Photoinduced Processes in Mixed Molecular Clusters $(CF_3I)_n(CF_3Br)_m$ under the Action of Femtosecond Laser Radiation

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Abstract—The dissociation dynamics induced in $(CF_3I)_n(CF_3Br)_m$ mixed molecular clusters by femtosecond UV radiation is studied. UV excitation and photoionization probing are used in combination with time-of-flight mass spectrometry. The process of electron-vibrational relaxation, which leads to the dissociation of clusters, is discussed. Data on the characteristic rates of the various stages of this process are obtained.

INTRODUCTION

The interest in studying the dissociation of molecular clusters is due to the specific channels of photoinduced reactions inherent in clusters, relative to monomers. One example of such reactions for iodide clusters of the $(R-I)_n$ type is the formation of molecular iodine among the products of their photofragmentation under the action of UV laser radiation. Molecular iodine has been observed as a neutral product of single-photon fragmentation of dimers $(CH_3I)_2$ [1], and as an I_2^+ ion during multiphoton ionization (MPI) of these objects [2]. The I_2^+ ion of the molecular iodine was later observed with UV MPI of $(CF_3I)_n$ [3, 4] and $(IF_2CCOF)_n$ [5] clusters. Ion I_2^+ has also been observed when femtosecond UV radiation was used for MPI of $(CF_3I)_n$ clusters. The characteristic times of intracluster processes leading to its formation [6] were measured using the pump–probe technique.

Spectroscopic data are needed to determine how neutral molecular iodine is formed during the photofragmentation of clusters. The electronic structure of the CF_3I and CH_3I molecules has been studied in considerable detail. Numerous studies devoted to the CH_3I molecule in particular have shown the decay character of first excited state $\tilde{A}$ that forms upon of the $5p\pi$ electron's transition to the antibonding σ^*-orbital of the C–I bond. The lifetime of this state is in the subpicosecond range [7]. Rydberg states of the CH_3I molecule are formed during electronic transitions from the $5p$ orbitals of the iodine atom to the $6s$ or $6p$ orbital. The decay of higher Rydberg states in this molecule was investigated in [8, 9], where it was shown that characteristic times lie in the 100 fs range, and the most probable decay channel is the dissociation of the molecule with the breaking of C–I bonds. The concept behind the energy diagram of the CF_3I molecule's levels can be understood from the data in [10]. The spectrum is determined by transitions which are analogous to the transitions in CH_3I molecule. The characteristic times of dissociative processes in the CF_3I molecule lie in the same time domain [10].

The ultrafast dynamics of the dissociation of $(CH_3I)_2$ dimers was first investigated in [11], where the authors used femtosecond laser radiation at a wavelength of $\lambda = 277$ nm for single-quantum UV excitation into the $\tilde{A}$ absorption band, and pulses with $\lambda = 304$ nm for the ionization of dissociation products. These experiments allowed ways of forming molecular iodine I_2 to be proposed, and the lifetimes of the excited complexes from which I_2 iodine is formed to be determined. The excitation of $(CH_3I)_n$ clusters into Rydberg states with two-photon absorption at a wavelength of $\lambda = 270$ nm and the femtosecond dynamics of their dissociation were investigated by the authors of [12]. They succeeded in tracing the decay evolution of highly excited electron states in a clustered CH_3I molecule on a timescale of up to several tens of picoseconds.

The dissociation dynamics of homogeneous clusters of the $(R-I)_n$ type was observed in [13] over a wide range of periods with electronic excitation of the molecules composing the cluster by femtosecond UV radiation at a wavelength of $\lambda = 266$ nm to the Rydberg states that lie below the ionization threshold. The process of cluster decay and the effect intracluster processes of energy redistribution had on its rate were revealed. The $(IF_2CCOF)_n$ clusters were chosen to demonstrate most of the experimental results in [13]. However, the patterns found in that work were similar for clusters of all three investigated molecules: $(IF_2CCOF)_n$, $(CF_3I)_n$, and $(CH_3I)_n$.

The aim of this work was to observe directly the decay dynamics of mixed clusters of the $(CF_3I)_n(CF_3Br)_m$ type while exciting the molecules composing each cluster with femtosecond radiation at a wavelength of $\lambda = 266$ nm under conditions analogous to those in [13]. It was of particular interest to determine the effect a mixed cluster's structure has on the decay and rate of intracluster processes of energy redistribution, and to compare these findings to ones for homogeneous clusters $(CF_3I)_n$.

EXPERIMENTAL

The setup described in [6] was used in our experiment, so we shall give only the conditions under which measurements were made. The basis of the experimental complex was a photoionization time-of-flight mass spectrometer (TOF MS) in combination with a pulsed nozzle (our source of molecular and cluster beams). A collimated particle beam was formed with a skimmer (Beam Dynamics, Model 1; diameter of the skimmer's aperture was $d_{skim} = 0.49$ mm) mounted at a distance of 55 mm from the pulsed nozzle (General Valve; diameter of the nozzle aperture was $d_{nozzle} = 0.8$ mm). It was directed to the TOF MS chamber, where it intersected with laser beams along with the axis of the mass spectrometer. The typical diameter of the cluster beam in the region of ionization was $D_{clust} = 1.8$ mm. Purely molecular beams and beams with different degrees of clustering up to purely cluster beams could be generated, depending on the conditions of the outflow from the nozzle. A purely molecular or purely cluster beam could be produced by controlling the duration of the pulse opening the nozzle. Mixed clusters $(CF_3I)_n(CF_3Br)_m$ were generated during supersonic expansion into the vacuum of a gaseous mixture of the investigated molecules with Ar at a ratio of $CF_3I/CF_3Br/Ar = 1/2/24$ and total pressure $P_0 = 200$ kPa at room temperature. Homogeneous clusters $(CF_3I)_n$ for which we also present results in this work were obtained using a mixture with Ar, in which the ratio was $CF_3I/Ar = 1/15$ at the same total pressure and temperature. The delay between the nozzle valve opening time and laser probing was chosen so as to act on the region of the cluster beam that contained the minimum addition of monomers.

An estimate of mean size N of the formed homogeneous clusters can be made using the Hagena relation in [14], along with the data obtained in experiments on the dissociation of $(CF_3I)_n$ clusters under the action of IR laser radiation [4, 15]. Under the abovementioned experimental conditions, we estimated that $N \approx 100$ for homogeneous $(CF_3I)_n$ clusters.

A titanium–sapphire laser (Spectra Physics; $\lambda = 800$ nm, $\tau_{pulse} = 50$ fs, $F = 1$ kHz), the radiation of which was converted using nonlinear BBO crystals, served as our source of femtosecond radiation to obtain laser pulses at frequencies of the second ($\lambda = 400$ nm) and third ($\lambda = 266$ nm) harmonics, and at durations of $\tau_{pulse} \approx 100$ fs. UV pulses at a wavelength of $\lambda = 266$ nm (pump pulses) were used to excite the molecules in a cluster into electronic states lying below the ionization threshold. Laser pulses at a wavelength of $\lambda = 400$ nm (probe pulses) were used for the MPI of the investigated particles, and the ions formed during MPI were detected by TOF MS. The delay time between a pump pulse and a probe pulse was smoothly regulated using an optical delay line; the energy in each of these pulses could be changed independently by means of disk attenuators. After the delay line, the pulses were brought together on a beam splitter and then propagated coaxially. Laser pulses were focused into the TOF MS chamber using the same lens with a focal length of $f = 30$ cm. The dispersion of the refractive index of the lens material (CaF_2) caused the focal distances for the pump pulse and the probe pulse to differ. The displacement of the lens along the axis of laser radiation propagation easily allowed us to obtain conditions under which the probe pulse acted only on the particles irradiated with the pump pulse, since the diameter of the probe pulse caustic in the region of ionization was much smaller than that of the pump laser pulse.

RESULTS AND DISCUSSION

To solve the problem of comparing the dissociation dynamics of homogeneous and mixed clusters over their UV excitation below the ionization threshold, we first need to detect mixed clusters in a beam using the mass spectra produced upon their ionization. IBr^+, $CFIBr^+$, and CF_3IBr^+ ions, which indicate the presence of mixed clusters $(CF_3I)_n(CF_3Br)_m$ in a molecular cluster beam, were found among the products formed upon the ionization of a cluster beam using femtosecond radiation at wavelengths of $\lambda = 266$ and $\lambda = 400$ nm, in combination with a mixture of $CF_3I/CF_3Br/Ar = 1/2/24$ at a total pressure of $P_0 = 200$ kPa. A typical mass spectrum for ionization using radiation with $\lambda = 400$ nm is shown in Fig. 1.

IBr^+ ions, the signal from which was the strongest among the detected mixed ion peaks, were chosen for observation, along with CF_3I^+ and CF_3Br^+ ions, which can form during the decay of mixed clusters $(CF_3I)_n(CF_3Br)_m$ as a result of electronic excitation of their molecules and subsequent relaxation processes.

Our pump–probe experiment was performed according to a scheme similar to the one for homogeneous clusters $(CF_3I)_n$ [13]. A UV pump pulse ($\lambda = 266$ nm) excited the electronic states in the molecules of mixed clusters $(CF_3I)_n(CF_3Br)_m$, after which a probe pulse ($\lambda = 400$ nm) that ionized the clusters and
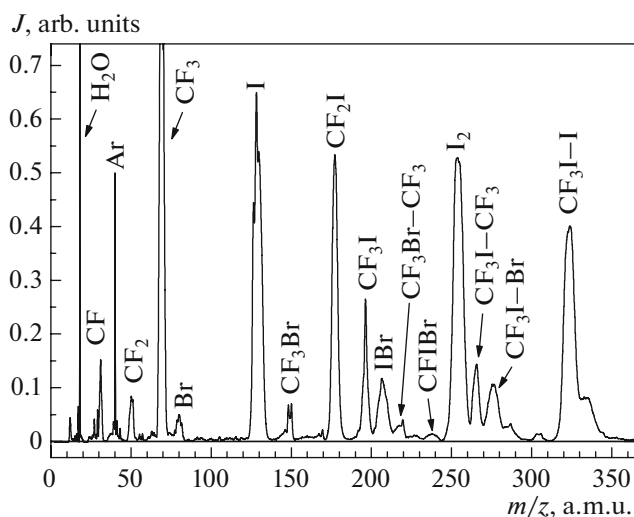
Fig. 1. Characteristic mass spectrum of the products of ionization of mixed clusters $(CF_3I)_n(CF_3Br)_m$ by femtosecond laser radiation at a wavelength of $\lambda = 400$ nm.

Fig. 2. Dependences of the yield of IBr^+ ions from mixed clusters $(CF_3I)_n(CF_3Br)_m$ and that of I_2^+ ions from homogeneous clusters $(CF_3I)_n$ on delay $\Delta\tau$ between the pump pulse ($\lambda = 266$ nm) and the probe pulse ($\lambda = 400$ nm).

their decay products was sent with an adjustable delay. Because of the way in which the problem was posed, the pump pulse produced no ions. It should be noted that CF_3I and CF_3Br molecules have different electronic structures and ionization potentials; these can also be shifted and/or broaden during clusterization. It is therefore even more difficult to identify the specific electronic states in which clustered molecules appear in a mixed cluster as a result of UV excitation than when dealing with a homogeneous cluster. The ionization potential of CF_3I and CF_3Br molecules is greater than 10 eV, so we can speak of two-quantum excitation in the 9.3 eV region (the quantum energy at a wavelength of $\lambda = 266$ nm is 4.66 eV) even with allowance for possible shifts in the electronic spectrum.

The kinetic curve of the yield of IBr^+ ions from mixed clusters $(CF_3I)_n(CF_3Br)_m$ is shown in Fig. 2 as a function of delay $\Delta\tau$ between laser pulses. The curve for the signal from the I_2^+ ions, obtained in a similar experiment with homogeneous clusters $(CF_3I)_n$, is also given for comparison in Fig. 2.

It can be seen that the signal from IBr^+ and I_2^+ ions decreases as delay $\Delta\tau$ between the pump pulse and the probe pulse grows. The behavior of the kinetic curves was analogous to that of homogeneous clusters $(CF_3I)_n$, and the characteristic times of signal changes lay in the range of 10^{-10} s. This indicates the scheme of relaxation processes described in [13] for homogeneous clusters of $(R-I)_n$ iodides is generally applicable to the case of mixed clusters as well, since the initial population of higher electronic states is converted to the ground electronic state over time. The vibrational
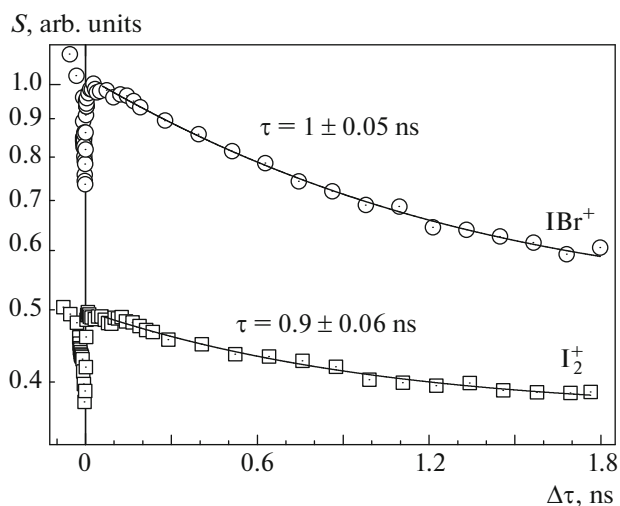
modes in molecules are in this case populated during relaxation. The energy contained in the vibrations of the molecules subsequently relaxes into the intermolecular vibrations of a cluster, raising its temperature and accelerating its dissociation with the formation of neutral molecules.

We can note several differences in the kinetic curves despite their apparent similarity in Fig. 2. If we compare the kinetics of the yield of I_2^+ ions from homogeneous clusters $(CF_3I)_n$ and that of IBr^+ ions from mixed clusters $(CF_3I)_n(CF_3Br)_m$, the signal for the latter reaches a level of around 60% of a signal unperturbed by a pump pulse. This level is about 75% for homogeneous clusters, and both of these experimental curves can be described with good accuracy by an exponential decay function with a characteristic time of ≈ 1 ns. This indicates the rate of energy transfer into the intermolecular vibrations of the cluster (the energy is originally stored in the electronic states of molecules) is the same. However, the possible differences between the amount of energy absorbed by the cluster (the cross section of two-photon absorption) and the bonding energy between the molecules in homogeneous and mixed clusters result in mixed clusters losing a higher percentage of molecules than homogeneous clusters during dissociation.

Let us consider the kinetics of the yield of CF_3I^+ ions from homogeneous clusters and that of CF_3I^+ and CF_3Br^+ ions from mixed clusters. All three curves are shown on one graph in Fig. 3, and the scale along the vertical axis is given in identical units for clarity. It can
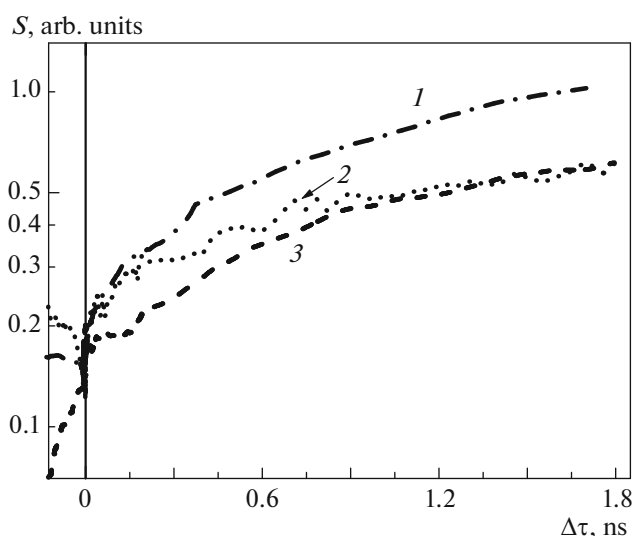
S, arb. units

Fig. 3. Dependences of yields of CF_3I^+ ions (curve *1*) and CF_3Br^+ ion (curve *3*) from mixed clusters $(CF_3I)_n(CF_3Br)_m$, and those of CF_3I^+ ions (curve *2*) from homogeneous clusters $(CF_3I)_n$ on delay $\Delta\tau$ between a pump pulse ($\lambda = 266$ nm) and a probe pulse ($\lambda = 400$ nm).

be seen that the rates of the rise in the signals from the molecular ions that form if there are mixed clusters in a beam differ from one another, and from those of the rise in the signals from molecular ions upon the dissociation of homogeneous clusters.

The difference between the rate of formation of molecular ions from homogeneous and mixed clusters could be due to the effect the structure of a mixed cluster has on the path of the initial excitation's relaxation, which leads to uneven evaporation of different components of a mixed cluster over time. This effect is most noticeable at fairly short delays between laser pulses when electron–vibrational conversion is not yet complete. This corresponds to a scale of times shorter than 500–600 ps under our conditions. Our experiment showed (see Fig. 3) that the growth rates of CF_3I^+ and CF_3Br^+ signals become virtually identical at times longer than 1 ns. More detailed study of the kinetic curves of the yield of CF_3I^+ and CF_3Br^+ ions is complicated, since there are both mixed clusters $(CF_3I)_n(CF_3Br)_m$ and homogeneous clusters $(CF_3I)_n$ and $(CF_3Br)_n$ in a cluster beam using a triple mixture of $CF_3I + CF_3Br + Ar$. Like mixed clusters, these homogeneous clusters will decay with the formation of neutral molecules that contribute to the signal from the CF_3I^+ and CF_3Br^+ ions during ionization. We may nevertheless conclude that the observed differences in the yield of at least CF_3I^+ ions are in two cases (if there are only homogeneous and mixed clusters in a beam) due to the exis-tence of mixed clusters and the effect their structures have on the formation of CF_3I^+ ions.

CONCLUSIONS

The results of experimental studies on the dissociation dynamics of mixed $(CF_3I)_n(CF_3Br)_m$ clusters, with electronic excitation of the molecules in a cluster using femtosecond UV radiation at wavelength of $\lambda = 266$ nm to the Rydberg states lying below the ionization threshold, show that relaxation of the energy stored by cluster molecules leads to the heating of clusters and the evaporation of molecules from them as a result of electron–vibrational conversion, as with homogeneous molecular clusters $(CF_3I)_n$. The molecules were detected by a time-of-flight photoionization mass spectrometer.

Analysis of the results indicates the initial excitation of electronic states in clustered molecules under the action of a UV pulse does not lead to instantaneous dissociation of mixed clusters on a time scale commensurate with the duration of the laser pulse. The vibrational excitation of molecules is transferred to intermolecular vibrations in the cluster on a 100 ps time domain. This is a slower process than electronic relaxation, but the cluster decays only after the energy has been transferred from intramolecular vibrations to intermolecular vibrations.

A mixed cluster's structure affects the process of its decay, which is most noticeable at times of 500–600 ps and is indicated in a faster yield of molecular ions from a mixed cluster than from homogeneous clusters.

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