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Observation of small metastable multiply charged CsI clusters embedded inside rare gas clusters

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Abstract. Medium size Kr and Ar clusters $\langle N \rangle \sim 200 - 400$ were used to pick up and aggregate CsI molecules. By varying the number of pick-up events it was possible to change the size of the guest cluster and the thickness of the rare gas coverage around the alkali halide cluster. "Soft" single (multiple) ionisation of the alkali halide core was achieved via charge transfer from the primary ionised rare gas shell. It turns out that the rare gas shell controls the vibrational relaxation of CsI cluster ions. Due to cooling by the rare gas shell shallow metastable states of multiply charged CsI clusters can be populated and detected. Clusters as small as $Cs_5I_3^{2+}$, $Cs_6I_5^{2+}$, $Cs_{13}I_{13}^{3+}$ and $Cs_{17}I_{14}^{3+}$ could be observed for the first time. The abundance of these multiply charged clusters steeply decreases if the thickness of rare gas shell shrinks.

PACS. 36.40.Qv Stability and fragmentation of clusters – 36.40.Wa Charged clusters

1 Introduction

After the discovery of appearance sizes [1] for doubly charged clusters the structure and stability of multiply charged clusters was studied in great details [2]. Since the long-range Coulomb interaction between different positively charged cluster fragments is repulsive all multiply charged clusters can be considered as unstable or at least metastable. The attractive part of the interaction potential at smaller intermolecular distances can have a local minimum in the total energy of multiply charged clusters [2, 3]. In such a minimum cluster fission is impeded by a barrier separating the local minimum and the repulsive part of the potential energy surface. The parameters of the fission barrier depend on the cluster structure, number and nature of atoms or molecules composing the cluster. As a result, the height and slope of the barrier is cluster size and element specific. In the mass spectra multiply charged clusters appear starting from well-defined clusters sizes. For rare gas, molecular, metallic and alkali halide clusters the measured appearance sizes are in good accordance with critical numbers obtained in theoretical calculations [2]. On the other hand, the probability to populate the metastable state or to overcome the barrier strongly depends on vibrational excitation of the clusters after the ionisation. Therefore, the appearance size for metastable multiply charged clusters can depend on experimental conditions [4]. In addition, because of the final lifetime of the multiply charged cluster in a metastable state, the flight time of the clusters before the detection has to be considered.

Recently a new pick-up technique of different kind of cluster production was introduced [5]. In this experimental approach rare gas (RG) clusters are used to pick up and aggregate a guest cluster inside the host. One of the advantages of this approach is the possibility to vary continuously the RG coverage around the guest cluster [6]. It was shown in the case of small clusters embedded inside big He clusters that the cold cluster environment can be considered as a thermal "sink" to dissipate the vibrational energy of the guest clusters [7]. Therefore, by varying the number of RG atoms around the guest cluster one can change the thermal capacity of the "sink". This provides the opportunity to control the thermodynamic properties of the guest cluster. In this paper, utilising the above mentioned method, we have investigated the influence of a Kr shell around the alkali halide clusters on the stability of the multiply charged clusters.

2 Experimental

Various combinations of alkali halides (NaCl, LiF, CsI) and rare gases (Ar, Kr) were used in this study. Here we concentrate on the combination CsI and Kr. CsI was chosen because it has a simple isotopic composition and high

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molecular weight, which simplifies the interpretation of the mass spectra. Primary Kr cluster beams with average cluster sizes $\langle \mathrm{N} \rangle \sim 200-400$ produced by an adiabatic expansion of cold rare gases through a conical nozzle. The skimmed beam entered a few cm long scattering cell where a vapour pressure of the CsI in the region of 10^{-6}–10^{-1} mbar could be maintained by heating the material. Guest molecules were picked up by the RG clusters depending on the scattering cross section, masses and interaction potentials of the collisional partners [7]. At alkali halide partial pressure of 10^{-4}–10^{-3} mbar the multiple pick-up and aggregation of these molecules inside RG clusters starts [6]. The coagulation energy of the newly formed guest clusters is dissipated by evaporation of an appropriate number of rare gas atoms thus cooling the clusters. If primary Kr clusters with $\langle \mathrm{N_{Kr}} \rangle \sim 200$ are used then bare alkali halide clusters could be produced when the number of picked up molecules exceeds $\langle \mathrm{N_{CsI}} \rangle \sim 20$ in average. Quantitative agreement of the conversion number $\eta = \langle N_{\mathrm{Kr}} \rangle / \langle N_{\mathrm{CsI}} \rangle$ with the reciprocal ratio of appropriate sublimation energies directly proves the CsI aggregation inside the host cluster [6]. In this study the thickness of the RG coverage around the guest clusters was controlled by varying the number of pick-up events. The resulting beam of bare or RG-covered CsI clusters was skimmed and entered the analytical chamber. The clusters were ionised by electrons ($E_{\mathrm{kin}} \sim 160$–$220$ eV) and probed with a reflectron time-of-flight mass spectrometer.

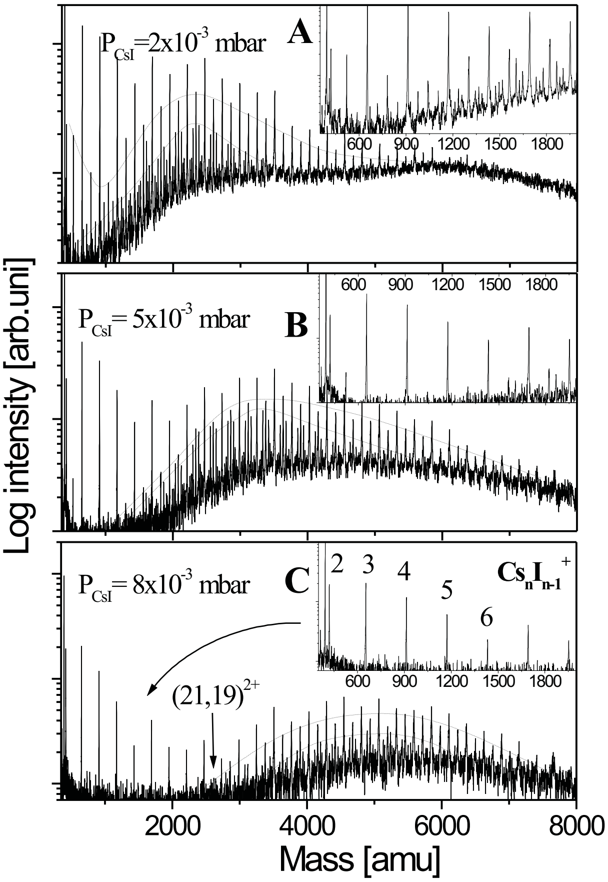

Fig. 1. Mass spectra of CsI clusters aggregated inside Kr clusters for the three different pick-up pressures. In the inserts the low mass range is shown in enlarged scale. The appearance size (n, m) for doubly charged bare $\mathrm{Cs}_n\mathrm{I}_m$ clusters is indicated in brackets.

3 Results and discussion

In the Fig. 1 mass spectra of CsI clusters aggregated inside Kr clusters are presented for three different pick-up pressures. The dominating mass peaks are due to non-stoichiometric $\mathrm{Cs}_n\mathrm{I}_{n-1}^+$ clusters. These clusters originate from the stoichiometric parent clusters by loosing a weakly bound neutral halogen atom after ionization [8]. The experimental conditions have been adjusted in such a way that top spectrum (A) in Fig. 1 represents CsI clusters embedded inside host Kr cluster, while bottom spectrum (C) corresponds to the bare CsI clusters. The spectrum in the middle (B) represents intermediate case. It is important to note, that as in the case of other rare gases, for Kr covered clusters the ionization of the guest aggregate proceeds through a charge transfer from the primary created hole in Kr shell [7,9]. Since the ionization potential of the RG cluster exceeds only in a few electron volts that one of the alkali halide aggregates, this mechanism of the guest cluster ionization can be considered to be “soft” in comparison with direct ionization with the primary 160 eV electrons. However, the presence of doubly and even triply ionized CsI clusters in spectra (A) and (B) (Fig. 1) reflects a multiple ionization in the case of the embedded clusters. This can be explained by a multiple sequential ionization in the Kr shell. The kinetic energy of the ionizing electrons 160–220 eV is well above the experimental threshold of ~ 63 eV for sequential production of Ar^{3+} [2]. Since the ionization potential of Kr is lower then of Ar the same holds for Kr clusters case. For the given kinetic energy of the primary electrons the mean free path in solid Ar and Kr is about 10 Å which is at least two times less than the average diameter of the parent rare gas cluster. In the mass spectra of Fig. 1 three observable distributions of singly, doubly and triply charged clusters can be distinguished (dashed envelope lines). All of them can be characterized by the few parameters: appearance size, maximum of the distribution and end of the distribution. Since doubly and triply charged clusters appear at mass numbers twice or three times reduced with respect to the single charged neutral precursors, their distribution parameters (excluding appearance size) are scaled correspondingly twice and three times with respect to case of the single charged clusters. Two major processes govern the evolution of the mass spectra with increasing of CsI partial pressure (Fig. 1). With increasing the vapor pressure the average guest cluster size develops while the Kr shell vanishes by evaporative cooling. The first factor is responsible for the continuous shift of the maximum in the distribution of the mass series towards higher masses,

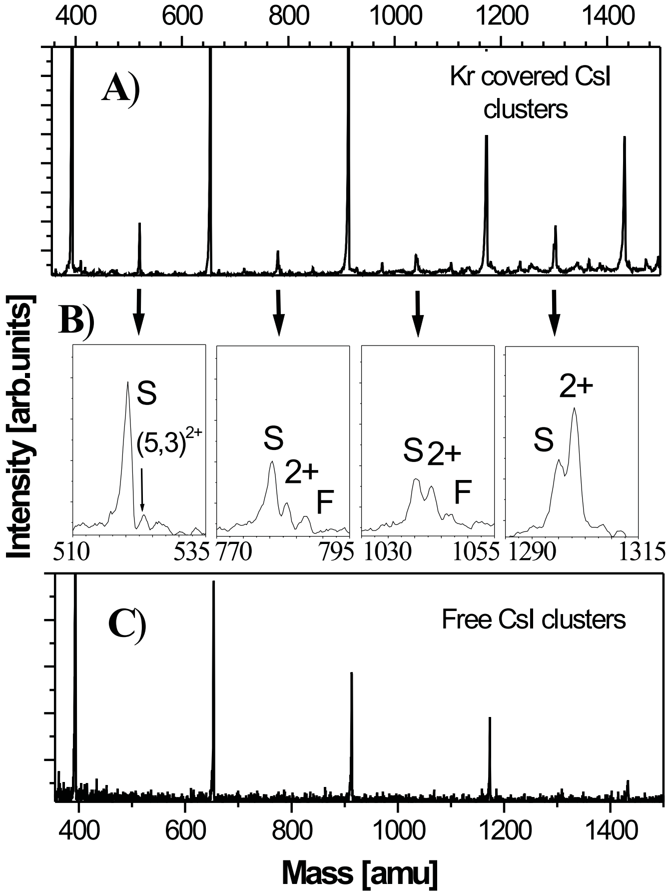

Fig. 2. Mass spectra of small CsI clusters embedded inside Kr clusters (A) and bare (C). In the middle (B) "intermediate peaks" are shown with high resolution. S: stoichiometric $Cs_nI_n^+$ clusters, 2+: doubly charged clusters $Cs_nI_{n-2}^{2+}$, F: clusters containing "F-center" with a composition $Cs_{n+1}I_{n-1}^+$.

while the second one controls the stability of small multiply charged clusters. Somewhat surprising is that all doubly and triply charged clusters at low masses vanish with increasing of the number of picked up molecules (see insertions in Fig. 1). We assume that the appearance sizes increase when the thickness of the Kr shell decreases. In the Fig. 2 the mass spectra for two limiting cases of embedded (A) and bare CsI clusters (C) are presented in an enlarged scale. In Fig. 2 (B) the fine structures of the "intermediate" peaks for the covered clusters are shown. As can be seen stoichiometric $Cs_nI_n^+$ clusters together with doubly charged and F-center containing clusters $Cs_{n+1}I_{n-1}^+$) [10] compose the "intermediate" peaks. While for the smallest cluster sizes stoichiometric clusters have a dominant intensity, the doubly charged clusters exhibit growing stability with increasing cluster size. Surprisingly, clusters as small as $Cs_5I_3^{2+}$ can be observed. To our knowledge it is smallest doubly charged alkali halide cluster being observed experimentally [4]. Already in the early eighties it was theoretically predicted that small ($N < 10$) alkali halide clusters are metastable [3]. The calculated fission barrier height was found to be on the order of a few tenths of electron

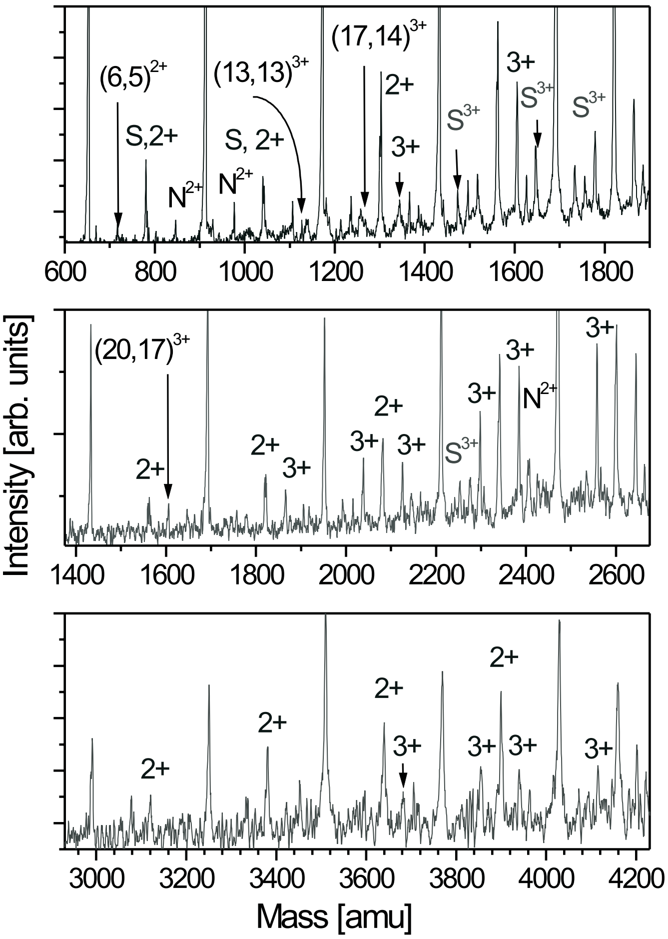

Fig. 3. Mass spectra showing the appearance of multiply charged clusters. 2+: correspond to the doubly charged clusters with composition $Cs_nI_{n-2}^{2+}$; 3+: to the $Cs_nI_{n-3}^{3+}$; N^{2+} indicate nonstoichiometric doubly charged clusters $Cs_nI_{n-1}^{2+}$; S and S^{3+} correspond to stoichiometric single and triply charged clusters. From top to the bottom the Kr coverage is decreasing. Bottom spectrum corresponds to bare CsI clusters. The composition of smallest multiply charged clusters is indicated in brackets.

volts (0.2 eV for Na_3Cl^{2+}). In the usual electron beam experiments a few eV of vibrational energy can be left in the cluster after ionization. Because of a reduced number of degrees of freedom in small clusters very high vibrational levels can be populated. As a result, the fission barrier can be tunneled or overcome and the cluster dissociates into two singly charged fragments. However, there is experimental evidence [4, 8] that the initial temperature of the alkali halide clusters and the excess of the energy above the ionization threshold have a dramatic effect on the stability of doubly charged clusters. In our case the presence of RG shell around the alkali halide guest provide an additional thermal "sink" which can accommodate the excess of vibrational energy. Indeed, the presence of stoichiometric clusters indicate that the vibrational excitation of the small ionized cluster is not enough for the sublimation of loosely bound (less then 30 meV) neutral halogen [3], which is almost an order of magnitude less than the height of the fission barrier. By removing of the Kr thermal "sink" all small metastable clusters vanish from the mass spectrum Fig. 2 (bottom) indicating the temperature of the clusters increases. Under these conditions the first doubly charged clusters appears at $N_\mathrm{a} \sim 20$ what is in a good accordance with the previous studies on alkali halides [8].

A detailed analysis of the mass spectra of RG covered clusters reveals the presence of unusual CsI cluster ions with a composition $\mathrm{Cs}_n\mathrm{I}_{n-1}^{2+}$ and $\mathrm{Cs}_n\mathrm{I}_n^{3+}$. In Fig. 3 the appearance regions for these clusters for three different Kr coverage are presented. Due to the limited resolution of the mass spectrometer an alternative assignment of these mass peaks to quadruply and six times charged clusters could not be completely excluded. Since to our knowledge there are no experimental or theoretical data on these clusters to compare with our observations we present only a few key results. Nonstoichiometric doubly charged clusters (with appearance size $N_\mathrm{a} = 6$) and stoichiometric triply charged clusters (appearance size $N_\mathrm{a} = 13$) are only observable if RG-covered clusters are produced. The appearance size increases if the thickness of the Kr shell decreases. This behavior is analogues to the previous observations on "usual" doubly and triply charged species and therefore tentatively can be explained in the same way. In the case if the alternative assignment would be valid then the appearance sizes for quadruply and six times charged clusters would be $N_\mathrm{a} = 13$ and $N_\mathrm{a} = 31$ correspondingly. In that case the appearance size for quadruply charged clusters at $N_\mathrm{a} = 13$ turns out to be less than for triply charged CsI ($N_\mathrm{a} = 17$) and in addition there is no evidence for the presence of five times charged clusters. Based on these observations one can speculate about an enhanced stability of clusters having an even number of positive charges with respect to the odd one because of structural symmetry reasons. An additional experiments and theoretical studies in order to shine some light into this interesting issue would be very helpful.

4 Conclusion

A mass spectroscopic study on the stability CsI cluster ions produced in a pick-up process with large Kr clusters is presented. It turns out that the RG layers covering the alkali halide clusters act as a thermal "sink" dissipating the excess of vibrational energy of the alkali halide cluster after ionization. We are able to observe metastable small multiply charged CsI clusters with unexpectedly low appearance sizes. By heating up the alkali halide clusters the fission barrier can be overcome and the metastable clusters dissociate.

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