

Photodesorption of high-energy iodine molecules from the surface of nanopore quartz under resonance laser excitation

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Photodesorption of iodine molecules from nanopore quartz, which were excited by a resonance electronic laser, has been observed. The energy of the translational motion of molecular iodine is 1.7 eV at photon energy of 2.3 eV. Thermal desorption of I_2 with much lower kinetic energies and photodissociation of iodine on the surface of nanopore quartz were observed at the same time. © 1995 American Institute of Physics.

Photophysical and nonlinearly optical phenomena on extended surfaces with small characteristic dimensions in nanostructure materials are now well known and are being studied extensively.^{1,2} Most studies of photoprocesses in nanopore materials have been concerned with the diffusion and sorption of molecules under the action of laser radiation.³ At the same time, the small pore sizes (10–100 Å), the branched surface, and other properties characteristic of nanomaterials can be seen under resonance laser action in elementary surface photophysical processes which lead to desorption and photodissociation of molecules located on the surface.

In the present paper we report the observation and the results of experimental study of the photodesorption of iodine molecules with high kinetic energies under resonance laser excitation on submonolayers of I_2 sorbed in nanopore quartz.

In the experiments we employed the second-harmonic radiation ($\lambda = 532$ nm) of a Nd^{3+} : LAG laser, operating in a one-mode regime, with a pulse energy of 60 mJ and a pulse duration of 8 ns. The radiation power density on the surface was equal to $(5 - 15) \times 10^6$ W/cm². The pores in the quartz samples (α quartz) had dimensions of 20–100 Å. Iodine saturation was conducted in an atmosphere of iodine vapor and was monitored according to the absorption coefficient of the samples (10 cm⁻¹). The degree of filling of the surface of the nanopore quartz with iodine molecules was less than 0.5 monolayer.

Time-of-flight dynamic mass spectrometry was employed. The sample—iodine-saturated nanopore quartz—was placed in a vacuum chamber on a liquid-nitrogen-cooled stand. The excitation mass-spectra were recorded with different delays relative to the laser pulse. The presence of a time-of-flight baseline (31 cm) from the sample to the ion source made it possible to obtain time-of-flight spectra, i.e., the dependence of the amplitude of the mass peak on the direct transit time of the products up to the ion source of

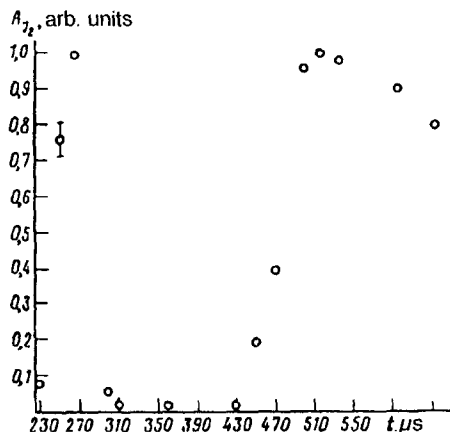


FIG. 1. Time-of-flight spectrum of iodine molecules desorbed from the surface of nanopore quartz. $\lambda = 532$ nm, $q = 1.5 \times 10^7$ W/cm².

the mass spectrometer. The purity of the surface was checked by the method of laser thermal desorption. A computer was used to analyze the results. The working vacuum was 10^{-8} torr and the maximum vacuum was 4×10^{-9} torr. All experiments were performed under conditions of collisionless separation of the products.

Emission of atomic iodine ($m/e = 127$) and molecular iodine ($m/e = 254$) were observed as a result of the action of the laser radiation. Residual-spectrum and impurity masses were not recorded. Figure 1 shows the dynamics of the flow of iodine molecules into the ion source of the mass spectrometer as a result of the direct passage of the molecules, i.e., the time-of-flight spectrum. The dynamics differs fundamentally from the case of thermal desorption of I_2 and consists of two pulses with peaks at 270 and 510 μs with complete absence of iodine in the time range 310–430 μs .

The high translational energies of the desorbed iodine molecules are worth noting. For a packet of high-energy molecules the most likely energy was found to be ~ 1.7 eV with 2.3-eV excitation photons and 0.5-eV photon for a packet of low-energy molecules.

Figure 2 shows the time-of-flight spectrum of atomic iodine. The spectrum contains two peaks. The spectrum does not reflect the real flow of the iodine atoms, which are formed as a result of the laser action, into the ion source, since the fragmentation of molecular iodine is ignored. Analysis of the fragmentation relations showed that the part of the distribution $A_{127}(t)$ with a peak at 270 μs is due completely to the fragmentation of the high-energy desorbed iodine molecules. Moreover, the analysis made it possible to separate the time-of-flight spectrum of the atomic iodine produced as a result of the photodissociation of I_2 molecules. This spectrum is shown in Fig. 3.

The products resulting from the action of resonance laser radiation on submonolayers of molecular iodine adsorbed on nanopore quartz thus contain iodine molecules with high kinetic energy (~ 1.7 eV), less energetic iodine molecules, and atomic iodine.

The high translational energies of I_2 , which are characteristic of a packet of fast

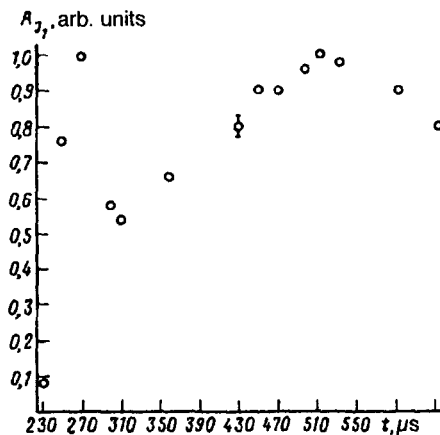


FIG. 2. Time-of-flight spectrum of atomic iodine. $\lambda = 532 \text{ nm}$, $q = 1.5 \times 10^7 \text{ W/cm}^2$.

particles, make it impossible to explain the appearance of such molecules by thermal desorption of the molecules. Our experiments on laser ($\lambda = 1064 \text{ nm}$) thermal desorption of iodine molecules from the surface of a metal showed that for surface temperatures which are much higher than in the experiments with nanopore quartz, the translational energies of the iodine molecules did not exceed 0.2 eV. We therefore attribute the high-energy peak of the time-of-flight distribution of the iodine molecules (Fig. 1) to a non-equilibrium process — photodesorption. It is important that the resonance laser excitation of iodine molecules sorbed on the surface of a bulk condensed medium (metal, dielectric,

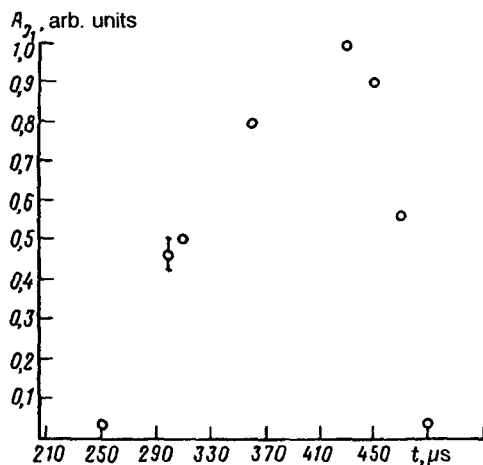


FIG. 3. Time-of-flight spectrum of atomic iodine formed as a result of the photodissociation of I_2 molecules. $\lambda = 532 \text{ nm}$, $q = 1.5 \times 10^7 \text{ W/cm}^2$.

including on the surface of fused quartz) does not lead to desorption with such high energies.

In most studies the photodesorption is treated as a Frank–Condon transition into either an antibonding state of an adsorbate–adsorbent complex⁴ or a bonding state of an adsorbate ion–surface complex (Ref. 5). In our case it is important that for the excited states of diatomic molecules in nanopore glasses the adsorption potential becomes deeper, and that this deepening of the potential is of a polarization nature which does not stem from the formation of an adsorbate ion.⁶

We assume on the basis of what we have said above that the observed photodesorption occurs via the formation of a stable state of an adsorbate–surface complex which corresponds to an excited adsorbate molecule.

We attribute the second (retarded) pulse, which peaks at 510 μs , in the time-of-flight distribution (Fig. 1) to the thermal desorption of I_2 . Analysis of the data shows that the heating of the surface under the action of the laser radiation is local, which could be due to the manifestation of size effects of the limitation of phonon relaxation in nanostructures.

The time-of-flight distribution illustrated in Fig. 3 is due to iodine atoms — the products of the photolysis of I_2 molecules. We know that laser radiation with $\lambda = 532$ nm excites iodine molecules in nanopore quartz into the upper bonding electronic state ${}^3\Pi_{0+u}$ near the dissociation limit of the molecule followed by photolysis from this state. Dissociation can also proceed via predissociation with a transition into an antibonding state ${}^1\Pi_{1u}$. Photolysis can proceed in the gas phase only via predissociation and under our experimental conditions it will be accompanied by the release of 0.5 eV of kinetic energy per two atoms. The corresponding atomic iodine should then be observed at times earlier than 100 μs , which, of course, does not occur. It thus follows that the time-of-flight distribution (Fig. 3) is due to iodine atoms — the products of the photolysis of iodine molecules on the surface.

In summary, in an experiment in which we used a resonance laser radiation to excite iodine molecules adsorbed in submonolayer coatings on the surface of nanopore quartz we have observed the photodesorption of iodine molecules with high kinetic energies and also thermal desorption and surface photolysis of I_2 . The character of the processes and the energy characteristics of the products in the case where the substrate consists of nanopore quartz are substantially different from the case of the sorption of iodine molecules on the surface of bulk condensed media. This shows that the surface photoprocesses are determined by the specific properties of nanopore media.

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