Photodetachment of rhodamine 6G molecular ions adsorbed on a surface by ultrashort laser pulses

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Heavy ionized fragments of rhodamine 6G were photodesorbed from the surface of a tungsten target by picosecond laser pulses of $\lambda = 0.53\ \mu$ wavelength and 10^7 W/cm^2 intensity. When the wavelength was changed to $\lambda = 1.06\,\mu$, there was no desorption of ions right up to intensities of 10^9 W/cm^2. It was concluded that photodesorption was nonthermal.

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1. INTRODUCTION

The use of ultrashort laser pulses for visualization, i.e., for obtaining direct data on the stereochemical structure of complex molecules (particularly, biomolecules), was suggested in Ref. 1. The idea is based on the hypothesis of feasibility of selective photoionization of individual fragments of molecules adsorbed on the surface of a point of a field-ion microscope. Until recently, there have been no experimental data on photodetachment of molecular ions or ionized fragments from the surface under the action of laser radiation. On the other hand, several interesting suggestions have been made on the possibility of interaction between laser radiation and surface-adsorbed molecules.[2–4]

We investigated experimentally this type of process and the possibility of selective photoionization by adopting the following experimental approach. The investigated surface with adsorbed molecules was placed inside the chamber of a transit-time mass spectrometer. Ions formed as a result of illumination of the surface with laser radiation of different wavelengths could be identified in accordance with their mass. It was thus possible to determine whether ionic fragments of a complex molecule were detached from the surface and to identify these fragments.

Successful experiments on the photodetachment of molecular ions of bases of nucleic acids and of anthracene from the surface of a molecular crystal illuminated with intense ultraviolet picosecond pulses were reported recently.[5]

We shall describe the first experiments on the photodetachment of heavy rhodamine 6G (Rh6G) ions adsorbed on the surface of tungsten and subjected to ultrashort (30 psec) pulses of the second harmonic of a YAG:Nd^{3+} laser, whose wavelength was $\lambda = 0.53\ \mu$ and intensity 10^7 W/cm^2. However, these ions were not detached by pulses of the $\lambda = 1.06\ \mu$ wavelength, which was outside the electronic absorption band of Rh6G, even when the intensity was increased up to 10^9 W/cm^2.

2. APPARATUS

The apparatus (Fig. 1) consisted of a transit-time mass spectrometer, whose ionization chamber contained the investigated target, and a YAG:Nd^{3+} laser emitting ultrashort pulses. The YAG:Nd^{3+} laser had the usual oscillator–switch–amplifier configuration and it was capable of producing single pulses of 30 psec duration and up to 10^{-2} J energy at the wavelengths of 0.53 or 1.06 μ. The laser radiation was directed at an angle of 80° on the target. The target was a tungsten plate of 6 × 6 mm dimensions. Before deposition of the adsorbate, the target was subjected to electropolishing and washing in distilled water and alcohol.

A solution of Rh6G in ethanol (10^{-3}–10^{-4} mole/liter) was deposited on the target surface in the form of a drop and then dried. The target was then placed in the ionization chamber of the mass spectrometer, which was evacuated to 5×10^{-8} Torr by a magnetodiode pump.

Each mass spectrum was recorded in one laser shot. A constant potential of +0.5 kV was applied to the target during recording of the mass spectra. This low acceleration voltage in combination with the long drift zone made it possible to use the broadening of the mass peak in estimating the density of the ions reaching the target (see Sec. 4). The ion beam was shaped by a stainless-steel aperture 3 mm in diameter, which was located on the axis of the mass spectrometer at a distance 15 mm from the target surface. This aperture had zero potential. The length of the drift zone of the mass spectrometer was 155 cm. Positive ions were detected with a secondary electron multiplier; the multiplier signal was amplified and then applied to the vertical deflecting plates of an S-8-12 storage oscilloscope. The oscilloscope sweep was triggered by a pulse from the electro-optic switch in the laser, which was locked rigidly in time to the selected laser pulse. A G-5-28 generator was used to delay the sweep, if necessary,

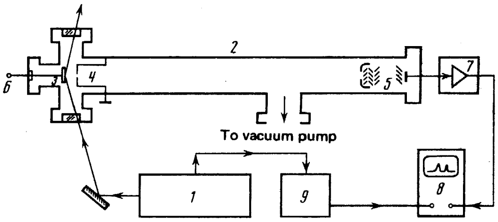

FIG. 1. Schematic diagram of the apparatus: 1) laser emitting ultrashort pulses; 2) transit-time mass spectrometer; 3) target; 4) aperture; 5) secondary electron multiplier; 6) terminal supplying high voltage to the target; 7) amplifier; 8) oscilloscope; 9) delay generator.

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by an interval from 0 to 90 μsec, and this altered the range of the investigated masses. The experiments were carried out under conditions such that the laser radiation did not create plasma on the surface of the illuminated target. These conditions could be verified rigorously since the appearance of a plasma resulted in a strong increase in the amplitude of the signal by three or four orders of magnitude and it caused anomalous broadening of the mass peaks.

3. EXPERIMENTAL RESULTS

It was found that the action of a single ultrashort laser pulse of the 0.53 μ wavelength gave rise to just one peak in the mass spectrum (at the threshold of 1.4×10^7 W/cm^2) and this peak corresponded to a transit time of 103 μsec, i.e., to a mass of $m/e = 434$ (Fig. 2a and 2d). An increase in the laser intensity caused considerable broadening of this peak in the direction of higher and lower transit times (Figs. 2b, 2c, 2e, and Fig. 3). Moreover, two additional peaks were observed and these were identified as due to Na and K (23.6 and 30.6 μsec); sometimes there was also a wide peak in the region of 150 μsec, corresponding to the double mass of the molecular ion $2M_i$ (Fig. 2e).

When the target was illuminated with laser radiation of the 1.06 μ wavelength, the mass spectrum appeared only when the intensity reached 1.2×10^8 W/cm^2 and it consisted solely of the K and Na peaks right up to 10^9 W/cm^2 (Fig. 2f).

A considerable broadening (up to 20 μsec) resulting from an increase in the laser intensity was exhibited only by the rhodamine peak, whereas the width of the K and Na peaks did not exceed 0.5 μsec. The broadening of the former peak could be attributed to a variety of factors. One of them could be secondary ionization by electrons and negative ions, resulting from the bombardment of the aperture with the primary ions.

A control experiment was carried out and this made it possible to eliminate this factor. The laser radiation was directed onto the aperture in the mass spectrometer (Fig. 1). This produced a mass spectrum of the target bombarded by electrons (and possibly negative ions) ejected from the aperture material and accelerated by the field to energies of about 0.5 keV. The threshold of appearance of this spectrum was at least an order of magnitude higher than that obtained for direct illumination of the target. A typical mass spectrum recorded under these circumstances is shown in Fig. 2g. We can see that, in contrast to Figs. 2d and 2e, only light fragments appear in the spectrum.

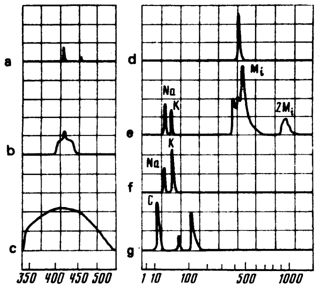

FIG. 2. Mass spectra obtained under different conditions of illumination of an Rh6G film: a)–c) 5 μsec/div., triggering delay 90 μsec; d)–g) 20 sec/div., triggering delay 0; a)–e) illumination with $\lambda = 0.53\,\mu$; f) $\lambda = 1.06\,\mu$; g) bombardment with 0.5 keV electrons. Intensity I of the laser radiation on the target (W/cm^2): a) 1.4×10^7; b) 1.6×10^7; c) 2.8×10^7; d) 2.2×10^7; e) 2.5×10^7; f) 1.2×10^8.

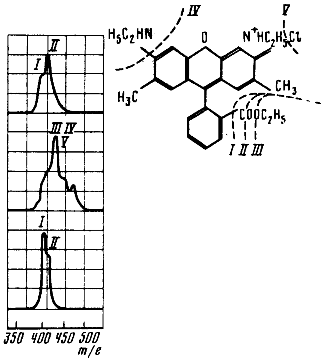

FIG. 3. Possible identification of the structure of a mass peak of Rh6G. Triggering delay 90 μsec; 5 μsec/div., $\lambda = 0.53\,\mu$, $I = 2\times10^7$ W/cm^2. I) Rh6G without $COOC_2H_5$ ($m/e = 406$); II) Rh6G with OOC_2H_5 ($m/e = 418$); III) Rh6G without OOC_2H_5 ($m/e = 434$); IV) Rh6G without H_5C_2H ($m/e = 431$); V) Rh6G without Cl ($m/e = 444$).

The width of the rhodamine peak at the threshold of its appearance did not exceed 0.5 μsec (Fig. 2a). This peak corresponded to the ion transit time of 102.5 ± 0.5 μsec. Precise identification of the mass of ions was not possible without calibration of the mass spectrum with the aid of peaks of ions with similar and precisely known masses. Therefore, we assumed that the observed peak was due to ions with a mass number in the range 430–440, characterized by zero initial velocities or due to heavier ions which entered the acceleration gap with a considerable initial velocity (which should be the same for all the ions). Figure 3 shows several mass spectra with a structure and gives a possible interpretation of the observed peaks based on the assumption that each of them corresponds to a specific mass.

The threshold of appearance of the mass spectra increased considerably as the target was illuminated with consecutive laser pulses. Moreover, after several series of experiments a noticeable deposit of Rh6G appeared at the edges of the aperture in the mass spectrometer. This indicated that the laser pulses removed rhodamine from the target surface.

In a separate series of experiments we recorded the mass spectra of a clean substrate (without rhodamine) in 5×10^{-8} Torr vacuum; we used ultrashort laser pulses of different wavelengths and also energetic electrons (Fig. 4). The results (Figs. 4a and 4b) showed no significant difference between the mass spectra obtained by illumination with $\lambda = 1.06$ and 0.53 μ.

An interesting feature of the spectra was the appearance of a strong but narrow hydrogen line when the laser radiation intensity was $I > 10^8$ W/cm^2 (the ionization potential of hydrogen was 13.6 eV) after illumination with the wavelengths $\lambda = 0.53$ and 1.06 μ (Figs. 4a and 4b).

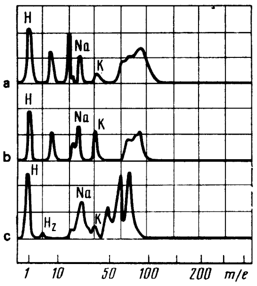

FIG. 4. Mass spectra obtained for a target without rhodamine using different excitation methods: a) $\lambda = 0.53\,\mu$ radiation ($I = 1.2\times10^8$ W/cm^2); b) $\lambda = 1.06\,\mu$ radiation ($I = 1.1\times10^8$ W/cm^2); c) 0.5 keV electrons or negative ions. Triggering delay 0; horizontal scale 10 μsec/div.

4. DISCUSSION OF RESULTS

The most interesting observation was the detachment of heavy Rh6G ions in the absence of significant fragmentation by the $\lambda = 0.53\ \mu$ ($\hbar\omega = 2.36$ eV) laser radiation. The absence of Rh6G from the mass spectra in the case when the target was illuminated with $\lambda = 1.06\ \mu$, which was the wavelength not absorbed by rhodamine, indicated that the substrate had little effect on the ionization process. This was supported also by estimates of the temperature rise of the substrate. Therefore, the primary process which produced these Rh6G ions was undoubtedly the absorption of the $\lambda = 0.53\ \mu$ radiation in the rhodamine film. In our experiments this film did not have a constant thickness because of the well-known tendency of the dye molecules to form aggregates during adsorption (under the action of the intermolecular van der Waals attraction forces).[6] Therefore, the thickness of the film probably varied from one point to another, ranging from zero to several hundreds of monolayers. Consequently the orientation of the dye film surface could vary greatly from point to point and one could then expect reflection of between 36% (in the case of normal incidence) to practically 100% of the radiation corresponding to the absorption band of the dye. Estimates of heating of Rh6G at the points of strongest absorption of the 0.53 μ radiation, on the assumption that all the absorbed energy was converted into heat, gave an increase in temperature of about 100 °C, which was insufficient for thermal ionization. In these estimates we assumed an intensity of 1.4×10^7 W/cm^2 at the threshold of the appearance of the mass spectrum and an absorption cross section of $\sigma = 2.5\times10^{-16}$ cm^2 for the electronic band in the vicinity of the $\lambda = 0.53\ \mu$ wavelength; the specific heat of solid Rh6G was assumed to be 0.3 cal$\cdot$g$^{-1}\cdot$deg^{-1}. Hence, we concluded that the photoionization of Rh6G in our experiments was of nonthermal nature. The actual ionization mechanism could not be identified without additional experiments. One of the possible mechanisms could be, for example, the collective energy transfer processes between electronically excited molecules.[7]

The process of ionization of K and Na impurities was sensitized by the absorbing rhodamine molecules. This was deduced from the experimental observation that in the $\lambda = 0.53\ \mu$ case the threshold of appearance of the K and Na ions in the presence of Rh6G was an order of magnitude less than in the absence of rhodamine. However, in the case of the $\lambda = 1.06\ \mu$ radiation, which was not absorbed in Rh6G, the threshold of appearance of the K and Na ions on a clean target was the same as that on a target with rhodamine.

Broadening of the Rh6G peak on increase in the laser intensity (Figs. 2a–2c) occurred in the direction of shorter and longer transit times. Therefore, it was mainly due to the Coulomb repulsion between the ions and not due to an increase in the initial velocities of the ions. This Coulomb repulsion could result in considerable (on the time scale) broadening of the mass spectrum in the case of large masses, in agreement with our observations.

The broadening of the mass peaks could be used to estimate the surface density of the charge in a packet of ions.[8] This value was 10^6–10^7 ions/cm^2 in the plane of the mass-spectrometer aperture; we assumed a uniform distribution of the charge and a small divergence of the ionic beam.

5. CONCLUSIONS

The first conclusion is that ultrashort pulses of the 0.53 μ wavelength can cause nonthermal detachment of Rh6G molecular ions from a thick film without significant fragmentation of the molecules. This is important for the development of a method of laser visualization of molecular bonds by selective excitation with laser radiation of a chemical label,[1] particularly of an intercalating dye in the DNA molecule. When a biomolecule is labeled with a suitable dye, it can then be adsorbed on the point of a field-ion projector and illuminated with a laser pulse at the absorption wavelength of the dye. The detached dye ions can identify the intercalation points on the projector screen, i.e., the positions of certain pairs of compounds. A set of dyes intercalating with different pairs and also differing considerably in respect of absorption bands can be used to determine the structure pattern of a biomolecule by illuminating it with pulses of different frequencies. An important advantage of this method is the fact that the absorption bands of the dye lie in the visible range and the biomolecules themselves are transparent in this range (the absorption bands of most of them lie in the ultraviolet range), so that it should be possible to excite the dye without affecting the biomolecule. Moreover, it seems quite feasible to identify the locations of the excited and ejected chemical labels and their masses from the transit time in a pulsed field-ion projector.[9]

Our results also indicate sensitization of the detachment of the K and Na ions by the Rh6G molecules excited electronically by ultrashort light pulses.

Finally, at ultrashort laser pulse intensities exceeding 10^8 W/cm^2 the hydrogen ions are detached from the surface and this effect is observed at the wavelengths $\lambda = 1.06\ \mu$ and $\lambda = 0.53\ \mu$.

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