Detachment of chromophore ions from a complex molecule on a surface by picosecond UV laser pulses

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A preferential desorption of chromophore ions has been observed during the bombardment of a solid-phase peptide containing an aromatic chromophore by 5-ps laser pulses at a wavelength $\lambda = 266$ nm. When the pulse length is increased to 20 ns, the mass spectrum of the ions produced is dominated by heavy masses, ranging up to the molecular level.

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Lekhotov[1] has discussed some new possibilities in ion mircoscopy for visualizing the spatial structure of macromolecules. The idea is to use ultrashort laser pulses to selectively detach ions of selected functional groups of a compound molecule adsorbed on the surface of a needle in a field ion microscope. The possibility of this selective action on molecules in the solid phase has not, however, been verified experimentally. It has been shown in some recent papers[2–4] that the bombardment of the bases of nucleic acids and other polyatomic molecules in the solid phase by laser pulses with a wavelength in the electronic absorption band of the molecules results in an effective detachment of the molecules as molecular or quasimolecular ions. The heating of the surface caused by this bombardment is very slight ($\Delta t < 20$–100 °C under the particular experimental conditions). Although the mechanism for this effect is not completely clear,[3] the fact that there is no pronounced heating of the surface indicates that it is possible in principle to selectively act on complex molecules on a surface.

For an experimental study of the role played by a specific chromophore in a complex molecule during photoionization and photodesorption of ions, we selected a peptide molecule consisting of a chain of amino acids; tryptophan, alanine, and glycine, with protective acetate and ester groups at the ends.

In the experiments of Refs. 2–4, we might note, aromatic molecules, in which the absorption of the laser pulses resulted from transitions of delocalized π electrons, were used. One of the amino acids in the peptide, namely tryptophan, contains an aromatic chromophore, which determines the absorption of the molecule in the near-UV region. The experimental procedure was to bombard a finely dispersed polycrystalline powder of the peptide by UV pulses [the fourth harmonic from a YAG:Nd laser ($\tau_{\text{pulse}} = 2\times10^{-8}$, 3×10^{-11} s) and a neodymium-doped phosphate glass laser ($\tau_{\text{pulse}} = 5\times10^{-12}$ s)] and to detect the desorbed ions with a time-of-flight mass spectrometer. The apparatus is discussed in detail in Refs. 2 and 3.

Figure 1 is a typical mass spectrum of the positive ions which are driven from the surface of the sample by the nanosecond laser pulse. The pulse energy was chosen at a

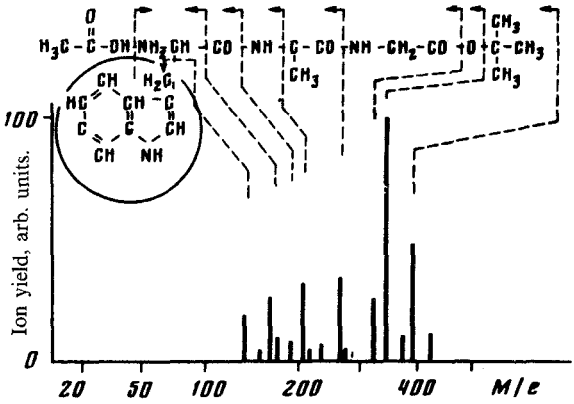

FIG. 1. Identification of the components of the mass spectrum of the ions desorbed from the surface of a solid peptide sample during bombardment by laser pulses with $\tau_{\text{pulse}} = 2\times10^{-8}$ s and $\lambda = 266$ nm.

level designed to keep the total number of ions detected in the linear region of the secondary electron multiplier (10^3–10^4 ions/pulse). It can be seen from Fig. 1 that the ion mass spectrum consists of several intense peaks, which correspond to the fragmentation of the molecule, with ruptures primarily at peptide bonds and with a charge localization at the aromatic chromophore. The lightest fragment, with $M/e = 130$, corresponds to the chromophore ion (shown in the circle of Fig. 1). Neither this mass spectrum nor any of the others have been corrected to allow for the different sensitivities of the detectors for the ions of different masses, so that the relationships between the ion peaks within a given mass spectrum are only qualitatively correct. We can, nevertheless, compare the different mass spectra. The dependence of the total ion yield on the energy of the laser pulses is very strong, as in the case of simpler molecules,[2,3] while the relationships between the peaks in the mass spectrum remain essentially constant from the threshold for the appearance of the ions [$\Phi_{\text{thr}} = (2-4)\times10^{-3}$ J/cm^2] up to the maximum detected value (10^4 ions/pulse).

Figures 2A–2C show mass spectra obtained during the bombardment of the peptide by laser pulses of various lengths: $\tau_{\text{pulse}} = 2\times10^{-8}$, 3×10^{-11}, and 5×10^{-12} s. Spectra A and B were recorded in the direct beam at the same (within the experimental error) energy flux density of the laser pulses, $\Phi = (7\pm3)\times10^{-3}$ J/cm^2. For spectrum C the laser beam was focused by a lens with a focal length of 1 m; in this case it was difficult to determine the energy flow density because of the inhomogeneity of the spot at the focus. Even in this case, however, the average value of the energy flux density is in the interval just specified.

Comparison of the mass spectra for various pulse lengths reveals that (1) a decrease in the pulse length leads to a significant increase in the fraction of desorbed chromophore ions, so that at $\tau_{\text{pulse}} = 5$ ps the corresponding peak in the mass spectrum reaches its maximum size, and (2) no new fragment ions appear in the mass spectrum under these conditions, indicating that there is no further fragmentation of molecules.

This result can be explained in the following way.

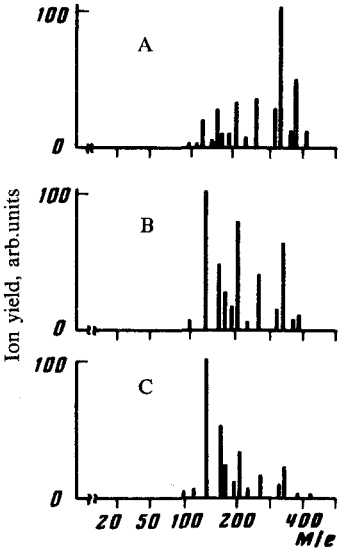

FIG. 2. Mass spectra of ions desorbed from the surface of a solid peptide sample during bombardment by laser pulses with an energy flux density $\Phi = 7\times10^{-3}$ J/cm^2 and a wavelength $\lambda = 266$ nm. A—$\tau_{pulse} = 2\times10^{-8}$ s; B—$\tau_{pulse} = 3\times10^{-11}$ s; C—$\tau_{pulse} = 5\times10^{-12}$ s.

The energy of the absorbed peptide molecule is initially in the form of an electronic excitation of the aromatic chromophore. Under these experimental conditions the electronic-excitation density is quite high: At a laser energy flux density of 7×10^{-3} J/cm^2, with the absorption cross section 6.8×10^{-18} cm^2 for the chromophore, each fifteenth molecule, on the average, participates in the absorption, near the crystal surface. The decay of the first excited electronic state in radiative and radiationless processes occurs in a time of order[5] 10^{-9} s, while the highly excited states decay much more rapidly. During the bombardment of molecules by picosecond pulses there is accordingly an increase in the probability for the absorption by the excited molecules of one or more photons at the energy of 4.7 eV. As a result, the chromophore, excited to a highly excited state in repeated excitation events, detaches in the form of an ion before the energy of the electronic–vibrational excitation is redistributed over the entire molecule and then through the crystal.

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