Photodesorption of sodium from the surface of sapphire

A. M. Bonch-Bruevich, T. A. Vartanyan, A. V. Gorlanov, Yu. N. Maksimov,
S. G. Przhibel'skiĭ, and V. V. Khromov

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Photodesorption of sodium atoms from sapphire has been studied experimentally under action of radiation in the transparent region of sapphire and in the absorption band of sodium adatoms. Quasithermal properties of photodesorption not related to the heating of the substrate have been identified. A phase transition between the 2-D gas of adatoms and islet films of sodium metal has been observed. A model accounting qualitatively for all the observed characteristics of photodesorption is proposed.

1. INTRODUCTION

Photostimulated processes on solid surfaces, associated with the excitation of an electronic subsystem, have long been studied, and in this area, extensive experimental data have been collected and theoretical concepts developed.[1] At the same time, photodesorption of atoms exhibiting resonance absorption of light from the surface of transparent dielectrics has been practically ignored by investigators. Yet such studies are of fundamental interest because this relatively simple case makes it possible to explain the basic properties of the photodesorption mechanism. In addition, the particular case of photodesorption is very close to the photodissociation of molecules in the gaseous phase—a process which has been closely studied and is often used for interpreting photodesorption effects. This paper is devoted to an explanation of the fundamental principles and mechanism of this type of photodesorption.

The system to be studied, i.e., sodium atoms adsorbed on the surface of sapphire, was chosen because of the chemical inertness of the substrate to alkali metals, the transparency of sapphire in the region of the electronic transition of the adatom, and the availability of information on this transition, obtained in experimental studies of the recently discovered[2] effect of laser radiation on the deposition of sodium atoms on a sapphire plate. This system has the following properties: sapphire is transparent in a wide spectra range, from 150 nm to 6 μm (the short-wavelength limit is due to interband absorption, and the long-wavelength limit is due to excitation of optical phonons[3,4]). The free sodium atom has a strong absorption line at a wavelength of 589 nm (resonance doublet of the $3S_{1/2}$–$3P_{3/2;1/2}$ transition with oscillator strength ≈ 1). As was determined in Ref. 5, when the atom is absorbed on sapphire, this line is transformed into a broad, structureless band with a maximum at 645 nm and a halfwidth of 200 nm (see Fig. 3, curve 1); this band is completely contained in the transparent region of sapphire.

Studies, carried out in Ref. 5 by the absorption method, of the concentration of sodium adatoms $N_{\rm ad}$ in equilibrium with the gaseous phase as a function of sodium vapor pressure and sapphire temperature T showed that this dependence is satisfactorily described by the Langmuir formula

$$N_{\rm ad}=RN_0\exp(E/kT), \qquad (1)$$

where N_0 is the atomic number density $R\simeq 2$–3 Å is the size of the region of interaction of an atom with the surface, and E is the adsorption energy. The linearity of the dependence $N_{\rm ad}(N_0)$ allows us to say that Na is adsorbed mainly in the atomic, not molecular, form. An estimate of E from Eq. (1) gives the value $E=0.75\pm 0.25$ eV, which appreciably exceeds the energies of physical adsorption.[6] The data of Ref. 7 yield $E\simeq 1$ eV, which is consistent with our result.[1)]

Knowing the adsorption energy of the atoms makes it possible to estimate their surface concentration and, by measuring the optical density, the absorption cross section of the adatoms, which was found to be $\sigma_{\rm ab}=3\times 10^{-16}$ cm^2. This value is in good agreement with the estimate based on the sum rule, $\sigma_{\rm ab}=\lambda^2\gamma/\Delta$, where γ is the radiation width of the transition, and Δ is the absorption bandwidth, formed from the atomic line on adsorption. Such agreement attests to a genetic relationship between the band and the atomic transition and makes it possible to assume that despite strong perturbation of the orbit, the optical electron of the adatom is localized around the atomic core in both the ground and excited states.

We do not know of any quantum-mechanical calculations of the Na atom adsorbed on sapphire. A qualitative idea of the bonding between the atom and surface is given by a comparison of the interatomic distances in the sapphire lattice with the size of a free Na atom. The average distance between adjacent oxygen anions in the hexagonal lattice on the surface of monocrystalline α-Al_2O_3 perpendicular to the (001) threefold axis is close to 5 a.u.,[8] and according the slow-electron diffraction data, the lattice does not rearrange up to 1000 °C.[9] The average diameter of the orbit of the Na valence electron in the ground $3S$ state is 8.4 a.u., and in the $3P$ excited state, 12 a.u. Therefore, the binding of this electron to the nodes of the substrate occurs essentially through multiparticle interaction and is probably associated with distortion of the equilibrium positions of many substrate atoms at the same time.

2. EXPERIMENTAL ARRANGEMENT

The apparatus used to study the photodesorption of Na atoms is shown schematically in Fig. 1. A certain amount of metallic Na was introduced (by vacuum distillation) into a sealed glass cell with a fused-on sapphire window after prolonged evacuation and degassing at 300–400 °C. The vapor pressure in the cell was determined by the temperature of the drop (at room temperature $\sim 10^{-11}$ torr), which according to Eq. (1) determined the concentration of adatoms in equilibrium with the gaseous phase (at room temperature $\sim 10^{10}$ cm^{-2}). Pulsed laser radiation (second and third harmonics

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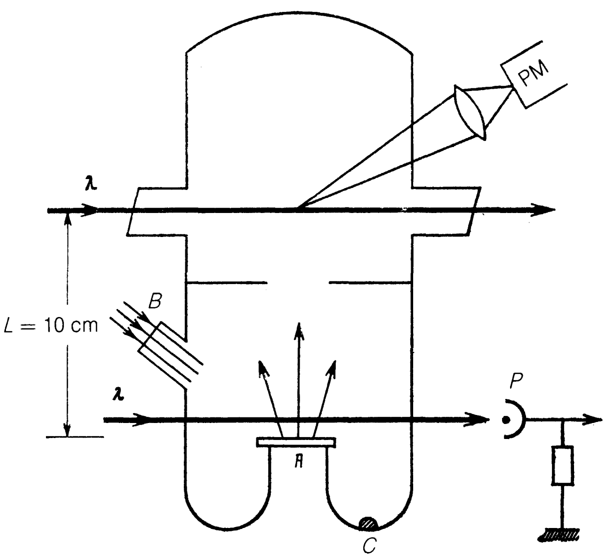

FIG. 1. Arrangements for detecting the photodesorption of sodium atoms: *A*—sapphire plate with adsorbed atoms; *B*—window for introducing pulsed exciting radiation; *C*—drop of metallic sodium; $\lambda = 5890$ Å—beam of continuous dye laser whose frequency is in resonance with the $3S_{1/2}$–$3P_{3/2}$ transition of sodium, PM—photomultiplier detecting the luminescence of a beam of photodesorbed atoms, *P*—photoelectric cell for measuring the absorption of the atomic beam

of neodymium laser radiation with pulse duration $\tau = 10^{-8}$ sec) and flashtube radiation (duration $\tau = 10^{-5}$ sec) monochromatized by a set of light filters were directed onto the plate through a side window. The radiation power density was changed by focusing. The flux of desorbed atoms was recorded by the intensity of their resonance luminescence by means of a photomultiplier, with recording on an oscillograph. The luminescence was excited by passing the beam of a dye laser at a frequency equal to that of the $3S_{1/2}$–$3P_{3/2}$ transition of the Na atom through the cell at a distance of 10 cm from the sapphire plate. Placing the luminescence excitation region at a distance of 10 cm from the sapphire surface made it possible to reduce the light interference considerably and obtain photodesorption signals with S/N amounting to 30–50. The sensitivity of the arrangement made it possible to detect 10^3–10^4 at/cm^3. In addition, this geometry made it possible also to measure the kinetic energies (velocities) of the desorbed atoms from the delay time of the luminescence pulse relative to the desorption pulse.

In the other variant, the number of desorbed atoms was detected by the absorption of the resonance radiation of a dye laser, passing at a distance of 1–2 cm from the sapphire plate parallel to its surface. By using the relative displacement of the desorbing and recording beams, it was possible to represent diagramatically the angle with which the atoms separated.

We did not have at our disposal methods for checking the cleanness of the sapphire surface, the chemical composition of its coating, or its structure. At the same time, various methods of cleaning of the surface (heating in a vacuum of 10^{-5}–10^{-6} torr to a temperature of 300–400 °C, annealing at the same temperatures in an atmosphere of hydrogen and oxygen, cleaning with an HF discharge in xenon at a pressure of 1 torr, high-vacuum oilless evacuation of the cell) did not result in any appreciable changes in the results of the experiments described below. The observed differences in the amplitudes of photodesorption signals from different plate samples, which were less than a factor of 2–3, are attributed to different degrees of roughness and imperfection of the surfaces.

3. BASIC EXPERIMENTAL CHARACTERISTICS OF RESONANT PHOTODESORPTION

It is our view that the experimental facts presented below indicate convincingly that the observed photodesorption is not due to the heating of the substrate. The weightiest argument in support of this statement is the observed linear dependence of the rate of desorption on the intensity of the incident light. This linearity was detected in the 10^2–10^5 W/cm intensity range. This fact, along with the low quantum yield of the process (see below), cannot be explained in terms of the thermal model, in which the dependence of the evaporation rate on the light intensity should be exponential. The experiment showed a sharp nonlinear increase in photodesorption intensity at power densities $> 10^5$ W/cm^2 (up to 10^7 W/cm^2), this being due to the thermal action of the radiation, i.e., heating of the substrate.

The dependence of photodesorption rate on surface temperature follows Langmuir's law (1) with an activation energy (Fig. 2) of 5500 ± 1000 cm^{-1}, which is close to the desorption energy.

Under the experimental conditions, prolonged action of radiation should have caused a shift of the dynamic equilibrium between the volume and surface phases toward a decrease in the concentration of adatoms. This was observed from the action of the second-harmonic radiation of a neodymium laser operating in the repetitive pulse mode ($\lambda = 530$ nm, repetition rate 12.5 Hz, power per pulse, 10^5 W/cm^2). At the same time, the steady-state concentration of adatoms decreased by a factor of 1.5. The characteristic time to establish the shifted equilibrium was $T_1 = 10$ sec. After the illumination was switched off, the concentration of adatoms

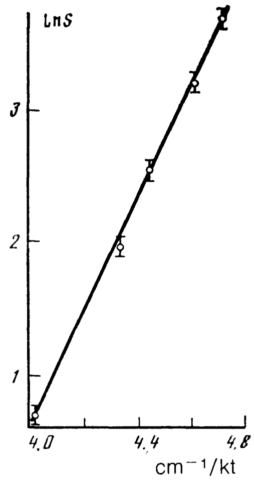

FIG. 2. Signal of atomic photodesorption vs substrate temperature.

was restored with a time constant $T_2 = 15$ sec. The concentration kinetics are satisfactorily described by the balance equation

$$N_{ad} = \Gamma(N^0_{ad} - N_{ad}) - WN_{ad}, \qquad (2)$$

where N^0_{ad} is the equilibrium concentration of adatoms without illumination, and Γ and W are the rates of thermal and irradiation-stimulated desorption, respectively. From the solution of Eq. (2) we have

$$N_{ad} = \overline{N} + (N^0_{ad} - \overline{N})\exp[-(W+\Gamma)t], \qquad (3)$$

where $\overline{N} = N^0_{ad}\Gamma/(\Gamma + W)$, and from the experimental data for the cases $W = 0$ and $W \neq 0$ we find $\Gamma = 1/T_2 = 0.07$ sec^{-1}, $W = 0.03$ sec^{-1}.

The value obtained for the thermal desorption rate Γ makes it possible to determine the accommodation coefficient α. Equating the flux of atoms becoming adsorbed to that of atoms becoming desorbed under equilibrium conditions, we obtain $\alpha \approx 10^{-2}$. From the luminous desorption rate determined above, we estimate the photodesorption cross section, which for $\lambda = 530$ has the value $\sigma_{pd} = 2 \times 10^{-19}$ cm^2.

The spectral dependence of the photodesorption cross section is presented in Fig. 3 (curve 2). Comparison of the photodesorption and adsorption spectra shows the similarity of the positions of their maxima and widths. Comparison of the absorption and photodesorption cross sections leads to the conclusion that the quantum yield of the photodesorption process near the maximum is $\sim 10^{-3}$. Note that the spectra are not identical: The blue wing of the photodesorption spectrum falls much more slowly than the red one, almost without changing in the 300–500 nm range, whereas the absorption spectrum is approximately symmetric. Unfortunately, experimental difficulties did not permit us to record the absorption and photodesorption spectra at the same temperatures, so that it would be possible to determine the spectral dependence of the quantum yield of the photodesorption process. It is clear, however, that the quantum yield increases appreciably as the irradiation wavelength decreases.

To find out more about how the absorbed luminous energy is transformed, we attempted to detect luminescence under action of the radiation of argon and krypton ($\lambda = 514$ nm and $\lambda = 676$ nm) lasers. The observations were conducted during continuous evaporation of atoms onto a surface with their simultaneous photodesorption.[2] The steady-state concentration of adatoms under these conditions was 10^{13}–10^{14} cm^{-2}. In the entire 0.5–5-μm spectral region, no luminescence associated with adsorbed atoms were detected. An estimate of the sensitivity of the recording arrangement employed and of the magnitude of stray luminescence of impurities in the volume of sapphire makes it possible to state that the luminescence quantum yield of the adatoms is less than 10^{-2}.

The radiation pattern of the flux of desorbed atoms was also studied. No deviations from Lambert's law were observed within the limits of experimental accuracy. This result can be explained by the surface roughness of the plates and therefore does not provide information on the characteristics of the elementary photodesorption event.

Figure 4a presents the result of time-of-flight measurements of the kinetic energy of desorbing atoms under action of radiation with different wavelengths. The time-of-flight spectra (TFS) correspond closely to those obtained in the case of a thermodynamic equilibrium source with an effective temperature determined by the energy of the photons undergoing desorption. Under the conditions of our experiment, an instantaneous thermal source with temperature T gives for the TFS, where t is the current time, m is the atomic mass, and l is the path travelled between the surface and the recording region.

The effective temperature is determined from the slope of the curve in the dependence of $\ln[t^3S(t)]$ on $ml^2/2t^2$ (Fig. 4b). In the case of irradiation with the second harmonic of the neodymium laser ($\lambda = 530$ nm), the effective temperature was 750 K, and for the third harmonic ($\lambda = 353$ nm), 1000 K. If the initial substrate temperature of 300 K is subtracted from these values, the radiating heating value obtained is found to be directly proportional to the photon energy of the radiation undergoing desorption.

We emphasize that the effective temperature determined from TFS is independent of the intensity of the applied radiation, and the photodesorption signal increases linearly with the intensity. All this indicates single-photon

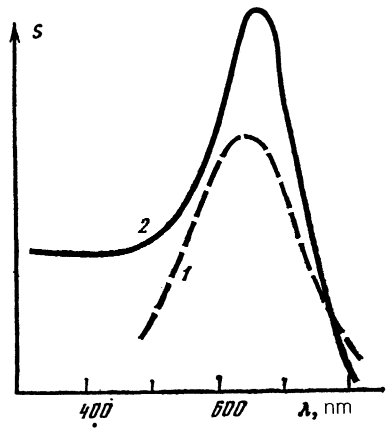

FIG. 3. Absorption spectrum of sodium atoms adsorbed on sapphire (curve 1, $T = 470$ K), and spectrum of sodium photodesorption from sapphire (curve 2, $T = 300$ K).

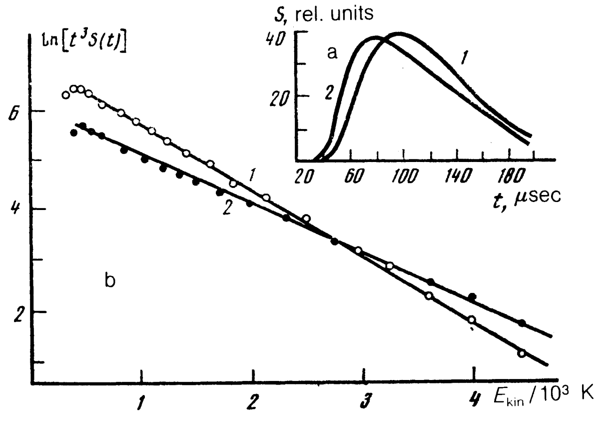

FIG. 4. Time-of-flight spectra of desorbed sodium atoms under action of radiation of the second (1) and third (2) harmonics of neodymium laser (a), and determination of effective desorption temperature (b); explanations are in the text.

heating mechanisms. Such an unusual process of quasithermal desorption finds an explanation in terms of the model presented below.

4. MIGRATION OF ATOMS AND PHASE TRANSITIONS IN THE ADSORBED LAYER

After rapid (4–5 sec) cooling of the sapphire plate to liquid nitrogen temperature (70 K), the photodesorption changed discontinuously. Initially, it increased for tens of seconds, then decreased to a level an order of magnitude below the initial one at room temperature. The establishment of a stationary desorption level lasted several minutes, which is substantially longer than the time of onset of thermal equilibrium. It may be assumed, therefore, that this is associated, not with the cooling process itself, but with the accompanying change in the concentration of adsorbed atoms. Under the experimental conditions sodium atoms deposit continually on the plate, so the increase in photodesorption in the first state is understandable; the further decrease in photodesorption rate is explained by a phase transition in the system of adatoms resulting in formation of islets of metallic film. This was directly confirmed by time-of-flight experiments, which recorded a constant rate distribution of the desorbed atoms at the beginning of the process as the desorption rate increased, then decreased.

At the final stage, when the desorption decreases by an order of magnitude, a new component appears in the rate distribution, corresponding to high escape energies (≈ 0.3 eV). The level and rate distribution of the new components correlates well with the values which we established[10] in the study of the photoevaporation of metallic sodium. Thus it is certain that what was observed here was a phase transition between the gaseous and islet phases of sodium adsorbed on sapphire.

Unfortunately, technical difficulties did not permit a detailed study of the characteristics of this transition. It is clear, however, that the density of adatoms at room temperature is strongly supersaturated relative to the corresponding density during the formation of metallic islets at 70 K. The fact that the surface concentration of adatoms decreases despite the steady deposition of atoms from the volume at a rate $\sim 10^{10}$ cm^{-2} sec^{-1} indicates a high rate of diffusion to the islets.

Making a number of assumptions, one can estimate the activation energy E_d determining the diffusion coefficient

$$D = a^2 \nu \exp(-E_d/kT), \tag{5}$$

where a is the atomic scale (≈ 1 Å) and ν is the characteristic oscillation frequency of the adatom ($\approx 10^{12}$ sec^{-1}). We shall assume from dimensional considerations that the velocity of the flux from the surface to the islets is proportional to $N_{\rm ad} N_{\rm is}$, where $N_{\rm is}$ is the density of the islets. Assuming this quantity to be an order of magnitude smaller than $N_{\rm ad}$, and considering that the experimental condensation rate exceeds the deposition rate by at least an order of magnitude, we find $E \approx 0.1$ Oe. This value is consistent with the 1/6 empirical rule[11] for the ratio of the activation energy of surface diffusion to the adsorption energy.

5. CONCLUSION

A detailed interpretation of the experimental results obtained here is impossible at the present time because of the insufficiently developed theory of surface phenomena. None the less, the data obtained in our study make it possible to construct a model of photodesorption of Na atoms from sapphire.

The most significant facts accounting for the photodesorption mechanism are: (1) The electronic excitation of Na atoms is effectively quenched when they strike sapphire;[12] (2) The quantum yield of the photodesorption process is low ($\sim 10^{-3}$) and increase sharply with increasing photon energy of the desorbing radiation, and, (3) The velocity distribution of desorbed atoms is similar to the thermodynamic equilibrium distribution with temperature proportional to the photon energy.

In light of the data cited, the photodesorption process can be represented as follows. The absorption of a photon by an optical electron of Na causes oscillations in the electronically excited complex consisting of the Na atom and its immediate environment. Then for 10^{-12} sec a nonradiative transition to the ground electronic state takes place with production of optical phonons. At the same time, strong oscillations of the atoms are excited, and a large number of substrate particles are set in motion. The large number of particles involved in the energy distribution makes it possible to assume that the latter takes place in a statistical manner. Then the energy distribution for adsorbed atoms, which is the only distribution determined in the experiment, follows the law of equilibrium thermodynamics, in which the "temperature" is specified by the average value of the energy corresponding to an atom of the complex, $\Theta = 2\hbar\omega/z$, where z is the number of degrees of freedom of the complex.

It is significant that although the electronic excitation lifetime of the complex is of the order of an oscillation period of the Na atom, the formation of the energy distribution takes place in a time shorter than this period, since the duration of the elementary event of nonradiative transition in the case of strong bonding usually is appreciably shorter than the vibration period. Such a picture of the instantaneous formation of the thermodynamic equilibrium distribution with respect to the energies of the adatoms makes it possible to estimate the photodesorption quantum yield. When the distribution is formed faster than the Na atoms can leave the region of the potential well, the fraction with an energy greater than the adsorption energy is

$$\eta \approx (E/\Theta)^{1/2} \exp(-E/\Theta),$$

which for $\Theta/k = 750$ K gives the value $\eta \approx 10^{-3}$, in satisfactory agreement with the experimental value.

After an Na atom has gone into the ground state, the optical phonons excited in the surface region rapidly (in a time $\sim 10^{-12}$ sec) escape into the volume of the crystal, and the adsorbed "heated" atoms cool slowly, in a time $\sim 10^{-11}$ sec. It can readily be shown that the contribution of these atoms to desorption is insignificant because of their heating by the "hot spot" of the substrate. This is due to the fact that the bonding between the Na atom and substrate atoms is appreciably weaker than their bonding to each other. An estimate of the desorption rate from the Arrhenius formula for such a heating process gives a value $\leqslant 10^8$ sec^{-1}.

The above model accounts for practically all the experimental results: the appearance of the TFS spectrum, the increase in the effective temperature and quantum yield as the energy of the photon causing the process increases, as well as the lack of a dependence of these quantities on irradiation intensity. Incidentally, the increase in photodesorption yield associated with an increase in photon energy is described by the Fischer theory,[13] which prescribes an exponential increase in the rate of a nonradiative transition as a function of excitation energy in polyatomic molecules and is constructed in terms of statistical models.

In the future, the development of the model will require a specific definition of an ensemble of essential vibrational modes in terms of statistical models of chemical reactions;[14] attempts to use such models in describing laser-stimulated desorption[15] and atomization[16] have already been made. A more complete experimental verification of the proposed model will require, first, an expansion of the temperature range of the studies, which is difficult to accomplish because of the formation of islet films at low temperatures, and because on heating, the number of relevant weakly bound adatoms rapidly decreases, and atoms from more strongly bound states begin to manifest themselves and to predominate in desorption.

[1)] The adsorption energy calculation,[7] obtained from an analysis of thermal desorption spectra, involves a considerable indeterminacy that is difficult to eliminate, whereas the inaccuracy of our measurements is due solely to the error in the temperature measurement.

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