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Energy transfer in heteronuclear rare gas clusters under multiphoton excitation and ionization

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Abstract. The ionization processes of the Ar_M, Xe_N and Xe_NAr_M clusters in a supersonic beam with multiphoton excitation were studied. The third 263 nm harmonics of a femtosecond Ti:sapphire laser were used for excitation and ionization. Kinetic energy spectra of photoelectrons has been recorded by a magnetic bottle time-of-flight electron spectrometer. Analysis of the electronic spectra of multiphoton ionization of clusters shows that, in heteronuclear clusters, the transfer of excitation energy between xenon and argon atoms plays a significant role in ionization.

1. Introduction

The study of non-radiative relaxation processes of electronically excited clusters of rare gases is of considerable interest from both fundamental and applied points of view. Indeed, clusters are a transitional stage from atoms and large molecules to a solid, and the study of relaxation processes in such nanoparticles sheds light on the ratio of bulk and surface relaxation processes. The practical significance of such research consists primarily in elucidating the role of the processes of relaxation of excitation and ionization, as the initial stage of the so-called "Coulomb explosion" of ionized clusters, which serves as a source of multiply charged ions to produce intense VUV radiation. Earlier [1,2], in our group, nonradiative relaxation processes of xenon clusters in an electronically excited states were investigated. Clusters were created in a supersonic beam during expansion into a vacuum and ionized by absorbing several photons of a femtosecond laser. The rates of the following processes were measured: desorption of excited atoms from a cluster, relaxation during electron-phonon interaction, and interatomic Coulomb decay (ICD). The rates of the above nonradiative relaxation processes of xenon clusters are in the range $10^{11} - 10^{12} \text{ s}^{-1}$. In this work, we measured the mass composition of xenon, argon, and xenon-argon mixed clusters. Using the time-of-flight spectrometer, photoelectron spectra of clusters were obtained. It was found that transfer of excitation energy from an excited xenon center to argon is observed in heteronuclear Xe_N Ar_M clusters.

2. Experimental set up

The pulsed supersonic cluster beam was produced by the adiabatic expansion of the gas mixture through a 200 μm diameter sonic nozzle at room temperature. The beam was skimmed at 20 mm distance from the nozzle by a 1.5 mm diameter skimmer. The cluster beam crossed the focus of a laser radiation. The composition of cluster beam was measured by time-of-flight mass spectrometer equipped with electron ionization source with energy of 30 eV, since at higher energies the cluster fragmentation increases significantly [3].



The third 263 nm (UV, $h\nu=4.71$ eV) harmonic of a femtosecond Ti : sapphire laser with a repetition rate of 10 Hz was used for excitation. The laser delivered pulses with duration of 50 fs. To avoid above-threshold ionization, the power density in the interaction region was governed by the position of the lens and did not exceed 10^{12} W/cm².

Kinetic energy spectra of photoelectrons emitted from the interaction zone has been recorded by a magnetic bottle time-of-flight electron spectrometer. The resolution of the spectrometer did not exceed 30 mV. A photoelectron spectrum of multiphoton ionized xenon atoms was used for energy calibration.

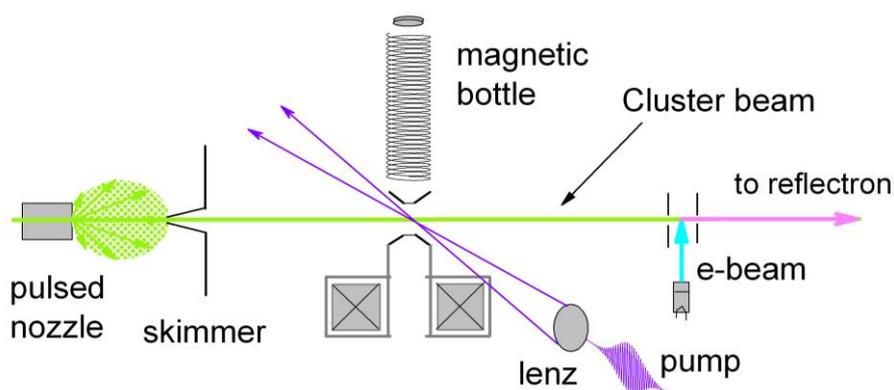


Figure 1. The scheme of the experimental setup.

3. Results and discussion

To create Ar_M , Xe_N and $Xe_N Ar_M$ clusters, pure argon, helium-xenon mixture (8% xenon in helium) and argon-xenon mixture were used in a ratio of 98:2, respectively. Figure 2 shows the mass spectra of the beam in argon, xenon, and argon-xenon mixtures at a pressure of ~ 4 bar. It can be seen that the peaks of xenon clusters are much wider than the peaks of argon clusters. In argon, 99.6% of the isotopic composition refers to the ^{40}Ar isotope. The mass spectrum of the Ar_M clusters actually consists of a single peak. Seven xenon isotopes from ^{128}Xe to ^{136}Xe have abundance above 1%. The mass spectrum of the Xe_N cluster is a set of peaks corresponding to clusters of different isotopic composition, which overlap each other in fig.2.

Part of the spectrum 358-442 Da for Xe_N and $Xe_N Ar_M$ cluster beams on a large scale is shown in Fig. 3. Only the Xe_3 cluster is contained in the xenon cluster beam in this region of the spectrum. It is seen that the mass spectrum of this cluster is a set of more than 20 peaks corresponding to different combinations of isotopes in the cluster. The spectrum of the xenon-argon cluster beam contains lines corresponding to the Ar_9 , Ar_{10} , Ar_{11} , Xe_3 clusters, as well as to all possible heteronuclear clusters: Ar_6Xe , Ar_7Xe , Ar_3Xe_2 , Ar_4Xe_2 , $ArXe_3$. The mass range of the isotopic distribution for each cluster is indicated in Fig. 3 by a black line. It is seen that the isotopic distributions for different $ArXe$ clusters overlap even for relatively small clusters. The observed mass set for $Xe_N Ar_M$ is much wider than Xe_N and Ar_M . As a result, it is possible to distinguish individual clusters only for masses not exceeding 1000 Da.

Despite the fact that the initial mixture contains only 2% xenon, the number of Ar_M clusters in the beam is small compared with the number of heteronuclear $Xe_N Ar_M$ clusters. A similar effect of a significant enrichment of the cluster beam of argon-xenon clusters containing xenon atoms as compared to the ratio of components in the initial mixture was observed in [4]. Note that an increase in the fraction of xenon in the initial mixture by 1-2% leads to the complete disappearance of argon clusters in the mass spectrum.

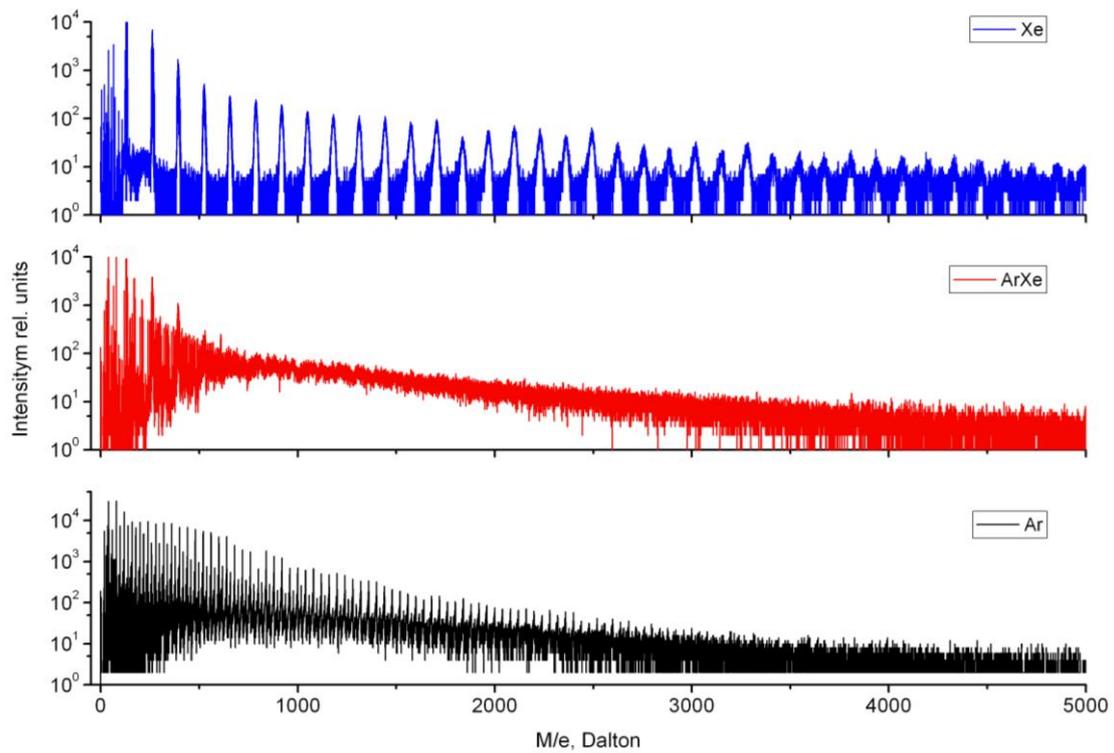


Figure 2. Mass spectra of a cluster beam for xenon, argon and xenon-argon mixture at stagnation pressure ~ 4 bar.

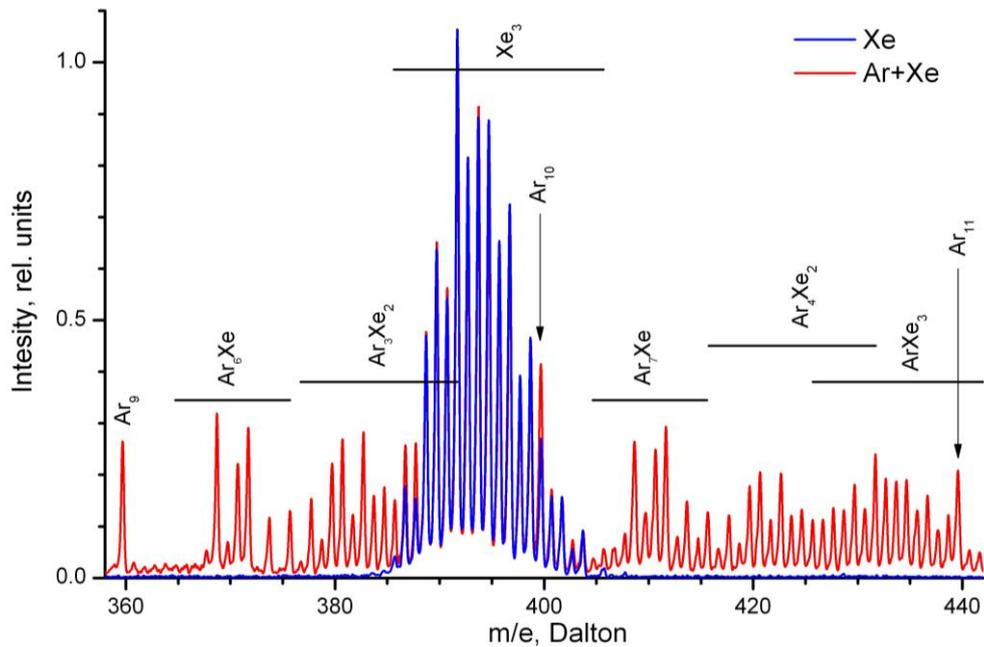


Figure 3. Isotope distribution for Xe and Xe+Ar beam in mass region 358-442 Dalton. Black lines indicate the mass range of the isotopic distribution with the intensity of individual lines of more than 1%.

Note that the comparison of the electronic ionization spectra for beams of different compositions is not trivial. The mass distribution in the beam depends on the stagnation pressure and composition of the mixture. At the same stagnation pressure, the mass distribution in the xenon and xenon-argon beams is different. By varying the pressure, it is possible to achieve approximately the same mass distribution in beams of pure xenon and xenon-argon mixtures. Obviously, in this case, the size distribution of the clusters in the beams will be different.

In [4,5], it was shown that the Xe_NAr_M cluster consists of a nucleus formed by xenon atoms and an outer shell of argon atoms. Taking into account that the ionization potential of argon atoms is higher than that of xenon atoms, it can be expected that the ionization processes of the Xe_NAr_M cluster will depend only on the xenon core of the cluster. Thus, the ionization spectrum of Xe_NAr_M clusters should correspond to the ionization spectrum of Xe_N clusters. However, in the experiment, significant variations are observed in the photoionization spectra of Xe_NAr_M and Xe_N clusters. Figure 4 shows the spectra of multiphoton ionization of a supersonic cluster beam for argon, xenon and an argon-xenon mixture. The stagnation pressures were chosen so that the mass distribution of clusters in the xenon and xenon-argon mixtures beams was approximately the same.

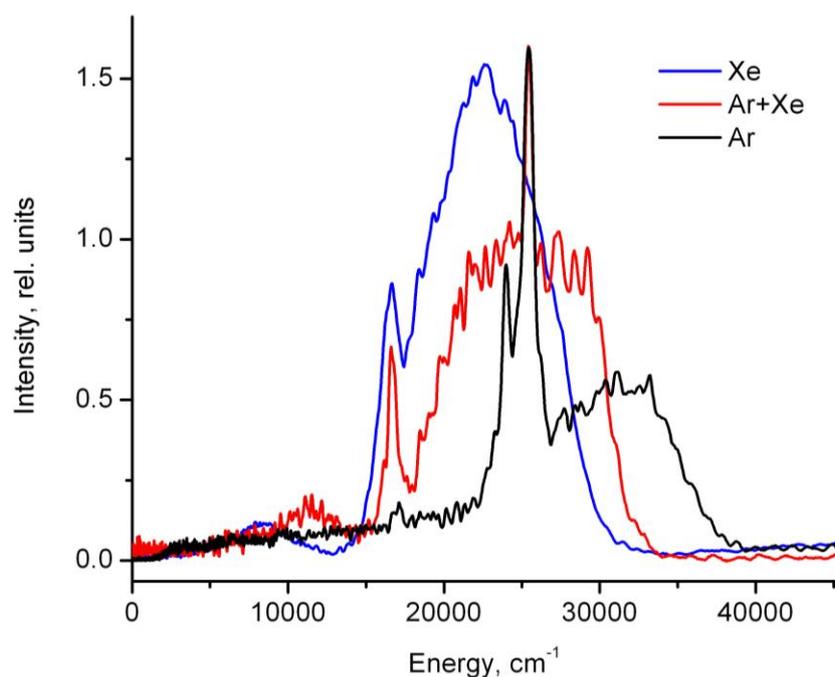


Figure 4. Photoelectron spectra of a cluster beam irradiated with the third-harmonic (263 nm) radiation of a femtosecond laser for xenon, argon and xenon-argon mixture. Stagnation pressure is about 8 bar for Xe, 5 bar for Ar+Xe mixture and 6 bar for Ar.

In the spectrum of the xenon beam, the intense line (electron energy 14530 cm^{-1}) correspond to three-photon ionization of xenon atoms to the $Xe^+(^2P_{3/2})$ states. The energy of two quanta (9.4 eV) is in the region of the effective two-photon absorption of xenon clusters. The ionization of these excited states of clusters by the third UV quantum leads to the formation of a broad, weakly structured ionization band in the energy range of $16000\text{--}25000\text{ cm}^{-1}$ [1].

Narrow lines of the multiphoton ionization of argon atoms (24000 and 25400 cm^{-1}) are also observed in the spectrum of the argon beam. The signal from argon clusters is in the region of $26000\text{--}35000\text{ cm}^{-1}$. The intensity of photoionization in an argon beam is noticeably lower than in a xenon beam, since in this case 4 photons are required for ionization.

Narrow lines corresponding to the ionization of xenon and argon atoms are also observed in the spectrum of an argon-xenon mixture. The wide photoionization band in the energy range of 18500–30500 cm^{-1} corresponds to the ionization of Xe_NAr_M clusters. Electrons with energies up to 25 000 cm^{-1} can be produced as a result of three-photon ionization of Xe_NAr_M clusters with the formation of xenon ions in a cluster in states $^2\text{P}_{1/2}$ and $^2\text{P}_{3/2}$. Electrons with energies greater than 25000 cm^{-1} cannot be produced as a result of three-photon ionization. Such electrons are born as a result of four-photon ionization with the formation of argon ions in a cluster. However, in Ar_M clusters, this process has very low efficiency. In Xe_NAr_M heteroclusters, this process effectively proceeds through the intermediate two-photon excitation of xenon centers. Thus, in this process, excitation transfer from the xenon center to argon inside the cluster with absorption of a UV quantum is observed.

Acknowledgments

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