

# Desorption of ions formed on the surface of a molecular crystal by a femtosecond-range laser pulse

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(Submitted 6 February 1988)

*Pis'ma Zh. Eksp. Teor. Fiz.* **47**, No. 6, 294–296 (25 March 1988)

The first mass spectra of ions formed directly on the surface of metal-free phthalocyanine have been obtained during illumination by a 300-fs laser pulse at 615 nm and 308 nm. A basic feature of these ions, which distinguishes them from ions produced in the gas phase, is the absence of a substantial fragmentation of the molecule.

When the surface of a molecular crystal is illuminated in the electronic absorption band by nanosecond UV laser pulses<sup>1</sup> and picosecond visible-range pulses,<sup>2</sup> the formation of molecular ions without a substantial fragmentation is observed. Egorov *et al.*,<sup>3</sup> have proposed and experimentally confirmed a mechanism for this effect in the case of UV pulses of moderate intensity. The mechanism consists of a thermal desorption of the molecules, followed by their stepwise ionization in vacuum. In some experiments<sup>4</sup> in which a complex molecule with an aromatic chromophore was illuminated with UV laser pulses with a length of about 5 ps, Antonov *et al.*,<sup>4</sup> observed an increase of the chromophore peak in the mass spectrum and a decrease in the fragmentation when the pulse length was reduced. In order to study the formation of ions directly on the surface of a sample, without going through the step of desorption of the molecules, however, one must resort to subpicosecond laser pulses, since in this case one can guarantee that the molecule will not be able during the pulse to move more than 0.3 nm away from the surface.<sup>3</sup>

This letter is the first report of an observation of a photodesorption of molecular ions formed directly on a surface, during the illumination of a polycrystalline sample of metal-free phthalocyanine by a 300-fs pulse of visible or UV light. In addition, the present experiments demonstrate that if the energy is deposited sufficiently rapidly, a slight fragmentation is a basic feature of the desorption of ions from a surface.

In the experiments we observed the mass spectra of the ions formed during the illumination by a laser pulse of a finely dispersed powder of metal-free phthalocyanine deposited in a thick layer on a metal substrate. The illumination was carried out in two geometric configurations, in which it was possible to produce ions either on the surface or in the gas phase. In the first configuration, a 300-fs pulse (at a wavelength of 615 nm or 308 nm) was focused onto the surface of a sample in the time-of-flight chamber of a mass spectrometer (Fig. 1a). In the second configuration, a femtosecond pulse was focused at a point a few tenths of a millimeter from the surface. The molecules of the sample were desorbed by a 10-ns laser pulse ( $\lambda = 532$  nm or 1064 nm), which preceded the femtosecond pulse by a time interval ranging from 0.5  $\mu$ s to several tens

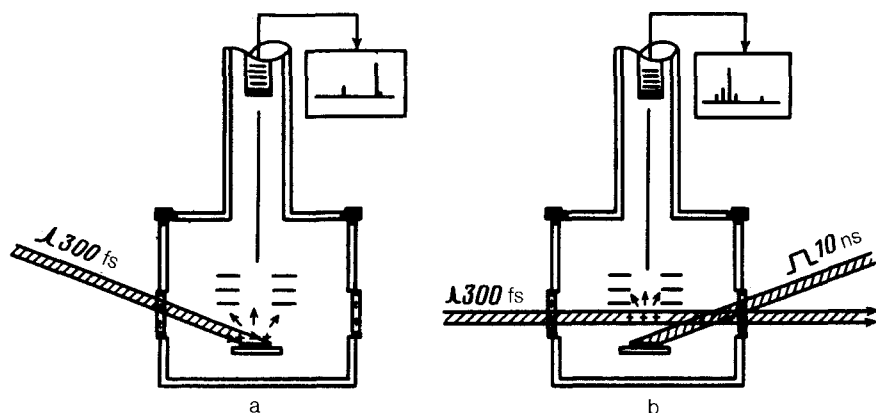


FIG. 1. Different arrangements for illuminating the sample in the mass spectrometer. a—To produce ions on the surface; b—to ionize desorbed neutrals in the gas phase. 1) Sample; 2) time-of-flight chamber of the mass spectrometer.

of microseconds (Fig. 1b). In the latter case, the experimental conditions were chosen in such a way that none of the pulses individually would produce an ion signal. Furthermore, special experiments showed that desorption by the 10-ns pulse did not cause a dissociation of the molecules.

Figure 2, a–c, shows mass spectra obtained under the experimental conditions shown in Fig. 1, a and b, respectively. The shape of the mass spectra in the case in which the surface is illuminated by femtosecond-range pulses at the wavelengths 615 nm and 308 nm is essentially the same: The molecular-ion peak with  $M/e = 514$  a.u. is predominant (Fig. 2a). However, the threshold energy density at which the ions are observed (the threshold sensitivity of the time-of-flight mass spectrometer was  $10^2$  ions) turned out to be  $10^{-3}$  J/cm<sup>2</sup> in the case of the pulse. In other words, in this case it was three orders of magnitude lower than for the pulse at 615 nm (0.5 J/cm<sup>2</sup>), although the absorption cross sections at these two wavelengths are approximately the same. It follows that the desorption of the ions is not a result of a heating of the sample. For the UV pulse, the heating does not exceed a few tens of degrees. Measurements of the width of the observed mass peaks lead to the conclusion that the kinetic energy of the molecular ions does not exceed 1 eV. It follows from this result that during the 300-fs pulse a molecule can move no more than 2 Å away from the surface. This distance is substantially shorter than the size of the molecule itself.

In the case of ionization in the gas phase, the mass spectra are dominated by peaks of fragmentary ions (Fig. 2, b and c). An interesting aspect of the fragmentation is the absence of ions with a mass greater than a quarter of the molecule. In view of the symmetry of the phthalocyanine molecule, it can be suggested that this molecule initially dissociates into four identical fragments with  $M/e = 128$  a.u. The threshold for the appearance of ions for the pulse with a wavelength of 615 nm was 1.4 J/cm<sup>2</sup>. For the UV pulses, as in the illumination of the surface, the threshold for the appearance of the ions turned out to be substantially lower (less than  $10^{-2}$  J/cm<sup>2</sup>). Furthermore, for

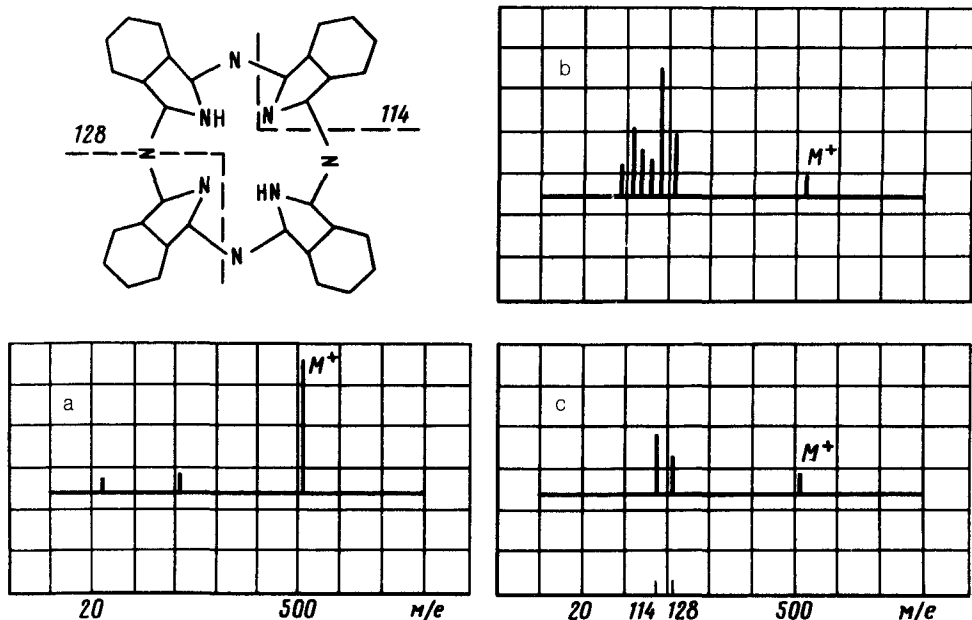


FIG. 2. Mass spectra obtained under various ionization conditions. a—Ionization on a surface by a 300-fs pulse with a wavelength of 615 nm or 308 nm; b—ionization in the gas phase by a 300-fs pulse at 615 nm; c—ionization in the gas phase by a 300-fs pulse with 308 nm.

the UV light (Fig. 2c) we observe fewer fragments and a slightly greater fraction of the molecular ion in the mass spectrum than for the wavelength of 615 nm (Fig. 2b).

In summary, it has been shown experimentally for the first time that the ions which appear during the illumination of a surface by a femtosecond-range pulse are formed directly on the surface. The molecules are ionized without any significant fragmentation. The role played by the heating of the sample during the desorption of the ions is inconsequential. It thus becomes possible to obtain information about the properties of complex molecules on surfaces, and new opportunities are opened up for realizing the idea of visualizing biomolecules<sup>5</sup> and for developing a femtosecond laser mass spectrometry of molecules on surfaces.

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<sup>5</sup>V. S. Letokhov, *Kvant. Elektron. (Moscow)* **2**, 930 (1975) [*Sov. J. Quantum Electron.* **5**, 506 (1975)].

Translated by Dave Parsons