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OPTICS
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# Dynamics of Photoreactions in $(CF_3I)_nXe_m$ Mixed Clusters Exposed to Femtosecond Ultraviolet Radiation Inducing Multiphoton Ionization

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The multiphoton ionization of $(CF_3I)_nXe_m$ mixed clusters formed at the outflow of a mixture of $CF_3I$ and Xe from an ultrasonic pulsed nozzle by femtosecond ultraviolet radiation ($\lambda = 266$ nm) has been studied. The formation of $XeI^+$ mixed ions and $I_2^+$ ions in intracluster reactions has been detected. It has been shown that the efficiency of the formation of $XeI^+$ ions significantly depends on the duration of a laser pulse: ultraviolet picosecond radiation is necessary for their formation. The kinetic yield curves of the $XeI^+$ and $I_2^+$ ions upon ultraviolet multiphoton ionization of $(CF_3I)_nXe_m$ mixed clusters have been measured. The characteristic times of their formation determined from these curves are $(53 \pm 8)$ ps and $(65 \pm 6)$ ps, respectively.

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## 1. INTRODUCTION

The multiphoton ionization and dissociation of molecular clusters by laser radiation, in particular, by femtosecond pulses are of interest because of the presence of specific channels of photoinduced reactions inherent in clusters compared to monomers. A striking example is the study of the so-called Coulomb explosion of clusters induced by intense femtosecond radiation. The perturbation of potential surfaces of molecules in a strong electric field results in the multiple electron detachment and in the formation of a multiply ionized core. The strong Coulomb repulsion leads to the fast dissociation of this core, which is often called the "Coulomb explosion," following [1]. One of the directions of study of this effect in the case of ionization of noble-gas clusters concerns its application to generate X rays [2]. Studies of this effect and its possible applications, in particular, to study intramolecular and intracluster dynamics are analyzed in detail in reviews [3, 4].

The Coulomb explosion in clusters is usually observed at the intensity of femtosecond pulses $\geq 10^{14}$–$10^{15}$ W/cm$^2$. However, photoinduced intracluster reactions are also observed at much lower radiation intensities $\leq 10^{12}$ W/cm$^2$. One of such reactions for clusters of $(R–I)_n$ iodides, where R is a radical, is the formation of molecular iodine among the products of their photofragmentation under ultraviolet laser irradiation. Molecular iodine was observed both in the form of a neutral product of single-photon fragmentation of $(CF_3I)_2$ dimers [5] and in the form of an ion upon the multiphoton ionization (MPI) of these objects [6]. Later, the molecular iodine ion $I_2^+$ was also observed upon the ultraviolet MPI of clusters $(CF_3I)_n$ [7, 8] and $(IF_2CCOF)_n$ [9]. Using the pump–probe technique, the characteristic times of intracluster processes resulting in the formation of $I_2^+$ upon the ultraviolet MPI of $(CF_3I)_n$ clusters by femtosecond pulses were measured [10]. The mechanism of the decay of $(R–I)_n$ clusters exposed to ultraviolet femtosecond radiation was studied in detail in [11].

The experiments mentioned above were performed with *homogeneous* clusters consisting of identical particles. However, comparative studies of the MPI of homogeneous $(CF_3I)_n$ clusters and $(CF_3I)_n$ clusters located inside or on the surface of large $Xe_m$ clusters with ultraviolet nanosecond pulses showed that the efficiency of fragmentation of particles, as well as the set of products, significantly depends on the environment and composition of clusters [12]. In this work, we study the MPI of $(CF_3I)_nXe_m$ mixed clusters, as well as the dynamics of specific reactions inherent in mixed clusters ionized by ultraviolet femtosecond radiation.

## 2. EXPERIMENTAL SETUP AND THE METHOD

The main elements of the setup used for the experiment were described in detail in [10]; here, we only describe the conditions under which the measurements were carried out. The setup consists of a photoionization time-of-flight mass spectrometer and a pulsed nozzle, which is a source of molecular and cluster beams. A collimated particle beam is formed with a skimmer (Beam Dynamics, Model 1, diameter of the orifice is $d_{skim} = 0.49$ mm) placed at a distance of 55 mm from the pulsed nozzle (General Valve, diameter of the orifice is $d_{nozzle} = 0.8$ mm) and is guided to the chamber of the mass spectrometer, where it intersects laser beams on the axis of the mass spectrometer. The characteristic diameter of the cluster beam in the ionization region was $D_{clust} = 1.8$ mm. Depending on the conditions of outflow from the nozzle, pure molecular beams and beams with different degrees of clustering up to pure cluster beams can be generated. $(CF_3I)_nXe_m$ mixed clusters were generated at supersonic expansion of the mixture of $CF_3I$ and Xe gases with the ratio $CF_3I/Xe = 1/100$ and the total pressure $P_0 = 200$ kPa at room temperature into vacuum. According to [12], under these conditions for such mixture including $CF_3I$, $(CF_3I)_nXe_m$ mixed clusters are formed with the central core consisting of $CF_3I$ clusters "coated" with Xe atoms. The shell structure of the mixed cluster under our outflow conditions is formed because of the difference in the binding energy between particles of different types: compared to atoms in the shell of a cluster, the binding energy of molecules in its core is higher and they are clustered earlier (at higher temperatures) in the process of gasdynamic cooling.

A Ti:sapphite laser (Spectra Physics, $\lambda = 800$ nm, $\tau_{pulse} = 50$ fs, and $F = 1$ kHz) was used as a source of femtosecond radiation, which was converted to obtain laser pulses at the frequencies of the second ($\lambda = 400$ nm) and third ($\lambda = 266$ nm) harmonics by means of nonlinear BBO crystals. The initial duration of ultraviolet pulses at a wavelength of $\lambda = 266$ nm used for the ultraviolet MPI of clusters in these experiments was $\tau_{pulse} \approx 160$ fs. Ions formed in the experiments were detected by the time-of-flight mass spectrometer. Probe pulses at a wavelength of $\lambda = 400$ nm were used to measure the formation kinetics of the corresponding products (see below). The time delay between the ultraviolet and probe pulses was smoothly controlled using an optical delay line. Ultraviolet pulses with different durations were used in the experiment. The pulse duration was varied by means of its chirping at the single and double transmission through a quartz block with a length of $L = 13.5$ cm. As a result, the initially unstretched ultraviolet pulse with a duration of $\tau_{pulse} \approx 160$ fs was transformed into a pulse with a duration of approximately 800 fs (one pass) and 2.2 ps (two passes through the quartz block). The duration of a laser pulse at a wavelength of $\lambda = 266$ nm was measured by mixing of this pulse with a 50-fs pulse at a wavelength of $\lambda = 800$ nm in the BBO crystal in terms of the effect of sum frequency generation. Radiation was focused into the chamber of the mass spectrometer by means of a lens with a focal length of $f = 30$ cm. The energy fluence of ultraviolet radiation on the axis of the cluster beam was usually no more than $\Phi = 0.15$ J/cm$^2$, which corresponds to a radiation intensity of $9.4 \times 10^{11}$ W/cm$^2$ for $\tau_{pulse} = 160$ fs.

## 3. RESULTS

The intense peaks of $XeI^+$ ions (in addition to $I^+$ and $I_2^+$ ions) were detected in the mass spectrum recorded in [12] upon the ultraviolet MPI of $(CF_3I)_nXe_m$ clusters by nanosecond pulses ($\tau_{pulse} \approx 7$ ns); the ratio of the intensities of the $XeI^+$ and $I_2^+$ peaks was approximately 1/1. The observation of $XeI^+$ peaks is direct evidence of the presence of $(CF_3I)_nXe_m$ mixed clusters in the beam and the occurrence of the photoinduced intracluster reaction of formation of this mixed ion. One of the main aims of this work was, using femtosecond pulses, to study the kinetics of this reaction and its mechanisms as in [10] for the $I_2^+$ ion upon the ultraviolet MPI of homogeneous $(CF_3I)_n$ clusters.

In this work, $XeI^+$ and $I_2^+$ ions were also detected upon the ultraviolet MPI of the cluster beam containing $(CF_3I)_nXe_m$ clusters by femtosecond pulses. At radiation intensities above $(2–3) \times 10^{11}$ W/cm$^2$, the mass spectrum has many peaks corresponding to fragment ions formed in the dissociative ionization of mixed clusters. We pay particular attention to ion signals near masses of about 260 and 130 a.m.u. The first group includes the $I_2^+$ ion peak (254 a.m.u.), as well as the $Xe_2^+$ and $XeI^+$ ion peaks. The last two ions provide a wide structure in the mass spectrum because of the existence of seven natural Xe isotopes with masses from 128 to 136 a.m.u. The model analysis of the recorded mass spectra, experiments with various durations of femtosecond pulses, and additional measurements with a purely xenon beam allowed us to determine contributions from various ion products near 260 a.m.u. The results are presented in Fig. 1.

We revealed that, compared to [12], the efficiency of formation of $XeI^+$ ions significantly depends on the duration of femtosecond radiation. This is seen in mass spectra in the region $m/z \sim 260$ a.m.u. containing $I_2^+$, $Xe_2^+$, and $XeI^+$ ion peaks presented in Fig. 1 for the ultraviolet pulse with a duration of approximately (a) 160, (b) 800, and (c) 2200 fs at a constant energy. The $XeI^+$ ion is hardly present at a short duration of

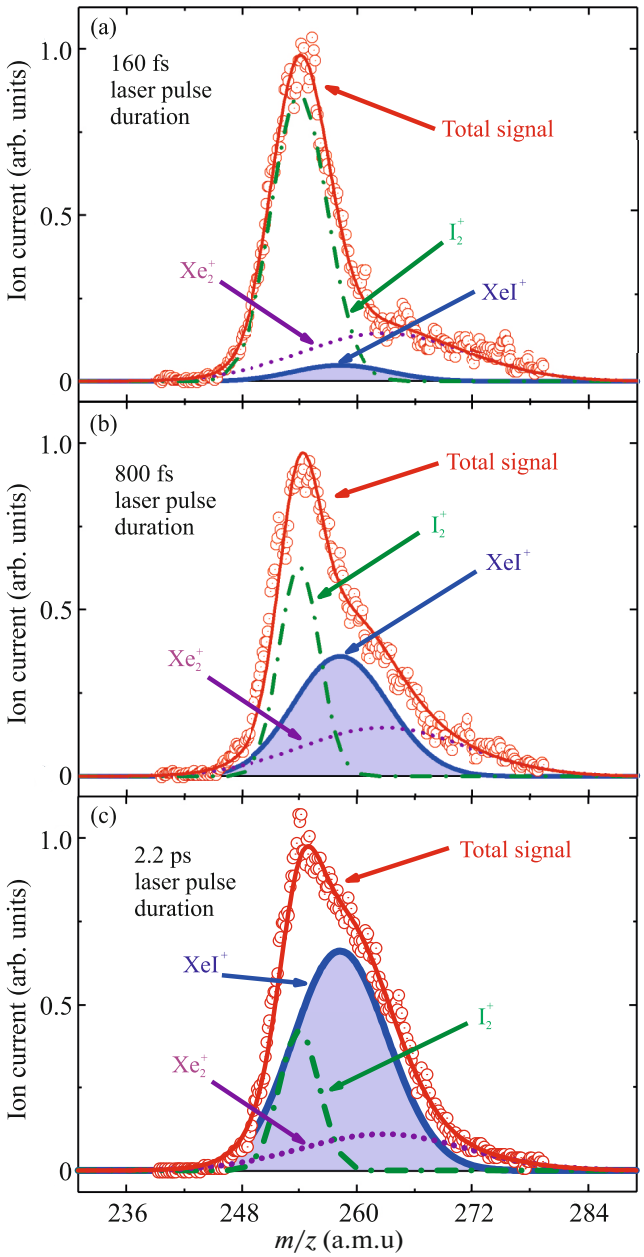


**Fig. 1.** (Color online) Mass peaks of the $I_2^+$, $Xe_2^+$, and $XeI^+$ ions obtained upon the multiphoton ionization of clusters by ultraviolet pulses with the duration approximately (a) 160, (b) 800, and (c) 2200 fs. The area proportional to the number of $XeI^+$ ions is colored for clarity. Circles are experimental points and smooth curves are the simulation results.

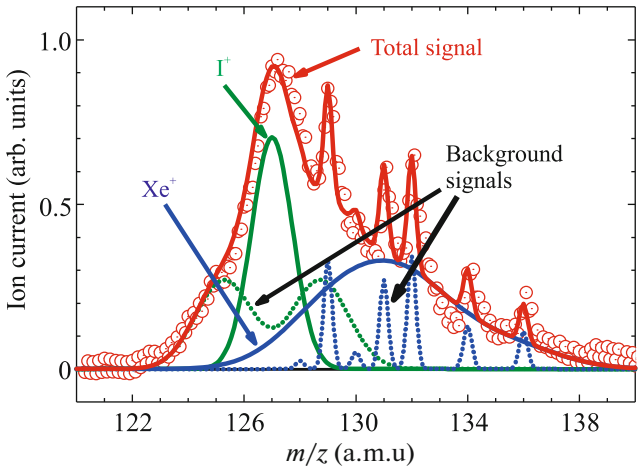


**Fig. 2.** (Color online) Fragment of the mass spectrum near 130 a.m.u. with overlapping peaks from the $I^+$ and $Xe^+$ ions at $\Delta\tau_{delay} = 200$ ps. The solid lines are the signals from the $I^+$ and $Xe^+$ ions formed upon the photodissociation of $I_2^+$ and $XeI^+$ by probe radiation, respectively. The dotted lines are the background signals from the $I^+$ and $Xe^+$ ions formed upon the ultraviolet multiphoton ionization of clusters and atoms of the carrier gas, respectively.

$\tau_{pulse} \approx 160$ fs and becomes dominant in the spectrum at $\tau_{pulse} \approx 2.2$ ps. We note that the absence of xenon ions in [12] is likely due to a higher ionization potential of xenon (≈12.13 eV) compared to the $CF_3I$ (≈10.28 eV) and $I_2$ (≈9.31 eV) molecules and to insufficient intensity of nanosecond radiation for its multiphoton ionization.

To understand the mechanism of formation of $XeI^+$, we measured the kinetics of its yield using the pump–probe technique. Ionization was induced by an ultraviolet pulse ($\tau_{pulse} \approx 2.2$ ps); after that, a relatively weak probe pulse ($\lambda = 400$ nm) induced single-photon dissociation of the $XeI^+$ ion, which was formed upon the ultraviolet MPI, into the $Xe^+$ ion and I atom: $XeI^+ \rightarrow Xe^+ + I$. According to the data from [13] on the energy levels of $XeI^+$, one photon at $\lambda = 400$ nm is sufficient to induce this reaction. The dissociation of the molecular ion is not an instantaneous process and the characteristic time of the formation of this ion should be taken into account. Below, we assume that the characteristic time of dissociation of $XeI^+$ can be estimated in order of magnitude from the time of dissociation of $I_2^+$ [10], which is about 1 ps.

However, it is noteworthy that the mass spectrum of ions near 130 a.m.u., where $I^+$ and $Xe^+$ peaks are located, has a complex structure (see Fig. 2). The mass spectrum in Fig. 2 demonstrates not only the $Xe^+$ ion formed upon the photodissociation of $XeI^+$ by a probe laser pulse but also $I^+$ ions formed upon the photodissociation of $I_2^+$ by a probe laser pulse: $I_2^+ \rightarrow I^+ + I$ (these $Xe^+$ and $I^+$ peaks are indicated by the solid lines in Fig. 2). This reaction was previously used to determine the rate of formation of $I_2^+$ upon ultraviolet MPI of homogeneous $(CF_3I)_n$ clusters [10]. In addition to

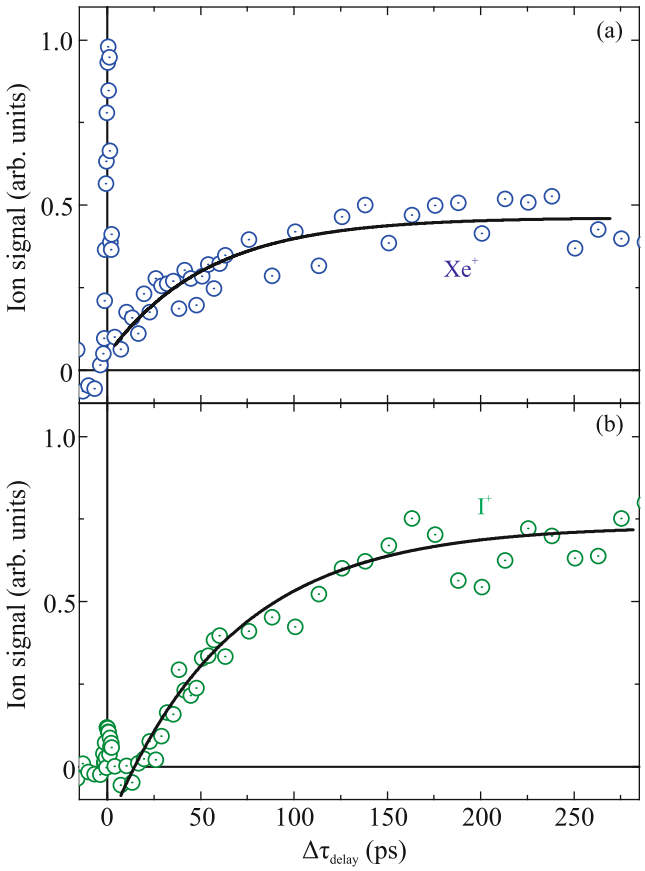


**Fig. 3.** (Color online) Kinetic yield curves for $Xe^+$ ions upon the dissociation of the (a) $XeI^+$ and (b) $I^+$ ions at the dissociation of $I_2^+$ upon the multiphoton ionization of $(CF_3I)_nXe_m$ clusters by ultraviolet pulses with a duration of $\tau_{pulse} \approx 2.2$ ps (each point is the area under the corresponding curve in Fig. 2). The solid lines are the approximations by the function $f(t) \sim 1 - \exp(-t/\tau)$ with the characteristic times $\tau_1 = (53 \pm 8)$ ps for $Xe^+$ and $\tau_2 = (65 \pm 6)$ ps for $I^+$.

signals from these two ions, Fig. 2 also demonstrates background signals from $I^+$ ions formed during dissociative ionization of clusters under the action of the pump pulse and from $Xe^+$ ions formed in ionization of atoms of the carrier gas and present in the beam (dotted lines).

The analysis of experimental mass spectra has made it possible to separate the contribution from $Xe^+$ ions formed upon the photodissociation of $XeI^+$ and from $I^+$ ions upon the photodissociation of $I_2^+$ by probe radiation at each time delay. As a result, we have obtained the kinetics of the yield of these ions (see Fig. 3), according to which the characteristic times of formation of the $XeI^+$ and $I_2^+$ ions upon ultraviolet MPI of $(CF_3I)_nXe_m$ mixed clusters are $\tau_1 = (53 \pm 8)$ ps and $\tau_2 = (65 \pm 6)$ ps, respectively.

The performed studies have shown that the characteristic time of formation of the $XeI^+$ and $I_2^+$ ions upon the ultraviolet femtosecond multiphoton ionization of $(CF_3I)_nXe_m$ mixed clusters is much longer (almost by two orders of magnitude) than the time of formation of the $I_2^+$ ion upon the ultraviolet MPI of *homogeneous* $(CF_3I)_n$ clusters [10]. We believe that this is primarily due to differences in the structure between the homogeneous and mixed clusters: in the former case, the yield of $I_2^+$ is at least not obstructed by the presence of the "coat" consisting of noble-gas atoms. It has also been revealed that the formation of the $XeI^+$ ion upon the ultraviolet MPI of $(CF_3I)_nXe_m$ mixed clusters depends on the duration of the laser pulse. The efficient formation of this ion requires the presence of ultraviolet picosecond pulses. In essence, an ultraviolet pulse triggers a sequence of intracluster reactions finally resulting in the formation of the free $XeI^+$ ion. The formation of ions upon the nonresonant MPI of molecular clusters by ultraviolet ultrashort laser pulses is accompanied by the fragmentation of clusters even at intensities of laser pulses far from the Coulomb explosion. The "shell" structure of $(CF_3I)_nXe_m$ mixed clusters limits the rate of the yield of ions formed from particles located in the core of the cluster. The observed time of formation of the $XeI^+$ and $I_2^+$ ions under such conditions represent the characteristic lifetime of the mixed cluster in the process of its dissociative ionization: the cluster shell consisting of xenon atoms apparently decays at times of about 50 ps; after that, the yield of free $XeI^+$ and $I_2^+$ ions becomes possible.

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## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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