmons at the interface. In the case of some special structures (such as diffraction gratings or structures with frustrated total internal reflection) these can be surface plasmon-polaritons.[11] In the case of a rough surface with separate granules one can expect excitation of localized surface plasmons representing collective dipole oscillations of the electron components of a plasma in a metal.[12] A characteristic feature of the electromagnetic mechanism is its *long-range nature: the enhancement effect does not require a direct contact between a molecule and a metal.*

The other surface enhancement mechanism is associated with an increase in the Raman scattering polarizability (or of the quadratic hyperpolarizability in the case of generation of a second harmonic) of a molecule as a result of its adsorption. This molecular-adsorption mechanism is feasible in the case of some types of adsorption of organic molecules when metal/adsorbate complexes are formed on the surface and the electronic spectrum of these complexes has an additional visible band associated with charge transfer between the molecule and the metal.[13] Raman scattering and second harmonic generation in such an adsorbate may be of resonant nature and this in turn may increase considerably their intensities. In the case of the molecular-adsorption mechanism direct contact between a molecule and a metal is of fundamental importance, i.e., the mechanism is of short-range nature. The dominant role of the electromagnetic mechanism, ensuring an increase in the Raman scattering intensity by four or five orders of magnitude, is now generally accepted.[14] The enhancement associated with resonant excitation of Raman scattering to a charge-transfer band is estimated to be a factor of 10–10^2 (Ref. 14).

However, experimental estimates of the relative contributions of these two mechanisms are subject to a large error due to the fact that these contributions are very difficult to distinguish in studies of GRS. In fact, an adsorbate molecule, the presence of which is essential for the observation of GRS, has a dipole moment induced by the pump field and is described the expression

$$d_{st} \propto \alpha_{\rm eff}\, L^2(\omega) E(\omega) \qquad (1)$$

and the intensity of GRS

$$I_{\rm GRS} \propto N_{\rm ad} d_{st}^2 \sim N_{\rm ad} \alpha_{\rm eff}^2 L^4(\omega) E^2(\omega) \qquad (2)$$

always contains a combination of three parameters: the surface density of the adsorbate $N_{\rm ad}$, the effective Raman scattering polarizability of the adsorbate molecules $\alpha_{\rm eff}$ allowing for the appearance of a charge-transfer band, and the local field factor $L(\omega)$ allowing for the change in the pump field near a rough surface.

Studies of generation of a giant SH give much more reliable experimental estimates of the relative contributions of the various mechanisms. The quadratic polarization of a surface layer of a metal at the SH frequency is given by the expression

$$P(2\omega)\propto(\chi_{\mathrm{m}}^{(2)}+\gamma_{\mathrm{eff}}^{(2)}N_{\mathrm{ad}})L(2\omega)L^{2}(\omega)E^{2}(\omega),\qquad(3)$$

where $\chi_m^{(2)}$ is the nonlinear susceptibility of the metal and $\gamma_{\mathrm{eff}}^{(2)}$ is the effective quadratic hyperpolarizability of the adsorbate molecules deduced allowing for the charge-transfer band. The intensity of a giant SH

$$I_{2\omega}\propto P^{2}(2\omega)\propto(\chi_{\mathrm{m}}^{(2)}+\gamma_{\mathrm{eff}}^{(2)}N_{\mathrm{ad}})^{2}L^{2}(2\omega)L^{4}(\omega)E^{4}(\omega)\qquad(4)$$

does not vanish even in the absence of adsorbed molecules ($N_{\mathrm{ad}}=0$) on the surface and this makes it possible to operate the electromagnetic mechanism in its pure form, excluding the adsorption effects and thus the molecular-adsorption mechanism, which is not true of GRS.

The photoactivation of giant processes and the surface enhancement itself may be of dual nature. Illumination during anodic etching may, in principle, alter the parameters of the rough surface (electromagnetic photoactivation mechanism) and can change the surface density of charge-transfer complexes (molecular-adsorption photoactivation mechanism). However, investigations of the photoactivation of GRS do not give an unambiguous answer to the question of the nature of this effect. The experimentally observed enhancement of the intensity of the scattered light can be explained either by the influence of illumination on the structure of the surface roughness[9] or by an increase in the surface density of charge-transfer complexes N_{CTC} (Ref. 10). As in the investigations of the mechanisms of surface enhancement, generation of a giant SH makes it possible to draw more reliable conclusions on the nature of the photoactivation effect because by eliminating the adsorption effects, we can isolate the contribution of the photoactivating illumination to the change in the roughness of a metal surface. However, in extending then the mechanism of photoactivation of a giant SH to the photoactivation of GRS, we must demonstrate that these specific surface nonlinear optical phenomena are of the same origin.

EXPERIMENTAL METHOD

A sample of pure (0.9999%) polycrystalline silver was placed in an optical electrochemical cell containing an aqueous solution of KCl in a concentration of 0.1 mol/liter. Pyridine C_5H_5N could be added to this electrolyte in a concentration of 0.05 mol/liter (molecules of pyridine are a model adsorbate in GRS studies). Before being placed in a cell the surface of a silver electrode was polished with a diamond abrasive and then it was etched electrochemically in order to roughen the surface at anodic potentials of silver amounting to $\varphi=+0.15$ V relative to the electrolyte (φ was measured by comparison with a saturated silver chloride comparison electrode). Reversal of the sign of the current for a given value of φ could initiate electrochemical oxidation of silver producing a film of chloride on its surface. Reversal of the current across the interface then reduced a film of AgCl to metallic silver. The two reactions occurred mainly at initial irregularities of the surface acting as crystallization centers. Anodic etching of the surface produced metal granules; the average size and the surface density of these granules were determined by the density of the surface charge q which crossed the interface during the anodic etching time. In all cases, except those mentioned specially, a charge of density $q\sim200$ mC/cm^2 passed through the electrode surface and the current density was $i\sim2$ mA/cm^2.

In addition to these surface granules, anodic etching created a large number of adsorbed silver atoms (adatoms) because the process of surface diffusion and incorporation in the crystal lattice of the metal was hindered in the case of these atoms by the adsorbed water molecules and electrolyte ions. These adatoms could form metalorganic charge-transfer complexes with pyridine molecules, known to be active in GRS and in giant SH generation.

The surface density of adatoms depended strongly on the potential of silver: when the potential was sufficient for etching, the density of atoms was maximal, but outside the cycle in the range $\varphi\lesssim0$ V it began to fall rapidly tending to zero for $\varphi\sim-0.7$ V. The addition of organic molecules to the electrolyte solution before and after anodic etching made it possible to alter the value of the surface density of charge-transfer complexes N_{CTC} and thus change the contribution of the molecular-adsorption mechanism to surface enhancement and photoactivation.

A giant SH was observed on reflection of YAG:Nd^{3+} laser pulses from the surface of silver; the parameters of these pulses were as follows: the wavelength was $\lambda_L=1064$ nm, the pulse duration was $\tau\sim15$ ns, and the power density was $W_L\sim10$–100 kW/cm^2. The radiation of an ionic argon laser emitting at $\lambda_L=514.4$ nm with a power of $P_L\sim100$ mW was used in the excitation of GRS. The systems used to record the intensities of GRS and giant SH were described earlier.[4,15] A region where excitation of nonlinear processes took place on the surface of silver was illuminated during etching with background radiation from an Ar$^+$/Kr$^+$ laser with different wavelengths λ_b and different power densities W_b.

EXPERIMENTAL RESULTS AND DISCUSSION

1. Dependence of photoactivation on background illumination parameters

In comparing the mechanisms of photoactivation of Raman scattering and of giant SH generation we considered the main characteristics of the photoactivation effect for these two separate processes. We studied the dependences of the photoactivation coefficients of GRS $K_{\mathrm{GRS}}=I_{\mathrm{GRS}}(W_b)/I_{\mathrm{GRS}}^{0}$ and of giant second harmonic generation $K_{\mathrm{SH}}=I_{2\omega}(W_b)/I_{2\omega}^{0}$ on the parameters of background illumination and on the conditions during photoacti-

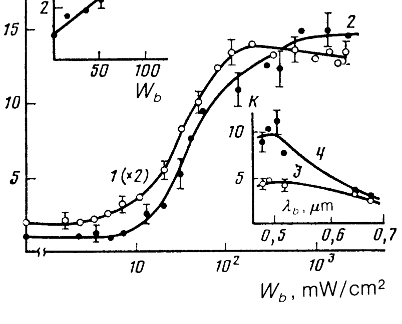

FIG. 1. Dependences of the photoactivation coefficients of GRS (1, 3) and giant SH generation (2, 4) on the power density W_b (1, 2) and wavelength λ_b (3, 4) of activating background illumination. Curve 5 shows the initial part of the dependence $K_{\mathrm{SH}}^{1/2}(W_b)$.

vation; here, $I_{\mathrm{GRS}}(W_b)$ and $I_{2\omega}(W_b)$ are the intensities of photoactivated giant (surface-enhanced) processes and I^0_{GRS} and $I^0_{2\omega}$ are the intensities of the corresponding processes in darkness. Figure 1 shows the dependences of K_{GRS} and K_{SH} on the power density of the background illumination W_b (curves 1 and 2) and on the background wavelength λ_b (curves 3 and 4). The dependences $K_{\mathrm{GRS}}(W_b)$ and $K_{\mathrm{SH}}(W_b)$ observed in the range $W_b > 10$ mW/cm^2 demonstrated an increase in the photoactivation coefficients by an order of magnitude or more, whereas in the range $W_b > 10^3$ mW/cm^2 the dependences reached saturation. The region of rise was linear in the case of GRS: $K_{\mathrm{GRS}} \propto W_b$. The photoactivation coefficient of the generation of a giant SH varied quadratically in this range of background illumination power densities: $K_{\mathrm{SH}} \propto W_b^2$. Curve 5 in Fig. 1 gives the $K^{1/2}_{\mathrm{SH}}(W_b)$ dependence obtained at $\lambda_b = 488.0$ nm and we can see that this dependence could be approximated satisfactorily by a straight line. The maximum value of the photoactivation coefficient in the region of saturation of generation of a giant SH was 2–3 times higher than for GRS.

The behavior of the spectral dependences of the photoactivation coefficients (curves 3 and 4 in Fig. 1) was similar for GRS and giant SH generation. There was no photoactivation in the infrared range. Moreover, the spectral dependence of the photoactivation coefficients was related qualitatively to the spectral dependence of the sensitivity of a surface film of AgCl to the process of photodissociation, which we used later in interpretation of the photoactivation mechanism.

All the measurements of the photoactivation of giant SH generation were made using pump (laser) pulses of power density $W_L \sim 20$ kW/cm^2. However, even this relatively low pump power density could affect the surface structure induced by the photoactivating illumination. We allowed for this possibility by investigating the dependence of the intensity of the second harmonic generated in the presence of photoactivation and in darkness $I_{2\omega}(W_L)$ in a wide range of W_L (Fig. 2). The values of W_L used in our experiments corresponded to the quadratic part of the dependence $I_{2\omega}(W_L)$, indicating the absence of degradation of the photoactivated surface. Moreover, the photoactivation effect was strong even when the conditions corresponded to those parts of the curves where the dependences deviated from the quadratic law.

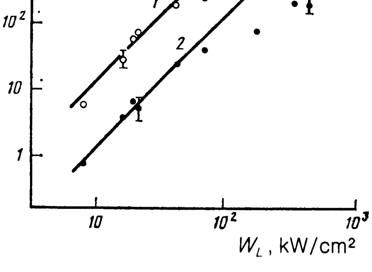

FIG. 2. Dependence of the intensity of a giant SH on the power density of the pump radiation W_L in the case of photoactivated (1) and dark (2) anodic etching cycles.

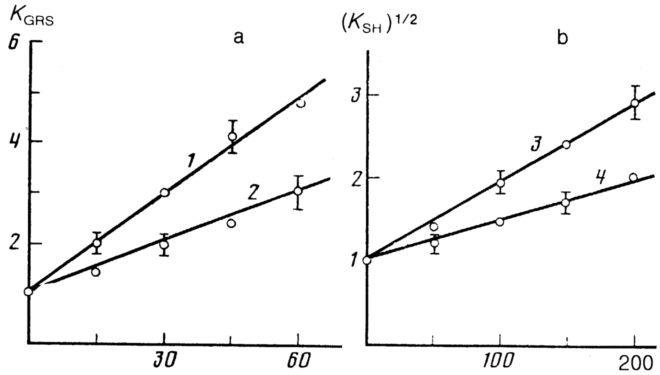

FIG. 3. Check of the validity of the Bunsen-Roscoe law in the photoactivation of GRS (a) and giant SH (b). Dependences of K_{GRS} and $K^{1/2}_{\mathrm{SH}}$ on the duration of background illumination t are approximated by straight lines with the slope proportional to the power density of the background illumination W_b. The results are plotted for the following values of W_b (MW/cm^2: 1) 50; 2) 25; 3) 60; 4) 30.

2. Relationship between photoactivation and exposure. Bunsen-Roscoe law

A detailed investigation of the dependence of the photoactivation of GRS and of giant SH on the parameters of the background illumination showed that in a certain range of the background power densities W_b the photoactivation effect obeyed the Bunsen-Roscoe reciprocity law. According to this law, the yield of a photoreaction product is proportional to the exposure $H = W_b t$ and that the duration of illumination t and the background power density W_b occurring in this expression are interchangeable.

Figure 3a shows the dependence of the coefficient $K_{\mathrm{GRS}}(t)$ for the $\nu = 1010$ cm^{-1} line of a molecular vibration of pyridine on the duration of illumination obtained for two values of W_b corresponding to the linear part of the dependence $K_{\mathrm{GRS}}(W_b)$ and differing by a factor of 2. The slope of the straight lines $K_{\mathrm{GRS}}(t)$ is such that in order to obtain the same values of the photoactivation coefficient at a lower background power density we would require twice the time. This confirmed that the Bunsen-Roscoe reciprocity law was satisfied by the process of photoactivation of GRS in the linear part of the dependence $K_{\mathrm{GRS}}(W_b)$.

Since the intensity of the second harmonic differs from the GRS intensity because the former is proportional to the square of the amount of the generated substance, we checked the Bunsen-Roscoe law in the case of the generation of giant SH by investigating the time dependences $K^{1/2}_{\mathrm{SH}}(t)$ for two values of W_b corresponding to the quadratic part of the dependence $K_{\mathrm{SH}}(W_b)$ and differing by a factor of 2 (Fig. 3b). The slope of the straight lines $W^{1/2}_{\mathrm{SH}}(t)$ demonstrated, exactly as in the case of GRS, that photoactivation of giant SH generation obeyed the reciprocity law in a certain range of the background power densities.

3. "Memory" effect in photoactivation

Investigations of the photoactivation GRS and of giant SH generation revealed a "memory" effect manifested as follows: when after roughening of the surface in the presence of photoactivating illumination the subsequent anodic etching cycles were carried out in darkness without preceding repolishing of the surface, the giant SH and GRS signals did not change greatly after the last cycle in darkness and remained practically at the level of the photoactivation signal. On the other hand, if there was no initial photoactivating cycle, the subsequent etching cycles in darkness not only did not enhance the signal, but even reduced it somewhat. Therefore even after complete renewal of the surface by thermal cycling a "memory" of photoactivation remained in the enhancement-inducing structure.

The results of the investigations described in this and the preceding two subsections demonstrate that the photoactivation mechanism is the same for GRS and giant SH. In fact, the spectral dependences of the photoactivation coefficients, their relationship to the power density of the background illumination, the reciprocity law, and the "memory" effect are similar for both these giant nonlinear optical processes.

4. Photoactivation mechanism

As pointed out above, the spectral dependences of the photoactivation coefficients are the same as the spectral dependences of the rate of photodissociation of silver chloride. This reaction results in photoreduction of neutral silver in a film of AgCl which covers the surface of a metal during anodic etching. Photoreduction increases the surface density of silver adatoms compared with the number of adatoms formed on the surface simply as a result of electrochemical reduction. The question is whether the additional (photoreduced) adatoms behave as crystallization centers for the formation of additional roughness granules or whether they participate in the process of formation of complexes and increase the surface density of metalorganic complexes.

We studied the influence of the background illumination on the electromagnetic enhancement mechanism by eliminating the adsorption effects. Cycles of anodic etching in darkness and in the presence of illumination were carried out using a pure solution of KCl without pyridine. In this case we found that metalorganic complexes did not form on the surface of silver and that illumination could influence only the process of formation of the surface roughness, but the intensity of a giant SH was not enhanced: $K_{SH} = 1 \pm 0.2$. In the next experiment involving illumination the process of formation of the surface roughness could be influenced only by such illumination. After anodic etching (photoactivated and in darkness) the silver electrode was removed from the electrochemical cell, washed thoroughly with water that was distilled twice; this removed the adsorbate and we were then able to study giant SH generation in air. We found that that again the SH intensity did not increase: $K_{SH} = 1 \pm 0.2$.

These results indicate a slight influence of the photoactivation on the surface roughness and electromagnetic enhancement of the local field. It should be stressed that, for fundamental reasons, similar experiments are impossible when the photoactivation of GRS is investigated.

The influence of the molecular-adsorption mechanism could be reduced significantly by adding pyridine *after* the anodic etching cycle. In this case the density of surface charge-transfer complexes was found to be considerably less because of the rapid reduction of the surface density of atoms at the end of anodic etching. Figures 4a and 4b give the dependences $I_{2\omega}(\varphi)$ and $K_{SH}(\varphi)$ obtained on addition of pyridine *before* and *after* anodic etching. In the former case when the process of electrochemical reduction of a film of AgCl occurred in the presence of pyridine, the surface density of adatoms and N_{CTC} were high and the photoactivation coefficient reached its maximum value of $K_{SH} \sim 20$. The addition of pyridine after the etching cycle at $\varphi \sim -2$ V reduced the photoactivation by a factor of 8–10 because of the low values of the surface density of adatoms.

It should be noted that for $\varphi \sim -(0.8\text{–}1.0)$ V the contribution of the molecular-adsorption mechanism to the enhancement of giant SH and GRS was maximal.[15] The intensity of a giant SH observed after the addition of pyridine before anodic etching, when the role of molecular-adsorption mechanisms was important, reached its maximum precisely in this range of potentials (curves 1 and 2 in Fig. 4a). However, when pyridine was added after roughening of the

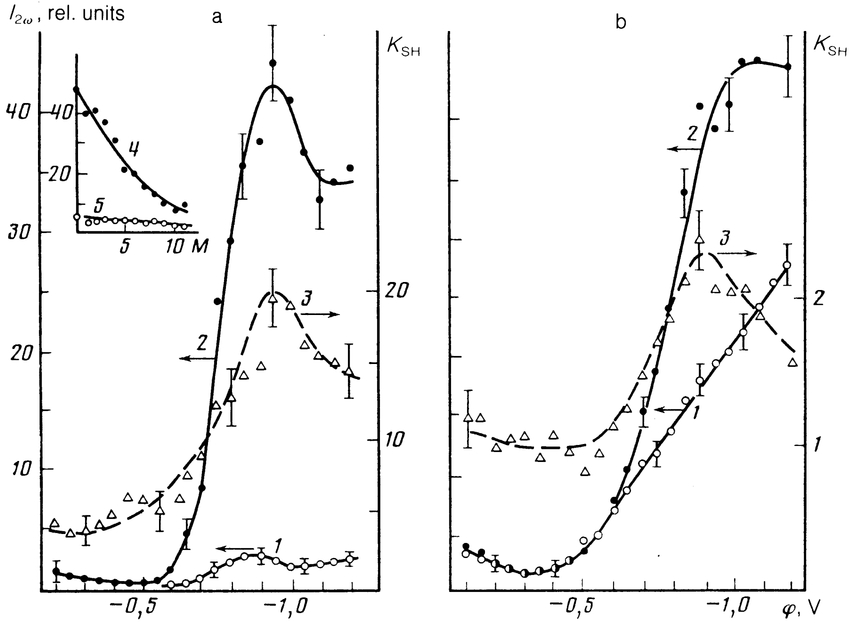

FIG. 4. Dependences of the SH intensity $I_{2\omega}$ on the potential φ obtained when pyridine was added before (a) and after (b) anodic etching in the case of dark (1) and photoactivated (2) giant SH. Curves denoted by 3 represent the dependence of the photoactivation coefficient K_{SH} on φ. The influence of the number M of the potential-scanning cycles on the intensity of the photoactivated (4) and dark (5) SH is shown in the inset.

TABLE I. Photoactivation coefficients of giant SH and GRS obtained for different values of the density N_{CTC} of metalorganic complexes of pyridine on the surface of silver.

Conditions during roughening of the surface	Conditions during measurement of SH and GRS signals	N_{CTC}	K_{SH}	K_{GRS}
In electrolyte without pyridine	in electrolyte without pyridine	0	1 ± 0.2	GRS spectrum of of pyridine absent
In electrolyte with pyridine	in air after washing with bidistillate	0	1 ± 0.2	ditto
In electrolyte without pyridine	in electrolyte with pyridine (pyridine added *after* etching)	small	1–2	5–7
In electrolyte with pyridine (added *before* etching)	in electrolyte with pyridine	large	15–20	5–7
Ditto	ditto, but after strong cathodic polarization	small	~ 1	

surface, this maximum did not appear in the dependence $I_{2\omega}(\varphi)$ (curves 1 and 2 in Fig. 4b) since the contribution of the adsorbate layer to the generation of a giant SH was then small and the nature of the dependence $I_{2\omega}(\varphi)$ was governed mainly by the influence of φ on the nonlinear susceptibility of the metal.[4] However, the maxima of the dependences $K_{\mathrm{SH}}(\varphi)$ were observed at potentials $\varphi \sim -(0.8\text{–}1.0)$ V in both cases (curves denoted by 3 in Figs. 4a and 4b) indicating an increase in the role of the molecular-adsorption mechanism of enhancement due to photoactivation.

An investigation of the photoactivation of GRS established that the addition of pyridine before and after anodic etching gave the same values of the photoactivation coefficient K_{GRS} (Refs. 7 and 9), so that we concluded that the photoactivation mechanism was of the electromagnetic type. However, this was clearly related to the fact that after anodic etching the density of photoreduced and chemoreduced adatoms and the density of charge-transfer complexes, formed as a result of roughening in darkness and during illumination, decreased by the same factor.

Metalorganic pyridine/silver complexes were unstable at high cathodic polarizations of the electrode and after exposure of the surface to a potential $\varphi \sim -1.0$ V the GRS and giant SH signals decreased irreversibly.[15] The inset in Fig. 4a shows the dependences of the intensity of the photoactivated (4) and dark (5) giant SH on the number of potential-scanning cycles in the range from -0.2 V to -1.3 V at a rate of 4 mV/s. The intensity $I_{2\omega}$ was measured at $\varphi = -0.9$ V after each scanning cycle. The much faster fall of $I_{2\omega}$ in the case of a photoactivated surface confirmed the dominant role of unstable metalorganic complexes in the photoactivation effect.

The results of our investigation of the photoactivation of giant SH obtained for different values of N_{CTC} are listed in Table I and they allow us to draw the conclusion about the molecular-adsorption mechanism of photoactivation: illumination of the surface during anodic etching increased the surface density of reduced silver adatoms and the surface density of metalorganic complexes. It should be pointed out that an investigation of the photoactivation of GRS, the results for which are given in the last column of the table on the right, could not be used to draw a definite conclusion about the nature of photoactivation.

5. Dependence of photoactivation on the parameters of an anodic etching cycle

We investigated the dependences of the photoactivation coefficients on the surface charge density q which passed during an anodic etching cycle. The exposure H was kept constant by altering q and this was done by varying the oxidation and reduction current density i while keeping the duration of the etching cycle constant at $T = 200$ s. Background illumination of the electrode during photoactivation was provided by light of $\lambda_b = 488$ nm wavelength and $W_b = 1$ W/cm^2 power density. We plotted in Fig. 5 the dependences of the giant SH intensity on q after roughening of the surface in darkness (curve 1) and after roughening accompanied by photoactivating illumination (curve 2). We plotted along the abscissa also the number of monatomic silver layers participating in the etching process (one monolayer corresponded to $q \sim 0.3$ mC/cm^2). In the range $q \lesssim 30$

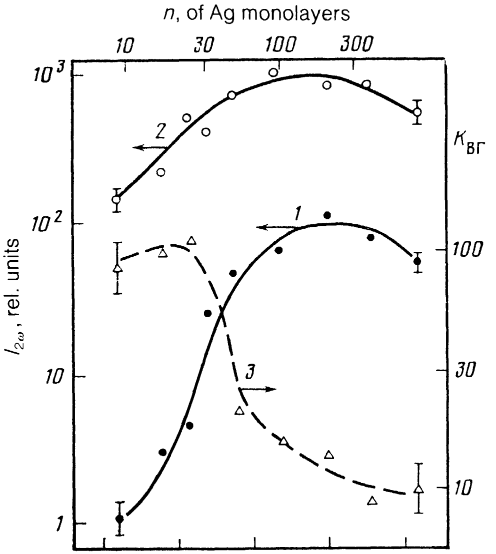

FIG. 5. Dependences of the intensity of the dark (1) and photoactivated (2) SH and of the photoactivation coefficient (3) on the charge density q and the number of etched silver monolayers n.

mC/cm^2 the dependence $I_{2\omega}^0(q)$ fell strongly, whereas the change in $I_{2\omega}(W_b)$ was considerably less in the same range of q. The dependence $K_{\text{SH}}(q)$ was represented by curve 3, which indicated that if $q = 100$–300 mC/cm^2, then $K_{\text{SH}} \sim 10$, whereas for $q \lesssim 10$ mC/cm^2, when the changes in the surface topography were small, we found that $K_{\text{SH}} \sim 100$.

This behavior of $I_{2\omega}^0$ and $I_{2\omega}(W_b)$ at low values of q was clearly associated with the fact that the amount of the activating background light depended weakly on q: in the case of photoactivation the important factor was only the presence of an oxide film on the surface. On the other hand, the number of charge-transfer complexes formed by chemoreduced silver adatoms during roughening in darkness depended strongly on the current density i and on the charge q in the case when $q \sim 10$ mC/cm^2.

CONCLUSIONS

We reported the results of photoactivation of giant second harmonic (SH) generation discovered earlier. We compared the characteristics of this effect with a similar phenomenon of photoactivation of giant Raman scatterint (GRS) of light.[6] We found that the photoactivation of GRS and giant SH exhibited a "memory" effect and obeyed the Bunsen-Roscoe reciprocity law.

The similarity of the dependences of the photoactivation coefficients K_{SH} and K_{GRS} on the power density and wavelength of the activating (background) illumination and the fact that the Bunsen-Roscoe reciprocity law was satisfied at the same values of the background illumination power density, together with the discovery of a "memory" effect, all pointed out to the same mechanism of photoactivation of GRS and giant SH. Since giant SH generation made it possible to distinguish experimentally the contributions of the electromagnetic and molecular-adsorption mechanisms to the surface enhancement, we determined the nature of photoactivation by investigating the features of these effects in the case of generation of a giant SH.

The magnitude of the photoactivation coefficient of giant SH was linked uniquely to the surface density of metalorganic pyridine/silver complexes. The absence of photoactivation in those experimental situations which were characterized by $N_{\text{CTC}} = 0$ indicated that background illumination had no significant influence on the surface roughening process or on the enhancement of the local field. An investigation of the photoactivation of giant SH for different values of N_{CTC} and also the dependence of the photoactivated SH signal on the SH signal led us to the conclusion that the photoactivation of GRS and of giant SH was due to the molecular-adsorption mechanism.

An investigation of the photoactivation of giant SH at low charges in an anodic etching cycle demonstrated that the photoactivation effect could be used to enhance the sensitivity of optical methods for monitoring the adsorption of organic molecules on metal surfaces when an essential requirement was a minimum change in the initial topography of the surface. Therefore, photoactivation made the generation of a giant SH a sensitive quasinondestructive method for the investigation of adsorption.

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