

# Formation of molecular ions as a result of irradiation of the surface of molecular crystals by UV laser radiation

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The observation of a nonthermal separation of molecular ions from the surface of molecular crystals under the influence of intensive UV laser radiation ( $\lambda = 249$  nm) is reported for the first time. The observed effect can be used in the development of new methods of investigation of the spatial structure of molecules and in mass-spectral analysis of the surface layer of solids.

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1. The detachment of molecular ions with preservation of molecular individuality, directly from the surface of a solid is of paramount interest for the development of methods of direct, visual representation of the spatial structure of molecules (photoion laser projector of molecules<sup>1</sup>) and analysis of molecular composition of the surface monolayer. Until now, we knew about the desorption of simple natural molecules due to the action of light<sup>2</sup> and evaporation of a mixture of different types of heating of the surface by laser radiation.<sup>3</sup> In this paper we report the observation, for the first time, of a detachment of molecular ions from the surface of a molecular crystal due to the action of UV laser radiation pulse, which is not associated with heating of the material. The experiment involved a mass spectrometric analysis of photoionization products after irradiating the surface of the molecular crystals of nucleic and bases and anthracene with KrF pulsed laser radiation. The use of the time-of-flight mass spectrometer also enabled us to investigate the velocity distribution of the produced photoions and the delay of the ion escape from the surface relative to the laser pulse.

2. Finely divided crystal powders of five nucleic acid bases ("Zellstoff-Fabrik Waldhof") and anthracene were deposited on  $0.4 \times 0.4$ -cm<sup>2</sup>, stainless-steel substrates and placed on the ejecting electrode of the ion source of the time-of-flight mass spectrometer (Fig. 1). The radiation of the KrF laser was directed through an attenuator and cylindrical focusing lenses to the substrate with the sample tilted at a 1° angle. The cross section of the laser beam directly in front of the sample was  $0.05 \times 0.4$  cm<sup>2</sup>. The radiation power density varied in the range of  $3 \times 10^4 \dots 3 \times 10^6$  W/cm<sup>2</sup> for a pulse duration of about 15 nsec. The produced photoions were ejected by a 120-V/cm field pulse to the region of the accelerating gap and further after separation according to masses in the region without a field, reached the cathode of the VEU-2B secondary-electron multiplier. The signal from the electron multiplier was recorded with a 50-ohm load using a C8-12 oscillograph with a memory. In a regular mode the ejecting pulse was supplied to the electrode with a delay of 3 to 6  $\mu$ sec relative to the laser generation pulse, which provided a velocity focusing of ions.<sup>4</sup> The resolution of the mass spectrometer in this case was better than 200 at the 0.5 level. The time was measured from the leading edge of the ejecting pulse using a G5-46 precision-delay

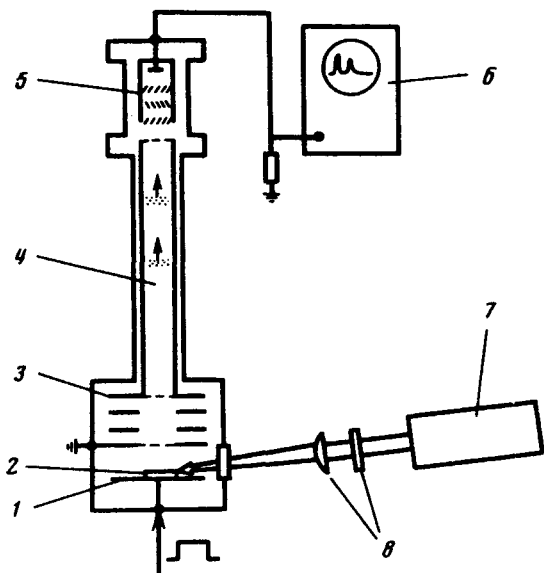


FIG. 1. Schematic of the experimental setup: 1, Ejecting electrode; 2, sample; 3, accelerating electrode; 4, field-free region; 5, secondary-electron multiplier; 6, oscillography; 7, KrF laser; 8, focusing lenses.

generator. The identification accuracy of the masses was equal to  $\pm 1$  unit. In a different mode the ejecting pulse was supplied at the same time the sample was irradiated by the laser pulse. In this case an analysis of the profile of the mass peak gives information on the velocity distribution of the photoions and the delay in the escape of ions from the crystals.

3. The characteristic mass spectra of ions, produced as a result of irradiation of the surface of molecular crystals, are shown in Fig. 2. The most important characteristic of the mass spectra is the domination of the molecular ions. In all the nucleic acid bases we can also see impurities of sodium, potassium, and molecules of the bases in which the hydrogen atom was replaced by sodium. In the case of cytosine we can see dimer ions of molecules. The existence of strong peaks  $m/e = 84$  in the thymine and  $m/e = 69$  in uracil can be accounted for by spontaneous dissociation of molecular ions or by the presence of impurities in the sample. At radiation intensities exceeding  $10 \text{ MW/cm}^2$  the number of components in the mass spectra increases considerably both due to the impurities and apparently as a result of fragmentation of the original molecules and ions. A typical signal level of molecular ions in the experiment amounted to  $10^4$ - $10^5$  ions/pulse.

4. An analysis of the signal profiles of the molecular ions of adenine and guanine, which were measured in the absence of velocity focusing, shows that these ions have anomalously high velocity corresponding to the kinetic energy of about 1 eV.

In the case of cytosine and uracil, a delay of up to  $3 \mu\text{sec}$  in the escape of molecular ions was observed at  $1$ - $2 \text{ MW/cm}^2$  radiation intensities. The presence of ejecting

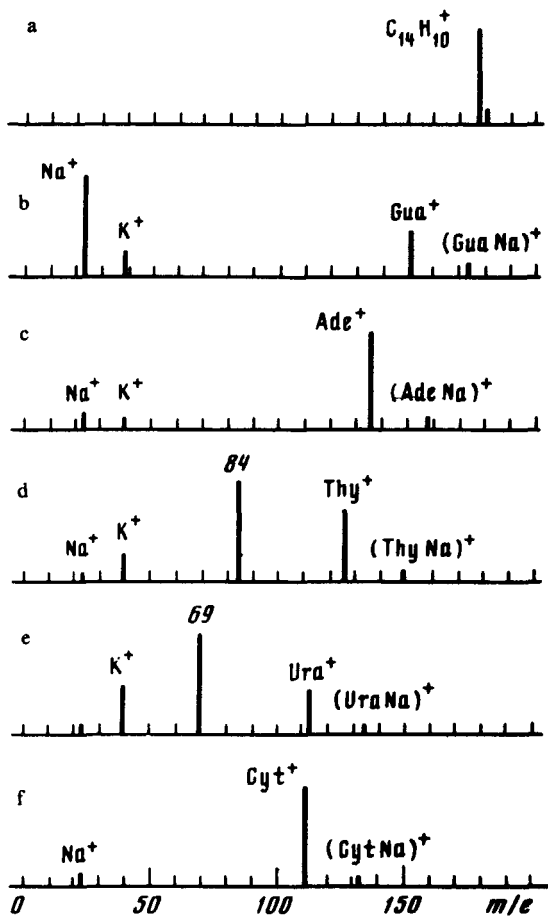


FIG. 2. Mass spectra of photoions produced by irradiating the surface of the molecular crystals: (a) anthracene,  $I = 150 \text{ kW/cm}^2$ ; (b) guanine,  $I = 3 \text{ MW/cm}^2$ ; (c) adenine,  $I = 25 \text{ kW/cm}^2$ ; (d) thymine,  $I = 1 \text{ MW/cm}^2$ ; (e) uracil,  $I = 1 \text{ MW/cm}^2$ ; (f) cytosine,  $I = 1 \text{ MW/cm}^2$ .

electric field or its absence in this case has an appreciable effect on the ion yield: in the presence of a  $120\text{-V/cm}$  ejecting field the signal in cytosine increases by a factor of 10 and that in uracil increases by a factor of 2.

A characteristic feature of the molecular ions formed in anthracene is the absence of a significant broadening of the mass peak due to anomalous velocities and due to a delay in the escape of ions from the surface. The average initial ion velocity in this case exceeds that of the thermal motion at room temperature by only a factor of 2 to 2.5.

An analysis of the experimental data answers the main question of whether the molecular ions break away from the surface or desorb the neutral molecules which are subsequently ionized in the laser radiation field. When the ion production is delayed relative to laser pulse (cytosine, uracil), the ions break away from the surface. For other cases this does not follow uniquely from the experiment. However, the desorp-

tion scheme of molecules with a subsequent two-stage photoionization does not account for the high level of the signal observed in the experiments with nucleic acid bases. This mechanism may play an important role for anthracene in view of easy sublimation of the crystals and high efficiency of the two-stage photoionization of the molecule.

5. Letokhov<sup>1</sup> expressed the idea of using an ion projector with a selective laser photoionization for visual representation of the spatial structure of a macromolecule, in particular for direct reading of the sequence of bases in DNA. Since the DNA bases retain their individuality after they break away from the surface in the form of ions, new possibilities open for the realization of the proposed scheme. By time sweeping the image in a laser ion projector, we could record the spatial structure of a molecule with a simultaneous time-of-flight mass analysis of fragments that produce the image.

The other possible practical application of this effect involves mass spectrometric analysis of trace amounts of organic compounds that are almost unvolatile and unstable to heating. This class of substances represents purine bases of nuclei acids used in experiments.

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<sup>2</sup>F. I. Vilesov, V. A. Kotel'nikov, and A. A. Lisachenko, *Sb. Molekulyarnaya fotonika* [A collection of papers entitled "Molecular Photonics,"] Nauka, L., 1970, p. 318.

<sup>3</sup>B. Noks, *Sb. Mass-spectrometricheskie metody opredeleniya sledov* [A collection of papers entitled "Mass Spectrometric Methods of Determining Tracks,"] Mir, M., 1975, p. 424.

<sup>4</sup>W. C. Wiley and I. H. Mc Larnen, *Rev. Sci. Instr.* 26, 1150 (1955).