Xenon clusters fragmentation in a supersonic beam under ionization by electrons and photons

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Abstract. Measurements of the mass distribution of xenon clusters in a pulsed supersonic beam during ionization by electrons and photons are carried out. For ionization by electron impact, an electron gun was used. The energy of the electron beam varied in the range 15 – 70 eV. Third harmonic of a titanium-sapphire femtosecond laser with a wavelength of 263 nm was used for multiphoton optical ionization. Clusters of xenon XeN with N < 1000 were observed in a supersonic beam. It is shown that the shape of the mass spectrum in multiphoton optical and electronic ionizations coincide at the electron energy near the ionization threshold (15 – 20 eV). At the electron energy of 30 – 70 eV the shape of the mass spectrum is substantially distorted in the region N ~ 2 – 150. The change in the shape of the mass spectrum is mainly due to the large fragmentation of multiply ionized xenon clusters due to Coulomb decay.

Introduction

In the supersonic beam, which is created when the gas mixture expands into vacuum through the nozzle, a significant decrease in the gas temperature to several kelvins and the formation of atomic (molecular) clusters occurs. Traditionally, the analysis of the composition of a supersonic beam is carried out by mass-spectrometry with ionization by electron impact.

Ionization potentials of xenon atoms into 2P3/2 and 2P1/2 ion states are 12.13 and 13.44 eV, respectively. The ionization potentials of xenon clusters are lower than the ionization potentials of xenon atoms [1]. Lowest adiabatic ionization potentials (Eₐ) of xenon clusters with N = 2 – 20 were measured in [2] and are 10 - 11 eV. Usually, mass spectrometry uses electron energies of ε = 70 eV, which is significantly higher than the ionization potential for xenon clusters.

Ionization of clusters of inert gases was considered in [3]. In the first approximation, it is assumed that the energy of the ionizing electron is not essential, since it only knocks out one electron from the outer shell of the atom and does not lead to the destruction of the cluster. R₂⁺ dimer inside the cluster is formed in the case of inert gas cluster ionization by electrons or photons. Energy ~ 1 eV is released during this process and a partial evaporation of the cluster occurs. About 6 atoms are evaporated in the case of xenon clusters [4]. Thus, the shape of the mass spectrum should not depend on the energy of the electron beam.

It is known that there is a significant fragmentation of noble gas clusters during ionization by electron impact [5] and the recorded ion spectrum differs from the original beam composition. We...
note that the mass composition of the beam can not be obtained from the widely used Hagena formula [6] for a pulsed supersonic beam of a gas mixture with a light carrier gas [7,8].

The purpose of this paper is to study the mass spectra of the supersonic beam of xenon clusters obtained at different energies of ionizing electrons and compare them with the mass spectra obtained in multiphoton ionization of clusters in the near-threshold ionization region.

**Experimental setup.**

Setup is shown in Fig.1. A pulsed cluster beam was created by an adiabatically expanding gas mixture through a sonic nozzle of 0.2 mm in diameter at room temperature. The gas pulse duration was about 200 μs, the repetition rate was 10 Hz. Stagnation pressure of the mixture (92% He and 8% Xe) ahead of the nozzle ranged from 1 to 9 bar. A skimmer with a diameter of 1.5 mm was located at a distance of 20 mm from the nozzle. The cluster beam speed is about 1 km/s. At a distance of 200 mm from the skimmer, the cluster beam enters the ion source of the time-of-flight reflectron mass spectrometer RFT10 (Kaesdorf, Munich). In the ion source the electron impact ionization of clusters occurs. Electron pulse duration was 5 μs. Electron energy varied in the range 15 – 70 eV. Third harmonic of a titanium-sapphire femtosecond laser with a wavelength of 263 nm (hν = 4.71 eV) was used for optical ionization. Laser pulse energy was 50 μJ, duration was 85 fs, repetition rate was 10 Hz. The laser radiation was focused into the same region of the cluster beam as the electron beam by a lens with a focal length of 160 mm.

The generated ions are extracted into the flight tube by means of a high-voltage pulse delayed by 0.2 μs after the ionization pulse. The MCP and the time analyzer recorded ions with a resolution of 250 ps. The resolution of the mass spectrometer is 10⁴ at 130 Da. Xenon of natural isotopic composition was used in the work. Xenon has 9 isotopes: from ¹²⁴Xe to ¹³⁶Xe, standard atomic weight is 131.293 Da. The mass spectrum of the Xeₙ cluster is a set of peaks corresponding to Xeₙ clusters of different isotopic composition. As an example, Fig. 1b shows the mass spectrum for the Xe₂ cluster. It can be seen that the isotopic distribution contains more than 20 peaks, in the range 386.7-407.7 Da. The width of the isotope distribution increases with increasing N, and at N > 11 the distributions begin to overlap. To ignore a significant number of individual peaks, mass spectrum was smoothed with a resolution of m/z ~ 20, which is sufficient to separate the peaks of the clusters of different sizes. The mass calibration was performed over the first 40 peaks of the clusters.

**Figure 1.** The scheme of the experimental setup (a), mass spectrum of a supersonic beam ionized by electron impact in range 380-410 Da (b).

**Experimental results and discussion**

*Ionization by electron impact*

An investigation of the mass spectra at different electron energies was carried out at the maximum stagnation pressure of the gas mixture (9 bar). Mass spectra at various electron energies from the near-threshold energy $\varepsilon = 15$ to 70 eV are presented in Fig.2. Such mass spectra are typical for cluster
beams of inert gases [4,9]. The ions of xenon clusters Xe$_N^+$ with $N = 2 – 1000$ are observed in the mass spectrum at all electron energies. The shapes of the mass spectrum at $\varepsilon = 20$ eV and $\varepsilon = 15$ eV differs slightly. The relative amount of Xe$_N^+$ ions with $N = 2 – 150$ in the mass spectrum increases with increasing electron energy. The strongest changes are observed in the range $N = 6 – 60$, where the number of ions increases by two orders of magnitude at $\varepsilon = 70$ eV.

Figure 2. Mass spectra of a supersonic beam ionized by electron impact. Upper: overview spectrum, bottom: part of the spectrum with $15 < N < 45$.

The Xe$_N^{2+}$ ions appear in the mass spectrum at electron energies above 30 eV. As is known in the case of small xenon clusters, the Xe$_N^{2+}$ ions decay into singly charged ions with a characteristic time less than 100 ps [10]. The appearance of the ions in the mass spectrum is clearly visible in the region of $N = 25 – 40$, see Fig.2. In this region of the spectrum there are peaks with a "non-integer" number of atoms in the cluster related to the doubly charged cluster ions with an odd number of atoms. Peaks from doubly ionized clusters with even N coincide with peaks from singly ionized clusters. The first peak from the doubly ionized cluster is at $N = 26.5$ and corresponds to the Xe$_{35}^{2+}$ cluster.
peak with n = 27.5 has a higher intensity and corresponds to a doubly ionized cluster with the number of atoms equal to the magic number N = 55. The threshold energy of the appearance of Xe\(_{N}^{2+}\) ions is 25 eV, which agrees with the results of [11]. The contribution of Xe\(_{N}^{2+}\) ions to the total intensity of the mass spectrum increases with increasing electron energy. At \(\varepsilon = 70\) eV, the contribution of the second ions in the spectral region with N = 26 – 60 is of the order of 50%.

Let us consider the possible variants of the formation of doubly charged clusters.

1. Sequential ionization. This process requires two collisions: in the first one, the cluster ionizes Xe\(_{N} + e \rightarrow Xe_{N}^{+} + 2e\), then the formation of the second ion occurs: Xe\(_{N}^{+} + e \rightarrow Xe_{N}^{2+} + 2e\). The ionization of a neutral atom in a cluster in the second collision requires an energy \(E = E_i + E_Q \sim 14\) eV, here \(E_i\) is the ionization potential of the xenon atom, \(E_Q\) is the energy of the Coulomb interaction. The value of \(E_Q\) depends on the arrangement of ions in the cluster and has a value of \(\sim 0.5 – 3\) eV. Thus, the threshold of this reaction is \(\sim 14\) eV.

2. The electron in one collision impacts out two external electrons from one atom of the cluster. The threshold of this process coincides with the potential of the second ion Xe\(_{2}^{2+}\) (34 eV).

3. The electron in one collision impacts out two external electrons from different atoms of the cluster. The threshold energy of this reaction is \(E = 2E_i + E_Q \sim 25\) eV, this value is close to that observed in the experiment.

4. The electron is knocked out from the inner shell. Next, the intraatomic transition of the electron from the outer shell to the newly formed vacancy occurs. In this case, an energy is released that can ionize another cluster atom via interatomic coulomb decay [12]. For the xenon atom, the energy required to knock out 5s and 4f electrons is 23.4 and 67.5 eV, respectively. Taking into account the ionization potential of the xenon atom the energy release is 11.3 and 57.4 eV. In the case of knocking out 4f electrons of the released energy is sufficient to ionize two more atoms and create Xe\(_{N}^{3+}\) ion. For 5s electron, an energy approximately equal to \(E_A + E_Q\) is released, which may be sufficient for ionization of the second atom in clusters.

In the experiment, the doubly charged ions appear at the electron energy of \(\sim 26\) eV, consequently, processes 1 and 2 are unlikely in conditions considered. The ionization thresholds of processes 3 and 4 are close to the observed in the experiment.

![Figure 3. Changes in the shape of the mass spectrum with increasing electron energy. The ratio of the intensities in the mass spectra at \(\varepsilon = 70\) (black circles) and 30 eV (blue circles) to the intensity of mass spectrum at \(\varepsilon = 20\) eV. Lines are smoothed data.](Image)
As mentioned above, the doubly charged ions of clusters with $N < 47$ are unstable and decay rapidly due to Coulomb repulsion. Note that the intensity of the peaks corresponding to $\text{Xe}_N^{2+}$ with $N = 47 – 51$ observed in [11] was low, in the present work, these ions were not recorded. In [10] it was shown that upon the decay of the $\text{Xe}_N^{2+}$ ions with $N < 51$, two singly-charged clusters of size $N >> 1$ are formed. Stable three-fold ionized clusters of $\text{Xe}_N^{3+}$ exist for $N > 108$ [11].

Figure 3 shows the change in the shape of the mass spectrum at an electron beam energy of 70 eV with respect to the shape of the spectrum at $\varepsilon = 20$ eV. It can be seen that in the region $N < 150$ a significant increase in the intensity of ions is observed. Two peaks corresponding to $N = 6 – 16$ and $N \sim 40$ are also observed. Apparently, the first peak corresponds to fragments formed during the Coulomb decay of doubly charged clusters with $N < 47$ and triply charged clusters with $N < 108$. The second peak in the mass spectrum corresponds to doubly and triply charged ions.

Photoionization

For the ionization of xenon clusters with 263 nm radiation, three quanta are required, the total energy of which is $\varepsilon = 14.1$ eV. This energy corresponds to the near-threshold ionization region. The intensity of multiphoton ionization depends nonlinearly on the radiation power density. To reduce the influence of nonlinear effects of high orders, photoionization was carried out at radiation power densities slightly exceeding the threshold for the appearance of ions. In this case, the shape of the mass spectrum in optical ionization (see Fig. 4) is close to the shape of the mass spectrum in electron ionization at $\varepsilon = 15 – 20$ eV.

![Mass spectra of a supersonic beam with electron (\(\varepsilon = 20\) eV) and multiphoton optical ionization (\(\lambda = 263\) nm).](image)

**Figure 4.** Mass spectra of a supersonic beam with electron ($\varepsilon = 20$ eV) and multiphoton optical ionization ($\lambda = 263$ nm).

**Conclusion**

In optical multiphoton ionization with UV radiation of 263 nm, the mass spectrum coincides with the mass spectrum upon ionization by electron impact in the region of near-threshold energies of 15–20 eV. In the case of ionization of a supersonic beam of clusters by electrons, a significant change in the shape of the mass spectrum is observed with a change in the electron energy from the near-threshold ($\varepsilon = 15 – 20$ eV) to 70 eV. At $\varepsilon = 70$ eV, the intensity of the peaks for clusters with $n > 150$
decreases, and the number of clusters with \( n < 150 \) increases. The intensity of small clusters \( n = 6–60 \) increases most strongly. The change in the shape of the mass spectrum is mainly due to the considerable fragmentation of multiply ionized xenon clusters due to Coulomb decay.

At electron beam energies of less than 25 eV, there is no distortion of the shape of the mass spectrum due to the decay of multiply charged clusters.

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