Eur. Phys. J. D **9**, 277–281 (1999)

THE EUROPEAN PHYSICAL JOURNAL D
EDP Sciences

Aggregation of small CsI clusters inside Ar clusters: ionization and fragmentation under soft X-ray excitation

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Received: 31 August 1998 / Received in final form: 16 October 1998

Abstract. Medium size Ar clusters $\langle N \rangle \sim 500$ were used to pick-up and aggregate CsI molecules. The primary Ar cluster beam can be converted into a beam of bare or Ar-covered alkali halide clusters by varying the number of pick-up events. Soft X-ray photoionisation was used to monitor the depletion of the Ar shell around the guest cluster. It was found that the Ar coverage controls the mechanism and degree of guest cluster ionization. For embedded CsI clusters charge transfer from the Ar shell is the dominant soft X-ray ionization process. Small alkali halide cluster fragments are ejected from the Ar host cluster. The detection of weakly bound stoichiometric $(\mathrm{CsI})_n^+$ clusters indicates that the Ar-shell prevents the desorption of neutral halogen atoms.

PACS. 36.40.Qv Stability and fragmentation of clusters – 36.40.Mr Spetroscopy and geometrical structure of clusters – 78.70.Dm X-ray absorbtion spectra

1 Introduction

The pick-up method of cluster doping introduced several years ago [1] is a very promising method for the investigation of the properties of both host clusters and guest atoms or molecules. Recent examples are the experiments on ultracold embedded metal clusters [2] and superfluidity in He droplets [3]. The next step in the development of the method was to produce bare guest clusters by multiple pick-up process and complete evaporation of the host cluster. This approach was successful for Xe aggregated inside Ar host clusters [4]. Since the host clusters are used as aggregation nuclei this technique is called the "cluster aggregation method". One advantage of this approach is the possibility to vary the thickness of the layer of rare gas atoms around the guest clusters which provides the opportunity to monitor the properties of embedded clusters as a function of coverage. The formation, ionization and fragmentation phenomena of such clusters are subject of the present paper. In order to get a deeper insight into the formation and ionization processes the spectroscopic techniques utilizing soft X-ray excitation were applied. These techniques probe very localized core electrons of atoms and molecules and thus are sensitive to the specific atom as well to its local environment. Spectroscopic methods like near edge X-ray absorption fine structure (NEXAFS), extended X-ray absorption fine structure (EXAFS) and photoelectron spectroscopy (XPS) are highly interesting for the cluster studies. In this paper we used the cluster aggregation method for the production of bare or Ar-covered CsI clusters. With the aid of soft X-ray photoionisation and mass spectroscopy we are able to probe the guest cluster and the Ar shell separately. Further, we can elucidate how the Ar shell affects the ionization and relaxation dynamics of encapsulated clusters after soft X-ray excitation.

2 Experimental

CsI was chosen for the following reasons: (i) Alkali halide molecules appear to be readily picked up by the primary cluster beam and aggregate inside Ar clusters (ii) Alkali halide clusters are model system which have been studied in great details both experimentally [5–7] and theoretically [8, 9] and are therefore good candidates to probe the new experimental approach. (iii) CsI has a simple isotopic composition and a large molecular weight, which simplifies the analysis of mass spectra.

Primary Ar clusters with a mean cluster size $\langle N \rangle \sim 500$ were produced by adiabatic expansion of the cold Ar gas through a conical nozzle. This beam was skimmed and entered a few cm long scattering cell where a vapor pressure of CsI in the region 10^{-6}–10^{-1} mbar was maintained by thermal heating. Multiple pick-up and aggregation of CsI

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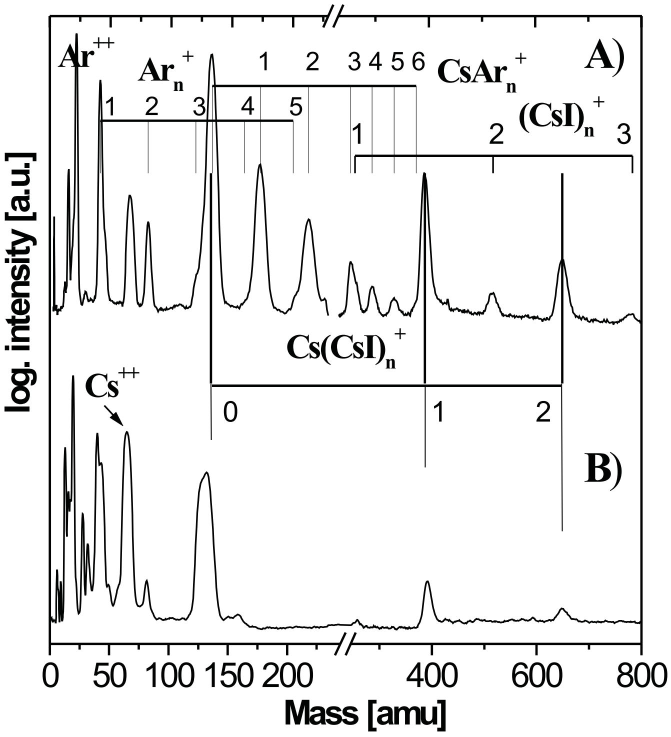

Fig. 1. Clusters produced in a pick-up process with Ar clusters passing through a scattering cell containing CsI vapor. Mass spectra of CsI clusters ionized with soft X-rays (257 eV). A) CsI clusters embedded inside Ar clusters. B) Bare CsI clusters.

molecules inside the Ar cluster started at the partial pressure in the range 10^{-4}–10^{-3} mbar. The resulting beam was skimmed and ionized by the intersecting soft X-ray beam. Synchrotron radiation with high photon flux in the region 30–800 eV from the undulator beamline BW3 at HASYLAB [10] was used to probe the clusters at alkali, halogen and Ar core edges. Mass spectra of the photoions were recorded with a short time-of-flight (TOF) mass spectrometer by exploiting the pulsed time structure of synchrotron light [11]. Partial ion yield curves of different ions were recorded simultaneously by scanning the excitation energy.

3 Results and discussion

3.1 Pick-up process

In Fig. 1 mass spectra of the cluster beam ionized above the Ar $2p$ edge (257 eV) for two different CsI vapor pressures are presented which reflect the two limiting cases of covered (A) and bare CsI (B) clusters. While the mass spectra of bare clusters exhibit exclusively the presence of non-stoichiometric $\mathrm{Cs}_n\mathrm{I}_{n-1}^+$ peaks [5, 6], the Ar-covered clusters give rise to a series of Ar_n, $\mathrm{Cs}^+\mathrm{Ar}_n$, $(\mathrm{CsI})_n^+$ and $\mathrm{Cs}_n\mathrm{I}_{n-1}^+$ ions. The development of the intensity for the main components as a function of CsI pressure is given in Fig. 2. Ar_2^+ is known to be a dominant fragment of

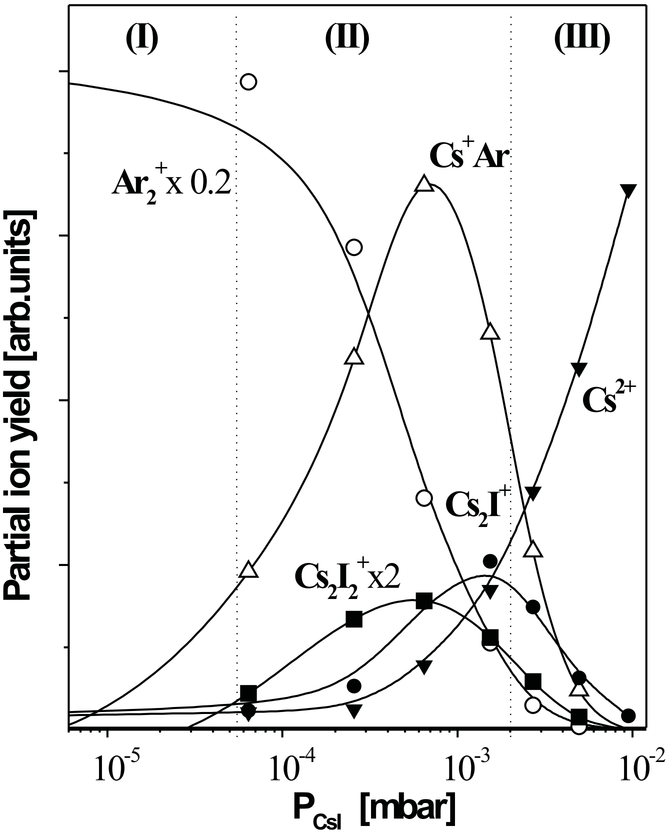

Fig. 2. Partial ion yields of Ar_2^+, Cs_2^+, $\mathrm{Cs}^+\mathrm{Ar}$, $\mathrm{Cs}_2\mathrm{I}^+$ and $\mathrm{Cs}_2\mathrm{I}_2^+$ as a function of CsI partial pressure under soft X-ray ionization at 257 eV.

Ar clusters [11, 12], while $\mathrm{Cs}^+\mathrm{Ar}_n$, $(\mathrm{CsI})_n^+$ and $\mathrm{Cs}_n\mathrm{I}_{n-1}^+$ ions are fragments of Ar clusters with singly and multiply picked up alkali halide molecules. Doubly charged Cs^{2+} ions represent the intensity of the molecular CsI component inside the beam. Three regimes (I, II and III in Fig. 2) can be distinguished which reflect the changes in composition of the cluster beam from free Ar clusters up to bare CsI clusters. At low alkali halide pressure (region I) the number of pick-up collisions is negligible and the Ar cluster beam passes the scattering region without attenuation. The pick-up process starts when CsI related fragments become seen in the mass spectrum (region II). At this stage single alkali halide molecules attached to the Ar clusters (mixed clusters), small alkali halide clusters and the remaining Ar clusters dominate the mass spectra (Fig. 1A). When the number of collisions increases the Ar components of cluster beam diminish in favor of a beam of bare CsI clusters (region III Fig. 2 and spectrum (B) Fig. 1). The variation of $\mathrm{Cs}^+\mathrm{Ar}_n$ and $\mathrm{Cs}_2\mathrm{I}^+$ peaks reflects the usual pick-up behavior observed on rare gas clusters [13–15] where an increase in scattering pressure favors picking up a greater number of molecules. However, in contrast to the work on He clusters [14, 15] the intensity distribution can not be fitted by the expected Poisson distribution. The aggregation of alkali halide inside parent medium sized Ar clusters lead to massive evaporation of the Ar thus reducing the average

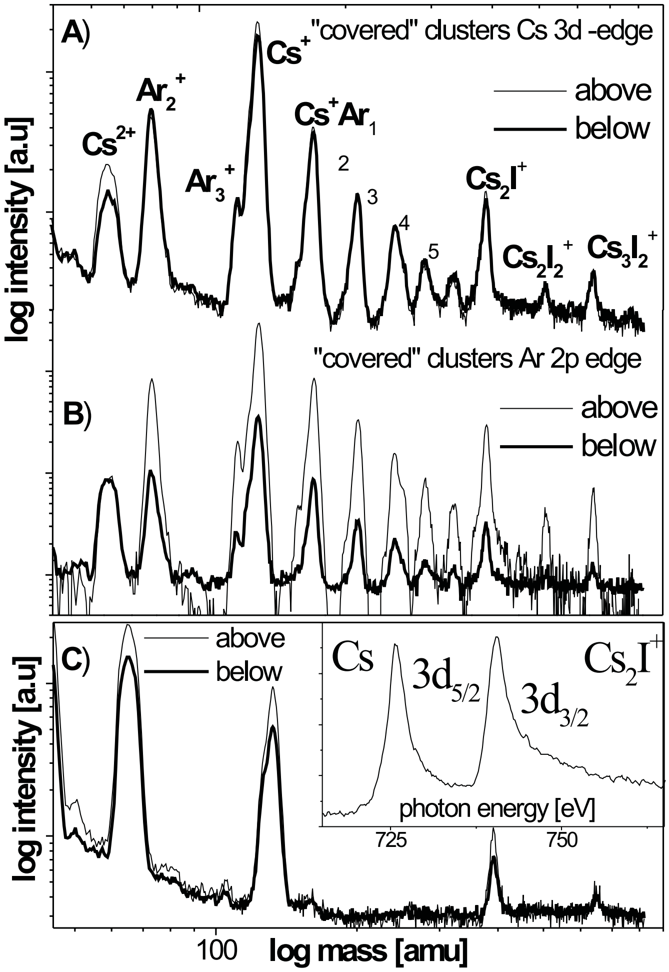

Fig. 3. Mass spectra of CsI clusters embedded inside Ar clusters and ionized A) below (720 eV) and above (730 eV) the Cs $3d_{5/2}$ edge, B) below (243 eV) and above (257 eV) the Ar $2p$ edge. C) Bare CsI clusters ionized below and above the Cs $3d_{5/2}$ edge (the insert shows the ion yield scan taken on the $\mathrm{Cs_2I^+}$ fragment).

size of the mixed clusters. As a result, both the pick-up and ionization cross-sections diminish. As we will see below, the steep drop of the cluster ion intensity is a result of a special ionization process. Finally in region III, a primary Ar cluster beam with $\langle N \rangle \sim 500$ is completely converted into bare daughter alkali halide clusters with an average clusters size of $\langle M \rangle \sim 25$. This has been checked with a reflectron time-of-flight mass spectrometer, which allows clusters up to 10^5 amu to be detected. The conversion coefficient agrees with the number estimated on the basis of the ratio between CsI and Ar sublimation energies [16, 17].

3.2 Ionization and charge transfer

It is important to note that the mass spectra reflect the properties of the cluster ions a few hundred nanoseconds *after* ionization event. During this time the energy deposited in the cluster during ionization is dissipated over all of the degrees of freedom of the cluster and massive evaporation of Ar from the host cluster and partial dissociation of the guest cluster can take place. Therefore, mass spectra alone can not give detailed information on the composition of the cluster beam. However, using ionization with tunable soft X-rays we can probe the composition of the mixed cluster *before* ionization and elucidate the role of different chemical constituencies of the cluster on the ionization process. This can be accomplished by ionizing the clusters below or above well-defined innershell thresholds which are characteristic of the different elements. In Fig. 3 the mass spectra for two limiting cases of Ar-embedded (A, B) and bare (C) CsI clusters are presented. The variation of partial ion yields at the Ar $2p$ and Cs $3d$ edges reflects the absorption of the mixed clusters. Surprisingly, for the embedded clusters all Cs-related ion yields reveal only weak changes in the relative intensity at Cs $3d$ edge (Fig. 3A). On the contrary, the same ions show a strong increase in intensity correlated with the Ar shell absorption at the Ar $2p$ edge (Fig. 3B). For the bare CsI clusters the opposite behavior was observed: a strong variation of ion yield at the Cs $3d$ edge (Fig. 3C and insert) together with the flat background at the Ar $2p$ edge (not shown). These observations demonstrate that for Ar-covered clusters, the production of the alkali halide fragments proceeds through the *intermediate ionization of the* Ar *shell followed by a charge transfer to the guest aggregate*. A similar two step ionization process was found to be very efficient for impurities embedded inside small He clusters [13–15]. It is important to note that the reverse process of ionization of the Ar shell through core excitation of alkali halide guest clusters can be observed as well but with lower probability. For covered clusters the $\mathrm{Ar_2^+}$ partial ion yield indeed reveals characteristic features at the Cs $3d$ edge (similar to the spectrum on the insertion Fig. 3C). Two mechanisms can be considered to account for this observation. The energy stored on a Cs ion after Cs $3d$ excitation is sufficient to ionize neighboring Ar atoms. Whether this process takes place or not depends on the relative reaction rates of CsI intramolecular relaxation and Cs → Ar charge transfer. On the other hand, Cs (MNN) Auger electrons with kinetic energy ∼ 690 eV emitted after ionization have a short mean free path in solid Ar [18] and can ionize some Ar atoms surrounding the alkali halide core. This could lead to a Coulomb repulsion of the positive ions with $\mathrm{Ar_2^+}$ being a most stable fragment.

3.3 Energy relaxation process

The "soft" ionization of the small alkali halide aggregates by charge transfer from the Ar-shell can lead to the deposition of about 2–3 eV into vibrational modes of the guest cluster [8]. Detailed analysis of the mass spectra can give insight how this energy becomes redistributed between the available degrees of freedom of such inhomogeneous clusters. The mass spectrum (A) in Fig. 1 was recorded under conditions when only few molecules were picked up by the primary Ar clusters with N∼ ⟨500⟩. We assume that about 100 Ar atoms were evaporated to dissipate the coagulation energy. Therefore, after aggregation CsI clusters will

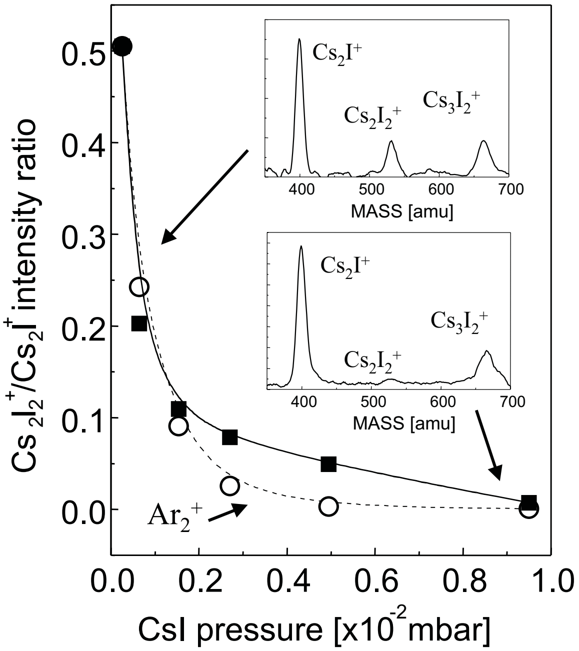

Fig. 4. The $Cs_2I_2^+$ / Cs_2I^+ intensity ratio as a function of CsI pick-up pressure. Ar_2^+ intensity is shown for comparison. Examples of mass spectra taken at different CsI pressures are shown in the inserts.

become surrounded with more than 400 Ar atoms. Surprisingly, such embedded aggregates appear as bare CsI cluster ions in the mass spectra. Indeed, the total binding energy of Ar_{400} cluster is above 30 eV [19]. The energy balance estimations indicate that energy deposited into the mixed cluster upon Ar $2p$ ionization and charge relaxation is not enough to desorb all Ar atoms of the Ar shell by an evaporative cooling mechanism [17]. An alternative explanation is that the guest aggregates are ejected after ionization. The Coulomb repulsion between the charged guest aggregate and the second positive charge left on the Ar shell as a result of primary Ar LMM Auger relaxation can be considered as a driving force for this ejection. In addition, the melting of mixed cluster can facilitate the process. For bigger CsI clusters and hence thinner Ar shells this relaxation mechanism merges into the usual evaporative cooling. Since the size of the mixed cluster is well above the critical size for Ar doubly charged clusters [20] the guest cluster ejection seems not to be an instantaneous process analogous to Coulomb explosion. Indeed, the observed CsI fragments indicate that partial thermalization takes place before (or soon after) ejection. This can be directly observed experimentally utilizing the fact that stoichiometric positively charged clusters of alkali halides are thermally unstable and under the usual conditions dissociate into non-stoichiometric $Cs_nI_{n-1}^+$ ions and neutral halogen atoms [5, 6, 8]. In Fig. 4 the development of the intensity ratio of stoichiometric and non-stoichiometric fragment ions as a function of CsI vapor pressure is presented. At the very beginning of aggregation the presence of stoichiometric clusters in the mass spectrum indicates that the vibronic excitation remaining on these fragments after electronic relaxation is not sufficient to evaporate loosely bound neutral halogen atoms. Thus, the appearance of this series in embedded clusters directly indicates partial thermalization even for ejected fragments. With increasing number of pick-up events the stoichiometric clusters vanish in favor of non-stoichiometric clusters and at the same time the evaporation of Ar atoms becomes inefficient. This indicates that the temperature of the guest cluster increases while the thickness of the Ar shell shrinks.

4 Conclusion

In this paper innershell spectroscopy with soft X-rays was used to investigate alkali halide clusters produced by the pick-up technique. These clusters are a new class of nanoparticles, which consist of an ionically bonded small cluster core surrounded by a few layers of Ar atoms. The thickness of the Ar shell can be varied in a controllable way enabling bare or Ar embedded clusters to be studied. Tunable soft X-ray excitation together with mass spectrometry allowed us to distinguish between direct core ionization and indirect ionization by a charge transfer from the Ar-shell. After ionization small alkali halide clusters are ejected from the Ar clusters. From the intensity ratio between stoichiometric and non-stoichiometric clusters it is concluded that the temperature of the alkali halide clusters increases with decreasing thickness of the Ar shell.

We gratefully acknowledge the financial support from the Deutsche Forschungsgemeinschaft under the grant SFB-508/C4 and Mo 719/1-1.

References

1. T.E. Gough, M. Mengel, P.A. Rowntree, G. Scoles: J. Chem. Phys. **83**, 4958 (1985)
2. A. Bartelt *et al.*: Phys. Rev. Lett. **77**, 3525 (1996)
3. S. Grebenev, J.P. Toennies, A.F. Vilesov: Science **279**, 2083 (1998)
4. M. Rutzen *et al.*: Z. Phys. D **38**, 89 (1996)
5. R. Pflaum, P. Pfau, K. Sattler, E. Recknagel: Surf. Sci. **156**, 165 (1985)
6. R. Pflaum, K. Sattler, E. Recknagel: Chem. Phys. Lett. **138**, 8 (1987)
7. X. Li, R.L. Whetten: J. Chem. Phys. **98**(8), 6170 (1993)
8. T.P. Martin: Phys. Rep. **95**(30), 147 (1983)
9. U. Landman, D. Scharf: J. Phys. Rev. Lett. **54**, 1860 (1985)
10. C.U.S. Larsson *et al.*: Nucl. Instrum. Methods A **337**, 603 (1994)
11. O. Björneholm, F. Federmann, F. Fössing, T. Möller: Phys. Rev. Lett. **74**, 3017 (1995)
12. E. Rühl *et al.*: Chem. Phys. Lett. **178**, 558 (1991)
13. M. Lewerenz, B. Schilling, J.P. Toennies: J. Chem. Phys. **102**, 8191 (1995)

14. A.A. Scheidemann, V. Kresin, H. Hess: J. Chem. Phys. **107**, 2839 (1997)
15. B.E. Callicoatt, D.D. Mar, V.A. Apkarian, K.C. Janda: J. Chem. Phys. **105**, 7872 (1996)
16. C. Rienecker: Ph.D. thesis, Universität Hamburg (1998)
17. A. Kolmakov *et al.* (in preparation)
18. N. Schwentner, E.-E. Koch, J. Jortner: *Electronic Excitation in Condensed Rare Gases*, Springer, Tracts in Mod. Phys. **107** (1985)
19. J. Xie *et al.*: J. Chem. Phys. **91**, 612, (1989)
20. T.D. Märk, P. Scheier, M. Lezius, G. Walder, A. Stamatovic: Z. Phys. D **12**, 279 (1989)