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Ultrafast Dissociation Dynamics Induced in $[Fe(CO)_5]_nXe_m$ Mixed Clusters by Resonant Femtosecond Infrared Laser Radiation

Denis G. Poydashev,* Olesya S. Ablyasova, and Evgeny A. Ryabov

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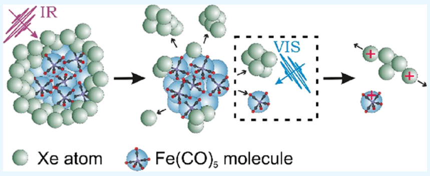

ABSTRACT: Real-time dissociation dynamics induced in $[Fe(CO)_5]_nXe_m$ mixed molecular clusters by femtosecond IR radiation in the 5 μm region was studied for the first time by means of time-resolved methods based on resonant excitation of $C\equiv O$ vibrations in the molecular core of the cluster and photoionization probing (λ = 400 nm) of its decay products. It was found that IR-excited clusters in the initially cold particle beam are heated and dissociated as a result of relaxation processes, giving rise to free neutral Xe aggregates and $Fe(CO)_5$ molecules. Thus, the formed particles are the origin of signal variations from Xe^+ and $Fe(CO)_5^+$ ions, which grow on a picosecond time scale. It is concluded that the initial laser excitation of $C\equiv O$ vibrations in clusterized molecules is followed by the process of cluster dissociation accompanied with the formation of free neutral particles according to the hierarchy of binding energies: weakly bound shells of Xe atoms are evaporated first and much faster than the $Fe(CO)_5$ molecules from the cluster core. The characteristic times of relaxation processes as well as the cluster temperature were estimated.

INTRODUCTION

The subject of this work is laser-induced dynamics in molecular clusters. A large number of studies have been devoted to the properties of these nanosized particles. Some data on the methods of producing clusters and their properties and applications can be found, for example, in monographs,[1] reviews,[2−4] and the literature cited therein.

The main objectives of studies performed in this work were to explore the excitation and subsequent fragmentation (dissociation) of mixed molecular clusters under the resonant action of IR radiation on vibrations of molecules in the cluster in their ground electronic state. These studies are closely related to the solution of a wider range of issues that are still rather poorly understood. In particular, the question of the degree of localization of the absorbed energy in "chromophore" molecules and the rate of its relaxation to internal degrees of freedom of the cluster—intracluster relaxation—are among them as well as the lifetime of an excited cluster (with respect to decay), the possibility of its significant overexcitation, and, finally, the statistical nature of fragmentation itself.

The binding energy in molecular clusters (with van der Waals or hydrogen types of binding) is comparatively low; usually, it does not exceed 0.5 eV.[1] Therefore, the absorption of even one IR quantum by a molecule, especially in the near-IR range, is often sufficient for the dissociation of clusters. At present, a considerable number of studies have been performed on the interaction of resonant IR radiation with molecular clusters, including the fragmentation of the latter. A summary of obtained results can be found in the review.[5] One of the first applications of IR photofragmentation of clusters was the use of this effect as one of the convenient tools for measuring IR absorption spectra in clusters (infrared photodepletion spectroscopy). Obtained in this way, photodissociation spectra were used in particular to obtain information on the intracluster dynamics, including the rates of cluster dissociation. For this purpose, the data on the width of the spectral lines were used as well as data on the shift of these spectra with respect to their position in free molecules.[6] Thus, comparatively simple systems based on dimers and trimers of HF (DF) and compounds of these molecules with noble gases were studied.[7,8] The obtained values of lifetimes with respect to dissociation for dimers lie in the range of 0.5−30 ns.[8] More complex systems were also studied—clusters based on polyatomic molecules, such as C_2H_4, CH_3OH, N_2H_4, and so on.[9] In the review,[9] obtained values of the lifetime τ were given, which lie in the range of 10^{-6}−10^{-12} s. It should be noted, however, that the interpretation of the results in this case is not unambiguous. This is related to the well-known problem of obtaining temporal information from spectral measurements when the nature of line broadening and/or the contribution of various mechanisms to the homogeneous component of this width is unknown. In the case of clusters of polyatomic molecules, a whole number of effects can

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contribute to the homogeneous width: (i) intramolecular relaxation (IVR) in an excited "chromophore" molecule, (ii) energy relaxation from the latter into intermolecular vibrations of a cluster, that is, "intracluster" IVR, and (iii) decay of the cluster itself. Therefore, the most reliable method for determining the dissociation rate of clusters is the direct measurement of the dissociation kinetics of the clusters themselves and/or the appearance of decay products—free particles.

One of possible methods for direct observation of the kinetics of cluster dissociation is the use of pulsed IR radiation sources for its excitation. In this regard, we can note works in which the IR dissociation of $(CF_3I)_n$ molecular clusters[10,11] and $(IF_2CCOF)_n$ molecular clusters[12] was studied. The dissociation was caused by resonant excitation of vibrations of the C−F bond (9.3 μm) in both molecules. Additionally, the IR dissociation of $(IF_2CCOF)_n$ clusters induced by excitation of the C═O bond (5.3 μm) in the IF_2CCOF molecule was also investigated. These vibrations were excited by radiation from a pulsed CO_2 laser and its second harmonic. The particles were detected by means of photoionization time-of-flight mass spectrometry, and the time resolution in these experiments was 10^{-8}[11] and 10^{-7} s.[12] The results of these experiments made it possible to conclude that all relaxation processes in the studied clusters, including their monomolecular decay, occur much faster than 10^{-8}−10^{-7} s. On this time scale, the process of IR dissociation is, in fact, a stationary or nearly stationary process of sequential evaporation of molecules.

Observation of the dynamics of intracluster processes, including non-stationary effects, became possible when IR pulses of picosecond and sub-picosecond durations were used to excite clusters. Here, we can point out to a work[13] in which the picosecond IR−UV pump−probe method was used to study the vibrational energy flow and decay of $(C_6H_5OH-C_2H_4)$ clusters. It was shown that, in these clusters, an intramolecular relaxation of the excited resonant mode (IVR-1) initially occurs then an intracluster redistribution of vibrational energy (IVR-2) takes place, which is accompanied by cluster dissociation. The latter dissociation proceeds with a characteristic time of 100 ps, and this time is virtually independent of the energy input channel. At the same time, the characteristic times of IVR-1 and IVR-2, which lie within no more than a few tens of picoseconds, turned out to be significantly dependent on the type of excited vibration.

In our work,[14] we studied the ultrafast dissociation dynamics of homogeneous $[Fe(CO)_5]_n$ clusters induced by IR resonant excitation of C≡O vibrational modes in the 5 μm range using a femtosecond time-resolved infrared pump−visible probe technique. Free $Fe(CO)_5$ molecules formed as a result of cluster dissociation were ionized by femtosecond laser radiation with $\lambda = 400$ nm and were detected using a time-of-flight mass spectrometer. The time dependence of the yield of free molecules was measured under different conditions of the IR laser excitation. An analysis of the results within the concept of "evaporative ensemble"[15] made it possible to obtain the profile of the temperature change of clusters in the process of their dissociation. It was found in particular that there is "overheating" of clusters with respect to the quasi-equilibrium "evaporation temperature". In this case, however, the subsequent dissociation of clusters can be well described by the mechanism of sequential evaporation of molecules. We also obtained estimates for the rates of intramolecular and intracluster vibrational relaxations in $[Fe(CO)_5]_n$ clusters; they lie in a 100 ps time domain.

Investigations of the IR fragmentation of molecular clusters showed that the intracluster dynamics and subsequent dissociation of clusters are considerably affected by their structure, including the external environment.[5] This, in particular, refers to mixed clusters of the form of $(M)_n(X)_m$, where M is a molecule and X is an atom of a noble gas. The above-said is clearly demonstrated by experiments[16] where the fragmentation of $(CF_3I)_n$ clusters of different types caused by the IR laser radiation of 150 ns pulse duration was studied. It was found that homogeneous $(CF_3I)_n$ clusters ($n = 45$ is the average number of molecules in the cluster) and $(CF_3I)_n$ clusters localized inside or on the surface of Xe_m clusters ($m = 100$ is the average number of xenon atoms in the cluster) have different stabilities with respect to fragmentation and different dependences of the fragmentation efficiency on the energy fluence of the IR radiation. The strongest dependence of the fragmentation probability on the energy fluence as well as the fragmentation at the lowest energy fluencies is observed for homogeneous $(CF_3I)_n$ clusters, the weaker dependence was observed for $(CF_3I)_n$ clusters localized inside Xe_m clusters, and the weakest dependence was obtained for $(CF_3I)_n$ clusters located on the surface of Xe_m clusters. Although no direct detection of the formation of free Xe atoms was performed,[16] it was concluded that the main reason for the higher stability (less efficient fragmentation) of $(CF_3I)_n$ clusters localized inside or on the surface of Xe_m clusters is the presence in the $(CF_3I)_n$ clusters of an efficient channel for the relaxation of the absorbed energy—the evaporation of xenon atoms.

In this work, we will present the results of studying the fragmentation dynamics of $[Fe(CO)_5]_nXe_m$ mixed clusters that were induced by resonant femtosecond IR laser radiation. The goal of these investigations is to study the specific features of intracluster processes and the mechanism of decay of this type of clusters (mixed ones) upon excitation of C≡O vibrations in $Fe(CO)_5$ molecules. Prior to proceeding to the presentation of the results obtained, let us briefly dwell on some particular features of the structure of small clusters, which will be required for the subsequent interpretation of the experimental results.

The structure of small clusters consisting of several tens or hundreds of particles has been of interest since the assumption by Mackay on the existence in nature of a packing of particles with a shell structure and icosahedral symmetry.[17] Considering the packing of equivalent spheres, the author concluded that the density of such a packing (in the limit of an infinite number of particles) is greater than that in the case of body-centered cubic packing but is smaller than those in the cases of cubic close-packed assembly or body-centered tetragonal packing. Subsequently, the sequence of the number of particles in each next shell in the case of an icosahedral symmetry, which was indicated in that work, is often referred to in the literature by the name of its author (so-called Mackay sequences).

With developing methods for obtaining clusters based on the outflow of a gas or a mixture from a nozzle, experimental data on the structure of clusters appeared. The structure of clusters of various types has been extensively studied by Farges and co-authors by an electron diffraction technique.[18−20] The subject of those investigations was not only clusters of noble gases[18−20] but also various molecules, such as H_2O,[21] N_2 and CH_4,[22] and SF_6.[23] Wide capabilities of the method used in the experiment, combined with mathematical modeling, made it possible to reconstruct the structure not only of small Ar_n clusters ($n \leq 50$) but also of argon clusters containing several hundred atoms. Small clusters had a poly-icosahedral structure,[19] and with an increase in the size of a cluster, it "overgrew" with additional atomic shells; up to $n \approx 750$, the atomic packing in the cluster had the shape of a multilayer icosahedron.[20] Comparison of clusters of noble gases, such as Ne, Kr, and Xe, with Ar clusters made it possible to conclude that these clusters exhibit the same structures as Ar clusters and the structural transitions occur for the same cluster sizes.[18]

If we turn to the structure of molecular clusters using the above water, nitrogen, methane, and sulfur hexafluoride molecules as an example, we can arrive at a general conclusion that, in the case of large clusters with the number of particles on the order of several thousands, their structure approaches that of a solid. With small clusters, the situation is more complicated: they may have signs of a poly-icosahedral structure (as in the case of N_2 and CH_4 molecules[22]), they may not have it at all as is the case with small $(SF_6)_n$ clusters,[23] or they may have an amorphous structure, like small water clusters.[21]

Numerous works were devoted to experimental studies of the structure of small clusters of metal carbonyls and their derivatives (containing several tens of atoms in the so-called "metal core" surrounded by various ligands) that were performed with the X-ray diffraction method[24] (lots of experimental data is conveniently summarized in the review[25]). The structure of such clusters may be different: they could have fragments of close packing just like crystalline bulk metals (face-centered cubic (fcc), hexagonal close packing (hcp), and body-centered cubic (bcc) packing) as well as mixed packing (fcc/hcp), local close packing with pentagonal symmetry, and strongly distorted amorphous packing. At the same time, there is evidence in the literature that metal clusters containing group 10 transition metals (Ni, Pd, and Pt) tend to form partial or complete icosahedral structures.[26] We are not aware of any experimental studies in which the structure of small $[Fe(CO)_5]_n$ clusters obtained in a molecular beam (with the number of molecules $n \approx 100$) was determined using either electron diffraction or X-ray diffraction methods. The structure of these clusters has also not been directly measured in experiments performed in this work. It is more important to us that there is the fundamental possibility of the existence of relatively small mixed $[Fe(CO)_5]_nXe_m$ clusters with values of n and m such that the structural forms considered above can be realized for them. Indeed, the average distance between Fe atoms in the cluster core is most likely close to $d(Fe{-}Fe) = 2.6$ Å (the value[27] for $Fe_3(CO)_{12}$). At the same time, this value for xenon clusters is noticeably larger: even in the limit of the low-temperature crystalline phase, the minimum bond length for Xe is r_{min} = 4.4 Å (the data for all noble gases were systematized, e.g., by Schwerdtfeger et al.[28]). Therefore, the problem of "matching" the molecular core of a mixed $[Fe(CO)_5]_nXe_m$ cluster with its atomic shell can be easily resolved in a way that is consistent with our results. The abovementioned molecular core/atomic shell structure of the mixed cluster will be justified in the Discussion section. We want to note here that, for identical numbers of particles in the outer layer of a molecular core and in the inner layer of the atomic shell of a mixed cluster, the atomic shell will completely surround the core (provided that the structures of the particle packing are considered to be identical).

■ EXPERIMENTAL SECTION

The experimental setup and experimental technique were largely similar to those described in our previous work.[14] Mixed $[Fe(CO)_5]_nXe_m$ clusters were obtained in the process of gas-dynamic cooling of a mixture of $Fe(CO)_5$ with xenon upon its outflow from a pulsed nozzle (General Valve; the aperture diameter was d = 0.8 mm, and the pulse duration was 300 μs). The total pressure above the nozzle was P_0 = 200 kPa with the proportion of the mixture being $Fe(CO)_5$/Xe = 1/300. The mixture was held at room temperature. A narrowly collimated cluster beam was formed using a skimmer (Beam dynamics, model 1; the orifice diameter was D_s = 0.49 mm), which was located at a distance of 55 mm from the nozzle edge. This particle beam was directed into the chamber of a linear time-of-flight mass spectrometer. At the point of intersection of the axis of the mass spectrometer with the cluster beam at a distance of 135 mm from the orifice of the skimmer, the particles under study were excited and probed by focused laser pulses. The nozzle valve was synchronized with the laser so that the particle beam interacted with the laser radiation in the middle of the pulse.

It is well known from the literature[29] that a rather deep dilution of molecules of the studied gas in the carrier gas (usually noble gases were used as the carrier) could lead to the formation of mixed clusters of the form $(M)_n(X)_m$, where M is molecules and X is carrier gas atoms. The ratio 1/300 was chosen due to the available information on the outflow from the nozzle used in the work[14] for the $Fe(CO)_5$/Ar = 1/50 mixture; such a dilution at the same total pressure and temperature of the mixture did not cause the formation of mixed clusters. Homogeneous $[Fe(CO)_5]_n$ clusters with an average size of $n \approx 300$ particles and a temperature of T = 100 K at the probing point were formed.[14] The presence of $[Fe(CO)_5]_nXe_m$ mixed clusters in the investigated beam under the specified outflow conditions was confirmed by the measured mass spectra (see below). Generally, it could be a challenge to produce mixed clusters using the gas mixture under the nozzle. In the case of $Fe(CO)_5$ molecules and our nozzle source, there are almost no signs of mixed clusters at a dilution of 1/100, and pure Xe_m clusters prevail in the beam at a dilution of 1/500.

To excite and probe clusters, we used radiation from a commercial Ti:sapphire laser system (Spectra-Physics, 1 kHz, 800 nm, 45 fs) of which the output was split into two channels. One of them was used to pump an optical parametric amplifier (Light Conversion TOPAS-C). The produced signal and idler pulses were subsequently guided to a non-collinear difference frequency generator (Light Conversion nDFG) to generate tunable broadband ultrafast IR pulses using a thin $AgGaS_2$ crystal. Generated IR pulses were centered at 2000 cm^{-1} with a pulse energy of up to 25 μJ and were used as pump pulses to excite C≡O stretching modes in the $Fe(CO)_5$ molecule. We used a KCl lens with a focal length of f_{IR} = 13.5 cm to focus the IR radiation into the vacuum chamber. The energy fluence φ_{IR} of these pulses was estimated to be not higher than 35 mJ/cm^2 inside the chamber. Pulses with a spectral FWHM of 150 cm^{-1} and duration of approximately 160 fs (intensity was ~2 × 10^{11} W/cm^2) were used in our experiments being controlled by a monochromator with a 2 cm^{-1} bandpass. The second channel of the master laser was used to generate a second harmonic of the fundamental output of the laser with a BBO crystal. Visible pulses at λ = 400 nm (with a typical pulse duration of 100 fs) were focused by a CaF_2 lens with $f_{VIS} = 30$ cm (the intensity was up to 5×10^{12} W/cm^2) and used as a probe for the multiphoton ionization of particles under study. The probe pulses propagated at an angle of approximately 2° with respect to the direction of the pump IR pulses and can be delayed with a 30 cm translation stage. The spatial positions of the focal spots of IR pump pulses and visible probe pulses were controlled by a Pyrocam III pyroelectric camera to ensure the necessary precise overlapping between them.

■ MEASUREMENTS AND RESULTS

Mass Spectra. Intracluster dynamics induced in $[Fe(CO)_5]_nXe_m$ mixed clusters as a result of excitation by femtosecond IR radiation in the range of 5 μm eventually leads to the formation of both free neutral xenon clusters/atoms and iron pentacarbonyl molecules upon a sufficiently high absorbed energy of the exciting radiation. These particles were detected by means of a time-of-flight mass spectrometer upon their multiphoton ionization by probing femtosecond laser pulses at a wavelength of $\lambda = 400$ nm. Free $Fe(CO)_5$ molecules in the ground electronic state could be ionized by the femtosecond radiation at the wavelength used in our experiment beginning from the laser radiation energy fluence values of $\varphi_{VIS} \geq 0.1$ J/cm^2 ($I_{VIS} \geq 10^{12}$ W/cm^2). To detect xenon clusters/atoms upon their multiphoton ionization, a greater number of radiation quanta is required than in the case of $Fe(CO)_5$ molecules due to the difference in the value of the ionization potential. In the experiment, a radiation energy fluence $\varphi_{VIS} \approx 0.4$ J/cm^2 ($I_{VIS} \approx 4 \times 10^{12}$ W/cm^2) was used at which the detection of Xe^+ ions by ionization of Xe atoms in the gas phase was possible.

A typical mass spectrum of ionization of clusters and their decay products is shown in Figure 1a for the mass range 50–1350 amu in the presence of an IR pump pulse ($\varphi_{IR} = 35$ mJ/cm^2) with a delay between the laser pulses of $\Delta\tau = 300$ ps. Without an IR pump pulse, a signal from Xe^+ and $Fe(CO)_5^+$ ions (marked in Figure 1a along with Xe_m^+ ion peaks) is noticeably smaller as there is no contribution to this signal from the mixed cluster dissociation products. As can be seen from Figure 1a, the particle beam indeed contains clusters, which are a source of signal from ions whose masses exceed the mass of the $Fe(CO)_5$ monomer (196 a.m.u.). Lots of peaks in the mass spectrum are a result of extensive fragmentation of clusters upon their multiphoton ionization by femtosecond laser pulses. It is a rather general phenomenon (so-called dissociative ionization), and it was observed for clusters of different types and compositions.[5]

The mass spectrum shown in Figure 1a contains peaks from different sources. One can designate peaks from the $[Fe(CO)_5]_n$ molecular core of mixed clusters, and those peaks have a structure of $Fe_x(CO)_y$, just like in the case of ionization of homogeneous $[Fe(CO)_5]_n$ clusters.[14] Another group of peaks in the mass- spectrum are Xe_m^+ ions. They could be formed from mixed clusters as well as from pure Xe clusters. Xe_{7-10}^+ ions are marked in Figure 1a as they could be relatively easily distinguished among others. Xe^+ and Xe_2^+ ion peaks are shown in Figure 1b,c, and the signal from Xe_{3-6}^+ ions was detected as well, but these peaks are significantly overlapped with $Fe_x(CO)_y^+$ ions mentioned above. The nature of the peak broadening in the case of heavy Xe cluster ions is mostly the isotopic structure of Xe. We should note that detected Xe_m^+ ions do not represent a "tail" of a real Xe_m cluster size distribution not only due to limitations of the instrument but also because of abovementioned dissociative ionization, which may cause extensive fragmentation. In the case of pure Xe expansion from our cluster source, Hagena scaling rules[30] will predict an average cluster size of approximately 500 to 1000 Xe atoms per cluster. As for m and n values of the $[Fe(CO)_5]_nXe_m$ mixed cluster, we expect a cluster size distribution with m and n values in the order of 100.

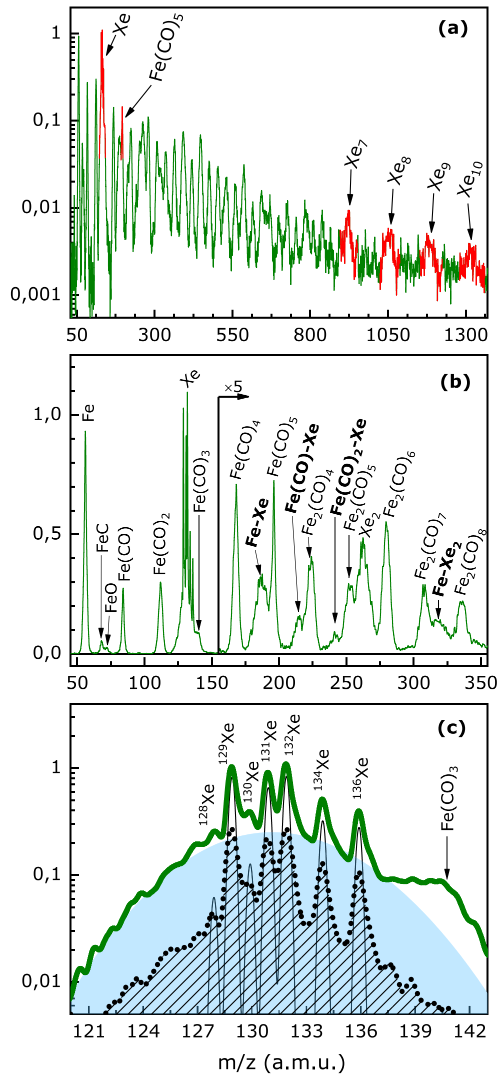

Figure 1. (a) Entire mass spectrum of ions formed upon ionization of clusters and their decay products in the particle beam. The delay between the pump and probe pulses was $\Delta\tau = 300$ ps. (b) Fragment of the mass spectrum with marked ions from $[Fe(CO)_5]_nXe_m$ mixed clusters. (c) Region of the spectrum of xenon ions formed via two channels: (i) ionization of the carrier gas (narrow peaks; seven main xenon isotopes were taken into account, and the ratio of their amplitudes corresponds to the natural isotopic ratio) and (ii) ionization of xenon produced from mixed clusters (wide base highlighted with a light-blue color). The curve in bold is the total ion current from mixed clusters. Dots are the signal from homogeneous Xe clusters (not to scale): a wide base band and narrow peaks are detected as well, plotted for convenience.

Although there are several mechanisms that could change the ionization rate for Xe clusters (compared to Xe monomers), including the ionization potential shift[31] or other phenomena related to excitonic bands in Xe clusters,[32,33] we will not discuss the details of the interaction of Xe clusters with ionizing femtosecond laser radiation ($\lambda = 400$ nm) as it does not affect the process of IR laser excitation and subsequent relaxation processes. The presence of pure Xe_m clusters in the beam and their possible interaction with other particles formed as a result of the mixed cluster dissociation will be discussed in the next section.

The presence of $[Fe(CO)_5]_nXe_m$ mixed clusters in the beam leads to the formation and detection of fragment ions of the form of $Fe-Xe^+$, $Fe(CO)-Xe^+$, $Fe(CO)_2-Xe^+$, and $Fe-Xe_2^+$ (see Figure 1b), which contain both atoms that enter into the composition of the iron pentacarbonyl molecule and xenon atoms. These ions are present in the mass- spectrum regardless of the presence of IR pump pulses. It should be noted that the process of gas-dynamic cooling of a mixture at the outflow from the nozzle does not rule out the simultaneous formation of homogeneous $[Fe(CO)_5]_n$ and Xe_m clusters along with $[Fe(CO)_5]_nXe_m$ mixed clusters. However, pure Xe_m clusters does not affect the dissociation of $[Fe(CO)_5]_nXe_m$ mixed clusters since they do not interact with IR laser radiation. Concerning the occurrence of homogeneous $[Fe(CO)_5]_n$ clusters in the beam, a considerable number of them in the beam seems to us unlikely due to a rather deep cooling required to form the mixed clusters. The majority of the $Fe(CO)_5$ molecules that were clustered on the axis of the cluster beam, preferably undergo further collisional cooling with Xe atoms and form the mixed cluster. Therefore, we will attribute the kinetics of the yield of $Fe(CO)_5^+$ molecular ions to the decay of mixed clusters.

An IR pump pulse of several hundred picoseconds prior to the visible probe pulse manifests itself in the mass spectrum by the appearance of peaks corresponding to free molecules (primarily, the parent $Fe(CO)_5^+$ ion) and by a change in the amplitude of the peaks corresponding to Xe_m^+ ions. In subsequent experiments, the dissociation kinetics of $[Fe(CO)_5]_nXe_m$ clusters was studied by means of two types of peaks—$Fe(CO)_5^+$ and Xe^+. We note that the mass spectra in Figure 1a that was obtained upon multiphoton ionization depends on the wavelength of the ionizing radiation, the energy in the laser pulse, and the pulse duration. In particular, upon multiphoton ionization of free $Fe(CO)_5$ molecules by femtosecond laser pulses, the mass spectrum may contain ionic fragments $Fe(CO)_x^+$, $x = 0-5$, which were also observed[34] as the ultrafast photodissociation dynamics of $Fe(CO)_5$ in the gas phase by femtosecond laser pulses at $\lambda = 400$ nm was studied. Unlike for the ionization of $Fe(CO)_5$ molecules by nanosecond pulses of which the ionic products contain only Fe^+ ions, the mass spectra in Figure 1 have a peak of the $Fe(CO)_5^+$ molecular ion, which ensures the possibility of a rather easy detection of free molecules in the particle beam as these ions are expected to be formed during the mixed cluster dissociation process (similar to the case of the pure $[Fe(CO)_5]_n$ cluster dissociation process).

A characteristic feature of the operation with xenon as a carrier gas is a signal from non-clustered Xe atoms as well as from pure Xe clusters that are present in the particle beam. The signal from non-clustered atoms appears as a set of relatively narrow peaks near 130 amu, which correspond to xenon isotopes (see Figure 1c). A background signal from pure Xe clusters is also a set of Xe_m^+ ions (with detected m values from 1 to 10). These peaks are significantly broadened by overlapping due to the isotopic structure and high translational kinetic energy of ions (in contrast to Xe^+ ions formed from carrier gas atoms). Figure 1c demonstrates the difference between narrow and wide Xe^+ peaks. Upon using a linear-type mass spectrometer under certain conditions (the type of a transition that precedes the dissociation and possible anisotropy in the angular distribution of the direction of velocity of ionic products), one can find out a relation between the shape and/or the width of the peak and the kinetic energy of particles that escape from the ionization region as a result of a particular decay event.[35,36] With the assumption of isotropic decay, the highest kinetic energy values of approximately 17 eV (corresponds to the value of 5 μm/ns of most probable velocity of Xe^+ ion in the Maxwellian distribution over absolute velocity values) among all detected Xe_m^+ ions refer to Xe^+ ions (m = 1). We made a special experiment on the ionization of pure Xe clusters produced with our nozzle at a stagnation pressure of 200 kPa. A similar set of Xe_m^+ peaks (with m in the range from 1 to 10) was detected. The signal from Xe^+ ions in this case is designated by the dotted line in Figure 1c (hatched area). As could be seen from Figure 1c, dissociative ionization of large homogeneous Xe clusters produces Xe^+ ions, which also have a broad peak in the mass spectrum.

In the presence of an IR pump pulse, Xe^+ ions that are formed as a result of the decay of the mixed cluster and ionization of its decay products also act as a source of the signal near 130 amu. Obviously, not all of these ions formed with high translational energy (assuming an isotropic spatial distribution) could be detected due to the finite size of the detector: only ions with velocities directed toward the detector (and to the opposite side) will be detected regardless of their energies. The radial component, v_r, of the detected ion's velocity (perpendicular to the direction toward the detector) is limited by the value of $v_r^{max} = R_{det}/ToF$ where R_{det} is the radius of the detector and ToF is the ion's time of flight. For the Xe^+ ions in our experiment, $v_r^{max} = 0.75$ μm/ns. It should be noted here that the shape of the peak in the mass spectrum will not be distorted by the fact that not all of the ions reach the detector due to the high translational energy. In the case of the isotropic spatial distribution, the signal will only be attenuated by a factor of $\alpha = 1 - \exp(-(v_r^{max})^2/v_0^2)$, where v_0 is the most probable velocity of the ion. There were no kinetic energy filters used in the apparatus: the maximum measurable value of the Xe^+ ion velocity is limited by the instrument sensitivity.

2. Kinetics of the Ion Yield. Information on the magnitude of signals corresponding only to products formed as a result of the cluster decay was obtained from mass spectra recorded at different values of the delay time between the IR pump pulse and the probe pulse at a wavelength of 400 nm. Experimental kinetic curves of the yield of Xe^+ and $Fe(CO)_5^+$ ions from $[Fe(CO)_5]_nXe_m$ mixed clusters are shown by circles in Figure 2a. Figure 2b shows a change in the value of most probable velocity v_0 of the Xe^+ ions during the course of the mixed cluster dissociation process. The highest values of $v_0 = 5$ μm/ns (most probable velocity of the Xe^+ ion) were measured at approximately 50 ps pump−probe delay times; the corresponding kinetic energy was approximately 17 eV.

To extract the kinetic curve of the yield of xenon ions only from a mixed cluster, first of all, the background signals from non-clustered Xe atoms and pure Xe clusters were separated from the signal produced by xenon ions that are formed from mixed clusters as a result of their IR-induced dissociation. The abovementioned background signals were subtracted from the total ion signal as these signals were found to remain one and the same during the whole process of the dissociation of mixed clusters. The magnitude of the signal from xenon ions that are

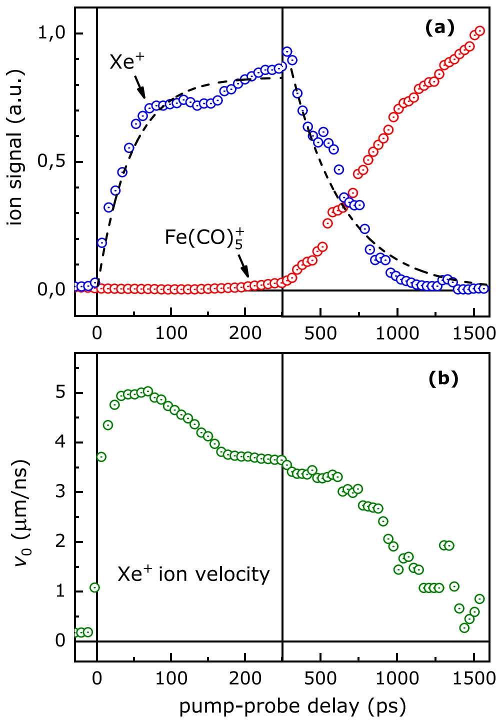

Figure 2. (a) Normalized kinetic curves for the formation of Xe^+ and $Fe(CO)_5{}^+$ ions as a result of the IR induced decay of $[Fe(CO)_5]_nXe_m$ mixed clusters (φ_{IR} = 35 mJ/cm^2). The dotted curve in the left side shows a single-exponential growth with a 45 ± 2.5 ps time constant, and in the right side, a 350 ± 8.5 ps exponential decay. (b) Time dependence of the most probable velocity v_0 of the Xe^+ ion obtained from the width of the ion's peaks. Note a different x-axis scale to the left and right from the vertical line.

formed from mixed clusters, therefore, will be a part of the area that is highlighted with blue color in Figure 1c.

For the signal from $Fe(CO)_5$ molecules, there is no such problem since without an IR pump pulse, $Fe(CO)_5{}^+$ ions are practically absent in the mass spectrum, and the background signal could be easily taken into account (so-called pump-off routine). In addition, in contrast to Xe ions, molecules that escape from the cluster do not have such a significant kinetic energy: $Fe(CO)_5{}^+$ peaks in the mass spectra are relatively narrow.

Apart from the background subtraction procedure, we have to take into account the abovementioned high translation energy of detected Xe^+ ions. At low pump−probe delay values, we observe Xe^+ ions formed with several-times higher velocities compared to ones formed at pump−probe delay times of ≥1 ns. This fact means that there is a significant loss of ions at the lowest pump−probe delay times ($\alpha(v_0 = 5\ \mu m/ns) \approx 0.022$). The other case is the delay times of higher than 1 ns at which we collect almost all Xe^+ ions. The magnitude of the signal on the kinetic curve for Xe^+ ions in Figure 2a was corrected to represent a change in the real number density of Xe^+ ions formed as a result of the mixed cluster dissociation process using the velocity values taken from Figure 2b. As a result, each point on the Xe^+ kinetic curve in Figure 2a was normalized with the values of α, which were calculated using the values of v_0 from the kinetic curve in Figure 2b.

Concerning the kinetics of the yield of molecular ions in Figure 2a, on the whole, it looks similar to the case of the IR-induced dissociation of homogeneous $[Fe(CO)_5]_n$ clusters.[14] In contrast to Xe^+ ions, the signal from molecules remains close to zero up to approximately 250 ps and then increases. A trend to saturation is weaker compared to the case of pure molecular clusters, but it could be still observed in the experiment.

■ DISCUSSION

Structure of Mixed Clusters. One can immediately note the difference in the rates of formation of particles that compose a mixed cluster upon its decay from Figure 2a: initially, Xe^+ ions appear, and then $Fe(CO)_5{}^+$ molecular ions do. This result can be easily predicted if we take into account the differences in the binding energy between particles in the mixed cluster and its structure. We upgraded the modeling procedure introduced in our previous work[14] and took into account a more essential, wide log-normal cluster size distribution (with FWHM ≈ N, where N is an average cluster size) instead of operating with only a certain cluster of an average size N. As a result, we have obtained slightly corrected values of the binding energy between neighboring $Fe(CO)_5$ molecules in the pure $[Fe(CO)_5]_n$ clusters: according to our latest estimates, ε_{mol} for large clusters is close to ε_{mol} = 0.3 eV. Similar values of the intermolecular binding energy are expected in the core of the $[Fe(CO)_5]_nXe_m$ mixed cluster. However, in the Xe_2 dimer, the binding energy is noticeably lower—ε_d = 0.0244 eV.[37] This fact affects the structure of the mixed cluster: in the process of its formation upon gas-dynamic cooling of a mixture of iron pentacarbonyl with xenon, small $[Fe(CO)_5]_n$ clusters are initially formed, which, upon further cooling, overgrow with a "coat" consisting of relatively weakly bound Xe atoms. Essentially, the average binding energy of Xe atoms in the mixed cluster is higher than the dimer value: it is close to the value for pure Xe cluster of a comparable number of atoms. Taking after the work of Farges and co-authors,[18] we estimate the binding energy of atoms and the temperature of pure Xe clusters formed from our nozzle source during expansion of the pure Xe gas at a stagnation pressure of 200 kPa to be approximately ε_{at} = 0.2 eV and 80 K, respectively. In the case of the expansion of the Xe + $Fe(CO)_5$ mixture, the temperature of the mixed cluster in the beam will probably be slightly higher, but the balance between the binding energy for Xe atoms consisting the "coat" of the mixed cluster and its temperature should satisfy the expression for the cluster dissociation rate in the evaporative model.[15] Indeed, clusters should exist in the particle beam at least a period of the time required to transfer them from the nozzle source to the probing region (∼1 μs in our experiment). In order to obtain an estimate of the initial mixed cluster temperature T_0, one could assume an equilibrium with pure Xe clusters of several hundreds of atoms, which are presented in the cluster beam along with $[Fe(CO)_5]_nXe_m$ mixed clusters.

Origin of the Xe^+ Ion Yield. Dissociative ionization of xenon clusters by femtosecond laser pulses, as was shown above, leads to the formation of $Xe_m{}^+$ fragment ions, and some of which (up to m = 10) are detected in our experiment. Small xenon aggregates could also be formed as a result of the IR-induced dissociation of mixed clusters and, in turn, during the dissociative ionization by probe laser pulses, act as sources of a signal from $Xe_{1-10}{}^+$ ions. The kinetics of signal changes from $Xe_{7-10}{}^+$ ions is shown in Figure 3. Unfortunately, it turned out to be extremely difficult to extract the kinetic curves for $Xe_{2-5}{}^+$ ions due to the significant overlap of peaks in the mass spectrum with peaks from $Fe_x(CO)_y{}^+$ ions. As can be seen

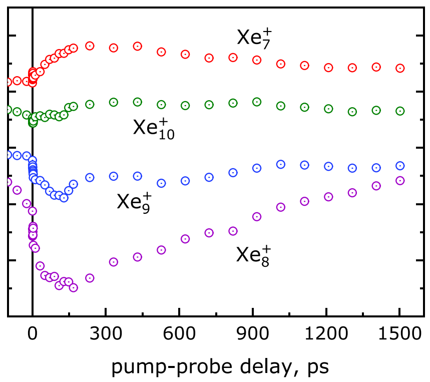

Figure 3. Kinetics of the yield of Xe_m^+ ions for $m = 7-10$ (not to scale; see text for details).

from Figure 3, two scenarios take place: the signal changes in a way that is similar to the signal from Xe^+ ions (Xe_7^+ and Xe_{10}^+ ions) and the signal changes in the opposite way (Xe_8^+ and Xe_9^+). We could note that all signals shown in Figure 3 have a turning point near the pump−probe delay values of 250 ps just like in the case of the Xe^+ ion signal. Taking into account this circumstance and due to the fact that large xenon clusters do not interact with the IR pump radiation, the change in the signals on the kinetic curves in Figure 3 is associated with the decay of mixed clusters. Several reaction channels could give a contribution to these ion signals as detected Xe_m^+ ions could be formed directly upon ionization of neutral dissociation products of the mixed cluster or through dissociative ionization of this products. It is more important to us that the changes in Xe_m^+ ion yields indicate the possibility of a formation of small neutral Xe_m aggregates from mixed clusters as a result of their IR-induced dissociation.

Among the signals from Xe_{1-10}^+ ions, we pick the Xe^+ ion signal because it is the final ionic product upon the dissociative ionization process. The fact is that we observe ion signals in the mass spectrum at times on the order of 10^{-6}–10^{-5} s (typical time-of-flight values). Based on the data from the literature,[38] at these times, the final spectrum of ionic and neutral products is formed from clusters and/or their decay products upon their dissociative ionization. In this case, the ratio between Xe_{1-10}^+ ions will depend on possibly the time-dependent size of neutral clusters/aggregates, which were a source of these ions. As small clusters are less stable, the dynamics of changes in the size of small xenon clusters formed as a result of the decay of mixed clusters could be apparently responsible for what is experimentally observed in Figure 3 of kinetic curves from Xe_m^+ cluster ions.

Precisely, the similarity in the kinetic energy values of Xe^+ ions formed from the mixed cluster that determined the most probable source of their formation is a relatively small xenon aggregate that escaped from the surface of the mixed cluster. In principle, there is no way to form lots of neutral Xe atoms with multi-electron-volt kinetic energy from mixed clusters by IR pump pulse only. Indeed, if we assume that the mixed cluster has, for example, 100 molecules in the core, an estimate for the absorbed energy gives us[14] a value of less than one absorbed IR quantum per molecule. It means that we only deliver less than 25 eV to the whole cluster. Consequently, we could expect five Xe atoms with 5 eV of kinetic energy per cluster. Hardly, we are able to detect such a low number of atoms, and, more importantly, hardly do we form clusters of several dozens of molecules with only five Xe atoms on the surface of them. We believe that the appearance of ions with multi-electron-volt kinetic energy during the ionization of xenon clusters is associated with the ionization of several atoms in the cluster and subsequent decay. In this case, apart from the transition to a state above the ionization threshold with a different configuration of interatomic distances, the cluster will receive an additional coulombic energy. An estimate of this energy can be obtained from the relation $U_c = 14.4 \cdot q_1 \cdot q_2 / r$ (U_c [eV], r [Å], q [e-charge numbers]). In the simplest case, for two singly ionized atoms located at a distance of, for example, 5 Å in a cluster, the coulombic energy is $14.4/5 = 2.88$ eV ($q_1 = q_2 = 1$). This energy will turn into the heat capacity of interatomic vibrations (if there is a corresponding "bath") and into the kinetic energy of particles emitted during the decay. At first glance, this is a small value, but if there are not two, but three charges, then, if we assume that the Xe^+ ions in the cluster are located at the vertices of an equilateral triangle with a side of 5 Å, the coulombic energy will be three times greater than in the case of two atoms. These estimates do not take into account the polarization of clustered particles. However, there is evidence in the literature that, as a result of such "multiple" ionizations, a part of the coulombic energy is spent for a relatively fast decay: 3−300 ps for clusters of different sizes with charge separation between two fragments (Ar_n^{++} was studied by Goldberg et al.[39]). Then, on a time scale of 10^{-6}–10^{-5} s, cluster ions (single-charged) undergo unimolecular fragmentation via the loss of small numbers of atoms or molecules.[38] In this case, the smaller the cluster, the more probable its fragmentation upon simultaneous ionization of several atoms: the cluster decays when the excess coulombic energy becomes comparable to the total binding energy of the particles in it.

Proposed Mechanism for IR-Induced Dissociation of Mixed Clusters. The proposed scheme for the decay of mixed clusters is shown in Figure 4. The initial excitation localized in the high-frequency vibrational modes of C≡O bonds in the $Fe(CO)_5$ molecules in the core of the mixed cluster is redistributed over time as a result of relaxation processes between the low-frequency vibrational modes in the molecules in the core and into the baths of intermolecular and interatomic vibrations of the mixed cluster. In this case, the experiment convincingly shows that the outer shells of the mixed cluster, consisting of xenon atoms, escape from its surface with a characteristic time of approximately 45 ps (see the dashed curve in Figure 2a). This is much faster than the characteristic times of relaxation processes in homogeneous $[Fe(CO)_5]_n$ clusters, which amounted to 280 ps,[14] and faster than the characteristic time of energy redistribution from excited CO vibrations in the iron pentacarbonyl molecule in the liquid phase in the solvent, which equals to 150 ps.[40] Thus, part of the energy stored in CO vibrations of molecules in the

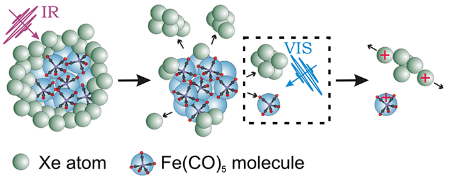

Figure 4. Proposed mechanism for IR-induced dissociation of mixed clusters and subsequent ionization of dissociated products.

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core of the mixed cluster is transferred to its shells in parallel with the process of populating low-frequency vibrations in "chromophore" molecules.

Taking into account the "shell" structure of the mixed cluster and weaker bonds between xenon atoms compared to iron pentacarbonyl molecules, it is quite natural to expect a faster decay of xenon shells. However, the experiment showed that a characteristic feature of the dissociation of the studied mixed clusters is the escape of small xenon aggregates from the surface of the mixed cluster, rather than the single-particle decay as in the case of homogeneous iron pentacarbonyl clusters. Moreover, Xe shells are dissociated from the surface of the mixed cluster completely within the first 250 ps before thermalization of initial excitation. At the same time, the character of the decay of the mixed cluster core corresponds to the case of unimolecular decay. A two-stage energy relaxation takes place: initially energy is redistributed from high-frequency vibrations of the molecule to low-frequency modes and then to intermolecular vibrations of the core of the mixed cluster. Relaxation processes are accompanied by an increase in the quasi-equilibrium temperature of the cluster core, and after which, it decomposes with the formation of free neutral molecules.[14]

It is worth noting here that the ionization of clustered molecules in the core of a mixed cluster, even taking into account possible shifts, requires fewer radiation quanta than for the ionization of xenon clusters due to the lower ionization potential of an iron pentacarbonyl molecule compared to a xenon cluster. Nevertheless, in the experiment, we did not observe the formation of a significant amount of $Fe(CO)_5^+$ ions with high kinetic energy by the same mechanism of dissociative ionization, which, apparently, takes place for xenon clusters. The main reason is the mechanism of dissociation of the mixed cluster core. In contrast to Xe shells, the molecular core is dissociated with the formation of slow, neutral $Fe(CO)_5$ monomers. These monomers are then singly ionized without any additional coulombic potential energy.

Upon dissociation of the mixed clusters, due to the indirect formation of Xe^+ ions, to estimate the fraction of absorbed energy that was redistributed into xenon shells, the quantitative sizes of small xenon clusters that escaped from the surface of the mixed cluster and the absolute probabilities of the formation of Xe^+ ions from them during dissociative ionization are required. It is impossible to obtain these data directly from our experiment; additional measurements are required to determine the quantitative characteristics. Turning to the values of the rates of relaxation processes in the mixed cluster, experiment shows that, as in the case of a homogeneous cluster, they lie in the ~100 ps range. The yield of molecules in Figure 2a could be easily modeled using a two-stage relaxation scheme proposed for homogeneous clusters[14] with relaxation rates of approximately 150 ps. However, to obtain quantitative values for the number of molecules in the mixed cluster core and the number of evaporated molecules, an abovementioned unknown fraction of the absorbed energy is required. Nevertheless, we could note a tendency toward a slightly faster escape of molecules from a mixed cluster compared to a homogeneous one, which point to faster relaxation times. As faster relaxation is characteristic of a condensed medium, the mixed clusters in the present experiment are probably colder than 100 K and therefore "more solid" compared to homogeneous ones.

Drop of the Xe^+ Ion Signal. Let us now discuss another important feature of the yield kinetics of xenon ions: its non-monotonic character compared to the kinetics of the yield of $Fe(CO)_5^+$ molecular ions: a relatively rapid growth up to the delay between the laser pulses of approximately $\Delta\tau = 250$ ps is followed by a signal decrease to almost zero at a delay of $\Delta\tau = 1500$ ps with a characteristic time constant of about 350 ps. Relaxation processes ultimately lead to the formation of neutral particles (Xe clusters and $Fe(CO)_5$ molecules) from the mixed cluster, but these processes do not describe a decrease in the signal in the yield kinetics of Xe^+ ions observed in the experiment (see Figure 2a). As was mentioned above, Xe^+ ions are formed as a result of dissociative ionization of small Xe clusters evaporated from the surface of mixed cluster. We could designate two possible causes of the Xe^+ signal decrease. First one is a process of charge exchange between the formed Xe^+ ion and a large neutral pure Xe cluster formed from the nozzle in the particle beam. A similar process of Xe^+ ions captured by neutral argon or neon clusters was described in the literature theoretically[41] and is demonstrated in the experiment[42] where thermal Xe^+ ions at a temperature of 550 K collide with neutral Ar clusters in the molecular beam produced by expansion of the pure Ar gas through a cooled (110 K) nozzle at a stagnation pressure of 1.5 bar.

The second process that could lead to a decrease in the Xe^+ ion signal is associated with the neutral source of the ion signal. The small Xe_n aggregate, which was evaporated in a possibly vibrationally excited state, could undergo dissociation to Xe_{n-m} and m Xe atoms. Efficiency of Xe^+ ion formation could strongly depend on the size of the neutral Xe aggregate, which produces them during the course of dissociative ionization. We could also assume that small neutral Xe aggregates formed from mixed clusters are completely dissociated due to the above-mentioned cooling process. In this case, the measured time constant of 350 ps shows the rate of this process.

Our experiment shows that the Xe^+ ion signal decrease is accompanied by the decrease in kinetic energy of these ions (see Figure 2b). The first process of charge exchange mentioned above should not be responsible for changes in the kinetic energy of detected ions. Dissipative inelastic scattering of Xe^+ ions due to collisions with other neutral or ionized particles does not look like the most probable mechanism too. More preferably Xe^+ ions are initially formed with a lower kinetic energy at high pump-probe delay values compared to early stages of the mixed cluster dissociation process. The process of dissociative cooling of the source of Xe^+ ions is consistent with the decrease in kinetic energy as the value of this energy is at least limited by the number of atoms in the parent Xe aggregate.

Summarizing all the observations, we concluded that the studied dissociation dynamics of $[Fe(CO)_5]_nXe_m$ mixed clusters induced by ultrafast IR pulses showed that the mechanism of the decay process is fast (compared to relaxation rates in the $Fe(CO)_5$ molecules that absorb IR quanta) evaporation of weakly bound shells of Xe atoms located on the mixed cluster's surface at first, and then $Fe(CO)_5$ molecules form the core of the cluster. The dissociation rate is limited by relaxation processes in the "chromophore" molecules (on a time scale of 100 ps) that proceed after the IR excitation on the one hand, but on the other hand, shells of Xe atoms are evaporated before the energy relaxation is completed (with characteristic time constant of about 45 ps) in the form of small Xe aggregates.

CONCLUSIONS

Dissociation dynamics induced in $[Fe(CO)_5]_nXe_m$ mixed clusters in a molecular beam upon resonant excitation of molecules that form the core of the cluster by femtosecond IR radiation in the range of 5 μm was studied for the first time. It is concluded that relaxation of the initial excitation localized in C≡O vibrations of $Fe(CO)_5$ molecules leads to the formation of (i) neutral, small Xe aggregates from the atomic shells of the mixed cluster with a characteristic time constant of 45 ps and (ii) neutral $Fe(CO)_5$ molecules from the mixed cluster's core on a time scale of 100 ps as a result of the energy redistribution to low-frequency vibrational modes of the molecule and a bath of intermolecular vibrations in the core of the mixed cluster. During the process of the cluster dissociation, relatively weakly bound shells of Xe atoms are completely evaporated within 250 ps. The core of the cluster that consists of $Fe(CO)_5$ molecules begins to decay only when the cluster core temperature rises as a result of relaxation processes.

In order to analyze and interpret the experimentally observed kinetic curves of the yield of detected mixed cluster decay products—Xe^+ and $Fe(CO)_5{}^+$ ions—we proposed a phenomenological mechanism, which took into account the structure of the mixed cluster and the hierarchy of binding energies between particles of different sorts in the $[Fe(CO)_5]_nXe_m$ mixed cluster. The sources of Xe^+ ions are small neutral Xe aggregates evaporated from the surface of the mixed cluster: these ions are formed with high translational energy similar to the case of dissociative ionization of pure Xe clusters by femtosecond laser pulses at a wavelength of $\lambda = 400$ nm. $Fe(CO)_5{}^+$ molecular ions are formed by ionization of free neutral molecules evaporated from the core of the mixed cluster. The process of dissociation of the mixed cluster's core most likely is a unimolecular decay similar to the case of dissociation of the homogeneous $[Fe(CO)_5]_n$ cluster.

High translational energy of Xe^+ ions observed in the experiment is a result of a dissociative ionization process: an excess energy source is a coulombic interaction between several singly ionized particles in the cluster. It is the property of Xe^+ ions that reveal the mechanism of the Xe shell dissociation process. At the same time, the experimental data available are insufficient to make numerical estimates on the size of the mixed cluster's molecular core and its atomic shells. We could not make an unambiguous conclusion about the structure of the mixed cluster too. More studies similar to that as the structure of noble gas clusters was revealed based, for example, on the electron diffraction method are required to reveal the structure of mixed molecular clusters as well as the structure of neutral products formed during the course of the dissociation process.

AUTHOR INFORMATION

Corresponding Author

Denis G. Poydashev − *Institute of Spectroscopy, Russian Academy of Sciences, Moscow 108840, Russia;* orcid.org/0000-0001-7026-3963; Email: poydashev@isan.troitsk.ru

Authors

Olesya S. Ablyasova − *Institute of Spectroscopy, Russian Academy of Sciences, Moscow 108840, Russia;* Present Address: Present address: Abteilung Hochempfindliche Röntgenspektroskopie, Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Strasse 15, 12489 Berlin, Germany; Physikalisches Institut, Albert-Ludwigs-Universität Freiburg, Hermann-Herder-Strasse 3, 79104 Freiburg, Germany

Evgeny A. Ryabov − *Institute of Spectroscopy, Russian Academy of Sciences, Moscow 108840, Russia*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c04367

Notes

The authors declare no competing financial interest.

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