THERMAL DESORPTION OF MOLECULES FROM METAL SURFACES INDUCED BY THE SEQUENCE OF LASER PULSES

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The thermal desorption kinetics of adsorbed molecular layers from the surface of bulk metals and metal films under the sequence of short laser pulses is considered. Analytical expressions for the activation energy of desorption of molecules for both types of samples are obtained. We carried out the experimental investigation in the reflection geometry of the second harmonic generation by silver and gold films, as well as bulk samples of copper and aluminum with adsorbed layers of pyridine molecules during the laser-induced thermal desorption. The values of energy of desorption activation of pyridine molecules on the surface of noble metals and aluminum are calculated.

1. Introduction

The discovery of the surface enhanced second harmonic generation (SHG) by a monolayer of pyridine molecules (C_5H_5N) during the reflection of laser radiation from silver [1, 2] stimulated intense studies of adsorbed monolayers at interfaces and solid surfaces by means of nonlinear reflection [3]. As a result, the nonlinear optical spectroscopy of surfaces became the most effective optical method to study adsorbed monolayers, especially in the presence of the surface enhancement [4]. This is related to the fact that the registered useful nonlinear optical signal appears only in the presence of adsorbed molecules (in case of Raman scattering) or differs from the signal from the bare surface (in case of SHG). The possibility to obtain a second-harmonic (SH) signal only from the adsorbed molecular monolayer on a metal surface was first shown in [5].

The influence of adsorbed molecules (air) on SHG during the reflection from metal surfaces (silver) was first observed in [6]. The possibility of the detection of molecular monolayers of pyridine with the help of SHG was first shown in [1, 2]. These and further investigations with in the SHG method of molecular monolayers of pyridine, benzene, water, methanol, and nitrogen on silver and copper surfaces [7–10] have shown the possibility to determine the surface density of molecules in the adsorbed monolayer by the magnitude of an SH signal. The absolute value of SHG intensity, including the contribution from adsorbed molecules to the SH signal, is strongly dependent upon surface characteristics of samples. The SH signal generated by the layer of pyridine molecules adsorbed on a silver surface depends on the surface roughness [1, 2, 7] and the crystal-lattice orientation of the silver surface [11]. However, it is always possible to assume that the intensity of SH generated by the adsorbed molecular monolayer is directly proportional to $|n\alpha^{(2)}|^2$, where n is the surface density of adsorbed molecules, and $\alpha^{(2)}$ is the average nonlinear second-order polarizability of molecules.

2. Experimental Technique

Under the action of a powerful laser radiation, the desorption of molecules from the surface of samples occurs. It was mentioned in [1, 2, 7] that changes in the laser radiation power lead to the relaxation of the SHG intensity by pyridine molecules to some new equilibrium value that corresponds to the equilibrium density of adsorbed molecules, which is set on the silver surface. The authors of work [12] proposed to estimate the desorption duration by the time necessary to achieve a constant value of SH signal.

In work [5], the dependence of the surface density of pyridine molecules during the desorption from copper

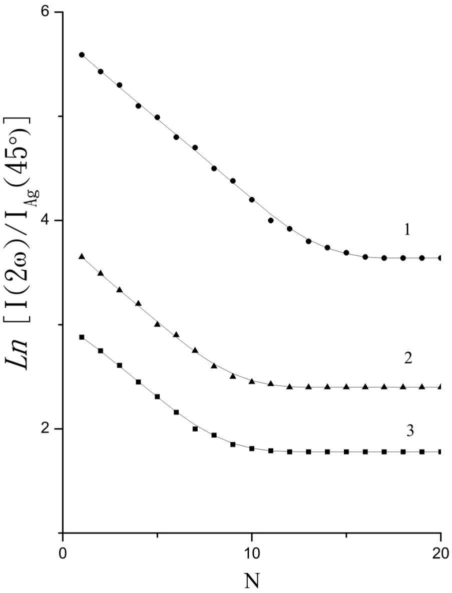

Fig. 1. Kinetics of molecular desorption from silver (*1*), gold (*2*), and aluminum (*3*) surfaces

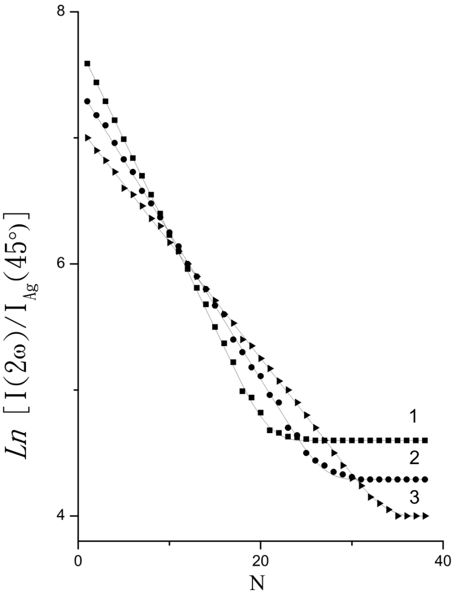

Fig. 2. Kinetics of molecular desorption from the Cu surface for different values of energy density of the incident radiation: *1* – 350, *2* – 300, *3* – 260 J/m^2

and aluminum surfaces under the action of laser pulses was observed. With the purpose to study regularities of the kinetics of desorption under the action of a sequence of laser pulses, we performed experimental investigations of the desorption of pyridine from the surface of silver and gold films and more detailed investigations of the desorption from the surfaces of bulk samples of copper and aluminum. The theoretical analysis of obtained experimental results for thin films and bulk samples was made.

In investigations, the opaque silver and gold films were used, their thickness was 500 nm; these films were prepared by the thermal sputtering of metals under ultrahigh vacuum conditions ($< 10^{-4}$ Pa) on smooth polished substrates and bulk smooth polished mirrors of copper and aluminum. The purity of metals was about 99.99%. To avoid the surface oxidation, the copper mirrors contained insignificant (0.37%) impurities of zirconium. The emission of a solid-state YAG:Nd^{3+} laser (1.064 μ) with active Q-switching falls on samples at an incidence angle of 70°. The energy of a giant laser pulse was 12÷16 mJ, pulse duration – 12 ns, and repetition rate – 0.1 Hz. Measurements of SH signals were carried out on a double-channel installation [13], which allowed us to register each laser pulse.

To obtain adsorbed layers, the alcoholic solution of pyridine (0.01 M) was applied on the surface of metal samples. Measurements started after the complete evaporation of the solvent. The adsorbed layer of pyridine, remaining on the sample surface, causes a sharp raise of SH signals. Pure alcohol applied in the same way didn't give the raise of the SH signal. Thus, the SHG enhancement was caused in this case only by adsorbed molecules of pyridine. After each probe pulse (beginning from the first), the SH signal decreased, and, after 15–20 pulses, the SH intensity $I(2\omega)$ restored to the typical value for the surface of a pure metal (Figs. 1 and 2). After the repeated applications of a pyridine monolayer to the metal surfaces, the dependence $I(2\omega)$ on the number of laser pulses is reproduced, and the SH intensity for a pure surface (after 10–35 laser pulses) always remains constant. Obviously, the laser radiation in such experiments causes no changes in the surface of samples and only "purifies" a metal from adsorbed pyridine molecules. Though the parameters of adsorbed layers obtained in such a way were not controlled in parallel by other independent *in-situ* methods, the repetition of results was good enough, the maximal values of enhanced SH signals (which correspond to the first excitation pulse) varied at most by 30% in each experiment. It can be noticed that the value of SH signal intensity gives an effective way for the control over the surface density of adsorbed molecules. The number of series of measurements was chosen with regard for the condition to ensure the random error to be less than 5% and was 20–30. From the results of work [14] concerning the thermal desorption of pyridine from the silver surface, it can be concluded that the covering degree of metals by adsorbed molecules in our experiments at room temperature does not exceed one monolayer, which always gives the main contribution to the reflected SH intensity [1, 2, 5, 7]. That is why we will consider an adsorbed monolayer which is formed as a result of the attainment of the thermodynamic equilibrium with air as the environment.

The molecular monolayer of pyridine adsorbed on the metal surface leads to a significant raise of the SH intensity during the reflection of laser radiation. The value of enhancement can be determined by the ratio of the intensity of the first SH pulse after the application of a monolayer to the SH intensity for the pure metal surface. For the p-polarized incident laser radiation, the following values of enhancement coefficients of SHG by the adsorbed pyridine monolayer on different surfaces were obtained: silver – 7.0; gold – 3.5; cuprum – 20; aluminum – 3.0 (Tables 1 and 2).

3. Results and Discussion

Under the action of a sequence of laser pulses, the desorption of adsorbed molecules on the surface occurs. It leads to a reduction of the intensity of SHG reflected from the surface of samples with the adsorbed molecular layer. In the case of pyridine molecules and nanosecond pulses, the laser thermal desorption is caused by the heating of a metal surface by probe laser pulses. Therefore, the light-induced acceleration of the desorption in a laser radiation field can reveal itself only at very high radiation fluxes ($\sim 10^{14}$ W/cm^2) [15], which is typical of femtosecond lasers [16]. Since the photodesorption is related to the resonance excitation of electronic or vibrational energy levels of adsorbed molecules, it cannot be observed, because in the frequency range of laser radiation does not contain the resonant absorption bands [17]. The thermal desorption of molecules from the surface of solids is described by the Polanyi–Wigner equation [18]

$$\frac{-dn}{dt} = n^m s \exp\left[\frac{-u}{kT(t)}\right], \qquad (1)$$

where n – surface density of molecules; u – desorption activation energy; $T(t)$ – surface temperature dependent on the time; m – desorption order; and s – entropy coefficient.

It follows from the theory of absolute reaction rates that $s \cong 10^{13}$ s^{-1}. If there is no dissociation or union of molecules during the desorption, the desorption is nonassociative, and $m = 1$. It will be shown further that, in our case, $m = 1$ (in general case $m = 0$–2, if additionally there is the associative or dissociative desorption).

Let us consider the desorption of molecules from the surface under the action of a sequence of laser pulses. After a short (12 ns) laser single pulse, the sample surface is rapidly overheated and then quickly cools down to the initial temperature due to the thermal conductivity. Therefore, we can consider that the desorption of molecules occurs only during the temperature increase, so the reduction of the number of molecules in the time interval between laser pulses can be neglected. This assumption is confirmed by the following experimental facts: first, the desorption kinetics does not depend on the repetition rate of laser pulses, the reduction of the density of adsorbed molecules is determined only by the number of laser pulses, which irradiated the sample surface till the moment of observation; second, the amplitude of the first SH pulse, which corresponds to the initial density of adsorbed molecules, does not depend on the time passed from the moment of the formation of the adsorbed layer. In this case, the solution of Eq. (1), which describes the desorption kinetics under the action of a sequence of short (in comparision with the characteristic time of thermal conductivity) heat pulses, can

Table 1. Results of the study of the kinetics of laser-thermal desorption from the copper surface

Metal	Cu		
Energy density, [J/m^2]	350	300	260
Maximal temperature $T_{\max}$, [°C]	63	52	48
Amplification coefficient		20	
Slope of desorption straight line	0.150	0.116	0.092
Permittivity 1.064 μ		$-26.9+i5.31$	
Activation energy u, [eV]	0.95	0.93	0.90
Sample type		bulk	

Table 2. Results of the study of the kinetics of laser-thermal desorption from surfaces of aluminum, silver, and gold

Metal	Al	Ag	Au
Energy density, [J/m^2]	300	330	330
Maximal temperature $T_{\max}$, [°C]	109	165	218
Amplification coefficient	3.0	7.0	3.5
Slope of desorption straight line	0.126	0.145	0.170
Permittivity 1.064 μ	$-23.7+i11.0$	$-45.9+i1.21$	$-35.3+i2.63$
Activation energy u, [eV]	0.29	0.16	0.21
Sample type	bulk	film	

be written as follows:

$$n_{N+1} = n_N \exp\left\{-s\int\limits_0^\infty \exp\left[\frac{-u}{kT(t)}dt\right]\right\}, \tag{2}$$

where: n_N — density of molecules before the action of the N-th laser pulse; n_{N+1} – density of molecules after the action of the N-th pulse or before the action of the $N+1$-st pulse. Since $T(t)$ corresponds to a short heat pulse, the limits of integration can be chosen from 0 to ∞.

As usual, the time distribution of a molecular flow under the action of a laser pulse is considered in the literature. In such a case, the limits of the integral in (2) is from 0 to t, and it is necessary to take the time shape of laser radiation pulses into account. This makes the analytical calculation of the integral impossible, and the integration should be performed numerically. Although we are interested only in the total molecular flow during the time of the heat pulse action, the time shape of a laser pulse is not significant, because the duration of a heat pulse is always much more than the duration of laser pulses, but much less than the time interval between N and $N+1$ pulses. So we can assume that at the time moment $t=0$, when a laser pulse comes, the instantaneous heat release proportional to the absorbed energy occurs. As the desorption kinetics under the action of short heat pulses was not discussed in the literature, let us consider it in detail. We consider the dependence $T(t)$ in two limiting cases: the semiinfinite bulk environment ($L^2 \gg 4a\tau$) and a thermally thin film ($L^2 \ll 4a\tau$), where L is the sample thickness; a is the thermal diffusivity coefficient; τ is the laser pulse duration. For an unfocused Gaussian laser beam, the instantaneous value of temperature of sample's surface after the heat radiation for bulk samples and films is given by following expressions [19]:

$$T_\mathrm{b} = \frac{IAd^2}{\rho c(4at+d^2)(\pi a t)^{1/2}}, \tag{3}$$

$$T_\mathrm{f} = \frac{IAa}{qL}\exp\left[\frac{-aht}{qL}\right], \tag{4}$$

where T_b – surface temperature of a bulk sample; T_f – film temperature; I – laser energy density; A – absorption coefficient of the sample; ρ, c, and q – specific density, thermal capacity, and thermal conductivity of sample's material, respectively; d – beam diameter; and h – heat exchange coefficient of sample's surface with the environment (for all metals in the vertical position of the surface in air $h \cong 5$ m^2/J). Let us make some assumptions about (3) and (4) to calculate integral (2). Since the functions $T_\mathrm{b}(t)$ and $T_\mathrm{f}(t)$ are rapidly damped in real time due to the high thermal diffusivity of metals, and $\exp[-u/kT(t)]$ gives the main contribution to the integral only at high values of temperature, it is possible to assume at small t with a good cause that $4at \ll d^2$ in (3) and $\exp(-aht/qL) \approx (1-aht/qL)$ in (4). Then, after the substitution (3) and (4) in (2) and the further integration, we obtain the following expressions for the desorption kinetics of adsorbed molecules from bulk samples and films under the action of a sequence of laser pulses:

$$n_{N+1} = n_N \exp\left[-\frac{s}{u^2}\frac{2k^2A^2I^2a}{\pi q^2}\right], \tag{5}$$

$$n_{N+1} = n_N \exp\left[-\frac{s}{u}\frac{kAI}{h}\exp\left(\frac{-uqL}{kAIa}\right)\right], \tag{6}$$

As was already mentioned, the intensity of SH generated by adsorbed layers of molecules depends quadratically on the surface density of molecules, i.e., $I(2\omega) \sim n^2$ [1–5, 7–11]. As the laser pulse length is smaller than the heat pulse length, the maximum of a heat pulse is shifted in time relative to a laser pulse, and the maximal temperature of the surface T_max is reached already on the trailing edge of a laser pulse with nanosecond duration [19], the SH signal generated by the N-th probe pulse will be proportional to $(n_N)^2$. So it corresponds to the density of molecules, which exists before the N-th pulse comes or after the $N-1$-st pulse stops its action. That's why the dependence of SH on the number of laser pulses N will be described by the following expressions in view of (5) and (6):

$$[I_N(2\omega)]^{1/2} = Cn_{N-1} = Cn_{N-2}e^B =$$

$$= \cdots = Cn_0 e^{-(N-1)B}. \tag{7}$$

Here, $N = 1, 2, 3, \cdots$; C – constant that takes the transformation coefficient of laser radiation in a harmonic signal (aperture and sensititvity of a measurement installation) into account; B – power exponent in expressions (5) and (6); and n_0 – initial concentration of adsorbed molecules before the first probe pulse. Then we have

$$\ln([I_N(2\omega)]^{1/2}) = -(N-1)B + \ln(Cn_0). \tag{8}$$

So, for the non-associative desorption, the dependence of $\ln\{[I(2\omega)]\}$ on the number of probe laser pulses N will be linear.

As was mentioned above, we have performed the experimental investigations of laser-thermal desorption kinetics of pyridine molecules from the surface of bulk samples of copper and aluminum and thermally thin (but optically thick) opaque films of silver and gold for the p-polarization of incident laser radiation. The experimental results are represented in the form of the dependences $\ln[I(2\omega)/I_{\mathrm{Ag}}(45)]$ of the normalized SH signal reflected from the sample's surface with the adsorbed layer of molecules on the number of probe laser pulses N (Figs. 1 and 2). The normalization was provided on the magnitude of SH intensity ($I_{\mathrm{Ag}}(45)$) that is generated during the reflection of p-polarized laser radiation from the clean surface of a silver film at the incident angle 45°. To avoid the migration of adsorbed molecules from lightless regions to the region of laser beam action, the whole surface of the sample was radiated. The average values of energy density of incident laser radiation were 260–350 $\mathrm{J/m^2}$. For copper, the investigations of the desorption kinetics were carried out for 3 different values of energy density of laser probe pulses. The corresponding values are shown in Fig. 2.

The linear initial region of this dependence at small values of N, where the contribution of adsorbed monolayers to the SH intensity considerably exceeds the contribution from the metal surface, confirms the previously made assumptions about the non-associative type of desorption. In other words, it is necessary to choose the first order of desorption in expression (1), i.e., $m = 1$. This is the most widespread case of the desorption phenomenon.

Using the slopes of linear parts of the experimental dependences $\ln[I(2\omega)] = f(N)$ and formula (8), it is easy to determine the exponents B in expressions (5) and (6) and then the energies of desorption activation u. For bulk samples (see (5)), the desorption activation energy is determined from the simple expression

$$B_{\mathrm{b}} = (s/u^2)(2k^2A^2I^2a/\pi q^2). \qquad (9)$$

For thin films, relation (4) yields

$$B_{\mathrm{f}} = (s/u)(kAI/h)\exp[-uqL/kAIa]. \qquad (10)$$

That's why to calculate the desorption activation energy u, it is necessary to numerically solve a simple transcendental equation of the type $ax = \exp(-bx)$. Experimental values of desorption activation energy for pyridine molecules from surfaces of noble metals and aluminum obtained with regard for formulas (9) and (10) are presented in Tables 1 and 2. For clearness, the maximal peak temperatures of sample's surface, which can be reached in the process of laser action on samples, are presented as well. Values of $T_{\max}$ were calculated by nomograms calculated in [19] for the dependences $T(t)$ for an unfocused giant laser pulse of the Gaussian form in space and the standard asymmetric form in time. The absorption coefficients of samples A were computed for the incident angle 70° by the Fresnel formulas for p-polarized incident laser radiation. In calculations, the values of optical constants of samples experimentally measured by elipsometric methods were also used. The corresponding values of complex permittivity ($\varepsilon = \mathrm{Re}\varepsilon + i\mathrm{Im}\varepsilon$) are presented in Tables 1 and 2. On the basis of the results on the kinetics of thermal desorption of pyridine during a linear heating of the surface of an Ag monocrystal (110) by infra-red laser radiation [14], it is possible to obtain the value of desorption activation energy $u \approx 0.2$ eV, which is in good correspondence with our results. Thus, we can see that the kinetics of laser-thermal desorption under the action of a sequence of laser pulses can be very well described by the obtained theoretical formulas (5), (6), and (8).

4. Conclusions

Thus, the usage of a sequence of short laser pulses for the activation of molecular desorption from the surface of metals (solids) and the simultaneous measurement of the reflected SH intensity for each pulse allow one to realize the continuous control over the surface density of adsorbed molecules and to calculate the desorption activation energy for bulk samples and thin films. This technique also allows one to study the processes of adsorption and desorption on surfaces and interfaces without the vacuum technique which is traditionally involved in investigations of such a kind.

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ТЕРМІЧНА ДЕСОРБЦІЯ МОЛЕКУЛ З ПОВЕРХНІ МЕТАЛІВ ПІД ДІЄЮ ПОСЛІДОВНОСТІ ЛАЗЕРНИХ ІМПУЛЬСІВ

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Резюме

Розглянуто кінетику термічної десорбції адсорбованих шарів молекул з поверхні масивних металів та металевих плівок під дією послідовності коротких лазерних імпульсів. Отримано аналітичні вирази для обчислення енергій активації десорбції молекул для обох типів зразків. Проведено експериментальні дослідження генерації другої гармоніки при відбитті імпульсів лазерного випромінювання від поверхні плівок срібла і золота та масивних зразків міді й алюмінію з адсорбованими шарами молекул піридину у процесі лазерно-термічної десорбції. Визначено значення величини енергії активації десорбції молекул піридину на поверхні благородних металів та алюмінію.