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The fragmentation dynamics of small $Cs(CsI)_n^+$ cluster ions under low-energy multiple collision conditions

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Dedicated to Professor Tilmann D. Märk, on the occasion of his 60th birthday.

Abstract

The collision-induced dissociations of small caesium iodide cluster ions of the type $Cs(CsI)_n^+$ where $n = 3$–7, have been investigated under low-energy multiple collision conditions. The collisions were performed in the rf-only quadrupole of a *BEqQ* hybrid mass spectrometer. Breakdown graphs of selected parent ions were obtained by varying the laboratory collision energy in the range of 0–400 eV. The fragmentation dynamic established under these conditions provides a link between the well-known decay behaviour occurring unimolecularly and the dissociations following high energy (keV) collisional activation. Of particular interest is the observation that the energy-dependent dissociation pattern supplies support for the occurrence of one-step fission reactions, featuring the evaporation of presumably intact $(CsI)_n$ neutrals as opposed to a sequential decay via *n*CsI losses. The breakdown graphs thus provide a valuable tool to enhance insight into the fragmentation mechanism of these clusters.

Keywords: Fragmentation mechanism; Caesium iodide clusters; Low-energy collisions

1. Introduction

Salt-like clusters of the general formula $C(CA)_n^+$, where C denotes a metal cation and A stands for an anionic counter ion, continue to represent a prime target of fundamental research. This is particularly true for alkali halide clusters, whereby caesium iodide clusters play an exceedingly important role, as these are easily accessible by a variety of methods and composed entirely of monoisotopic elements. Besides desorption-based methods, electrospray ionisation has advanced as a competitive means of production of such clusters [1–3], also enhancing the occurrence of higher charge states [2,3]. Recent investigations include ion mobility studies for the differentiation of cluster structures [4], as well as the use of trapped ion diffraction to obtain information about the cluster lattice [5]. The fragmentation dynamics has also been a focal point of several recent studies [1–3,6].

The fragmentation behaviour of caesium iodide cluster ions has been extensively studied, covering both the unimolecular decompositions, applying for instance mass-analysed ion kinetic energy spectrometry (MIKES) [7–10], as well as high energy collision-induced dissociations (CID) [7,11–14]. The fragmentation efficiency of metastable ions has been correlated with the magic number pattern observed in the mass spectra of such clusters [15]. Collision theory has been developed, studying the translational energy loss of fragment ions during keV collisions [11–14]. The fragmentation mechanisms governing the unimolecular and collision-induced dissociations have been a further focal point of interest. The unimolecular decompositions of small caesium iodide clusters, $Cs(CsI)_n^+$, are characterised by loss of one and/or two CsI moieties. A central issue has been in this context the question as to whether a particular fragment ion has been formed through a one-step fission reaction involving the loss of an intact $(CsI)_n$ unit as opposed to a succession of events via the loss of individual *n*(CsI) units [9,10]. Kinetic energy release data derived by MIKES [9] and the spatial separation of individual processes through the use of an electrically floated collision

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cell [10], showed that unimolecularly the loss of an intact dimer ($(CsI)_2$) prevails over a successive evaporation of two CsI monomers. High-energy collisional activation of $Cs(CsI)_n^+$ clusters in the keV laboratory energy frame led to the formation of a complete set of daughter ions through the formal loss of up to *n*CsI units [11]. It has been possible to collisionally re-ionise the neutral fragments derived from high-energy CID [16], leading to the identification of intact $(CsI)_n$ fragments with *n* being as large as 4, providing further support for the importance of the evaporation of intact neutral moieties (one-step fission) within the decay reactivity of these cluster ions. In order to shed further light onto the fragmentation dynamics of such clusters, the present report investigates the translational energy dependence of low-energy collision-induced dissociations occurring under multiple collision conditions.

2. Experimental

Caesium iodide clusters were produced by fast atom bombardment (FAB) of a solid salt surface applying Xe atoms at 8 keV inside the ion source of a VG-ZAB-HSQ mass spectrometer of *BEqQ* configuration. *B* stands for magnet, *E* denotes the electric sector and *qQ* represents a quadrupole system. The parent ions were initially accelerated by 8 kV, selected by *B* and *E* and decelerated to a particular translational energy in the range of 0–400 eV before entering the "rf-only" quadrupole *q* which operated as the collision region. The second quadrupole *Q* was scanned in order to sample those ions emerging from the collision region. Air was used as the collision gas and introduced into the collision quadrupole to reduce the transmission of the $Cs(CsI)_7^+$ parent ion to 80%. For a given laboratory collision energy, several successive scans were accumulated for one spectrum and stored on a data system. Breakdown graphs were obtained by plotting the relative intensities of all product ions obtained for a given collision energy as a function of the collision energy.

3. Results and discussion

Fig. 1 shows the breakdown graphs of $Cs(CsI)_3^+$ (Fig. 1a) and $Cs(CsI)_4^+$ (Fig. 1b and c). At low collision energies, the $Cs(CsI)_3^+$ ion dissociates into $Cs(CsI)^+$ by the net loss of two CsI units. Unimolecularly, this reaction proceeds via evaporation of an intact dimer ($(CsI)_2$ loss) [9,10], which has also been identified in high-energy collision/re-ionisation experiments [16]. It is thus reasonable to assume that also during low-energy collisions the dimer formation prevails. With increasing collision energy, Cs^+ daughter ions are formed. The onset of the Cs^+ fragment ion formation coincides with the $Cs(CsI)^+$ abundance going through a relative maximum and as the $Cs(CsI)^+$ ion abundance declines, Cs^+ ions are increasingly formed. This strongly suggests that Cs^+ ions are not directly formed from the $Cs(CsI)_3^+$ parent ion, but through a reaction sequence which involves $Cs(CsI)^+$ as an intermediate. The breakdown graph thus clearly indicates a succession of events as the collision energy increases, commencing with the loss of $(CsI)_2$ (as established earlier) from the parent ion and followed by CsI evaporation from the intermediate $Cs(CsI)^+$ fragment ion. The formation of $Cs(CsI)_2^+$ via loss of a single CsI unit remains inaccessible under the applied conditions.

The breakdown graph of $Cs(CsI)_4^+$ is shown in Fig. 1b. This parent ion undergoes at low collision energies the loss of a single CsI unit to form $Cs(Cs)_3^+$. As the $Cs(CsI)_3^+$ ion production reaches its maximum, a further increase in collision energy results in a dissociation pattern that is an almost exact replica of the $Cs(CsI)_3^+$ breakdown graph (Fig. 1a). $Cs(CsI)_3^+$ is thus established as an intermediate of further reactions. The breakdown graph thus reveals a succession of reactions whereby $Cs(CsI)_4^+$ dissociates first into $Cs(CsI)_3^+$ which continues to fragment into $Cs(CsI)^+$ from which eventually Cs^+ is produced at higher collision energies.

Fig. 1c shows also a breakdown graph of $Cs(CsI)_4^+$ precursor ions entering the collision quadrupole at the same range of translational energies as in Fig. 1b. These ions, however, were generated by unimolecular decomposition in the second field-free region of the *BEqQ* instrument employing the mass selection of $Cs(CsI)_6^+$ ions by *B* and using *E* for the selection of $Cs(CsI)_4^+$. The breakdown pattern of these unimolecularly generated $Cs(CsI)_4^+$ ions shows a decay behaviour that may be expected of ions possessing a lower internal energy content than their source-generated counterparts. The maxima for the resulting daughter ion abundances are clearly shifted towards higher collision energies (Fig. 1c) compared to the source-generated $Cs(CsI)_4^+$ ion (Fig. 1b). Unexpected, however, is the simultaneous co-formation of $Cs(CsI)_3^+$ and $Cs(CsI)^+$ ions at low collision energies. As Fig. 1b clearly indicated that both these ions are formed in a successive reaction sequence, therefore, the expectation for Fig. 1c would be that the onset of the $Cs(CsI)^+$ formation is even more shifted towards higher collision energies. The immediate formation of a relatively low abundant amount of $Cs(CsI)^+$ ions may indicate that also a direct fission from the $Cs(CsI)_4^+$ precursor is feasible for these ions. Unfortunately, it can only be speculated if the low internal energy precursor ions might possess a minor isomeric component which may directly decompose into $Cs(CsI)^+$. This finding, however, is the first clear indication from this set of data that entities larger than CsI and $(CsI)_2$ may be expelled directly from such caesium cluster ions.

This interpretation is even more clearly collaborated by the breakdown graph of $Cs(CsI)_5^+$ shown in Fig. 2a. The co-formation of $Cs(CsI)_n^+$ daughter ions with $n = 3$ and 4 is expected because these dissociations are also observed as unimolecular fragmentations involving the loss of $(CsI)_n$ with $n = 1$ and 2 [9]. The relative abundant formation of $Cs(CsI)^+$ in this energy range, however, may be taken as indication of the simultaneous loss of four CsI entities.

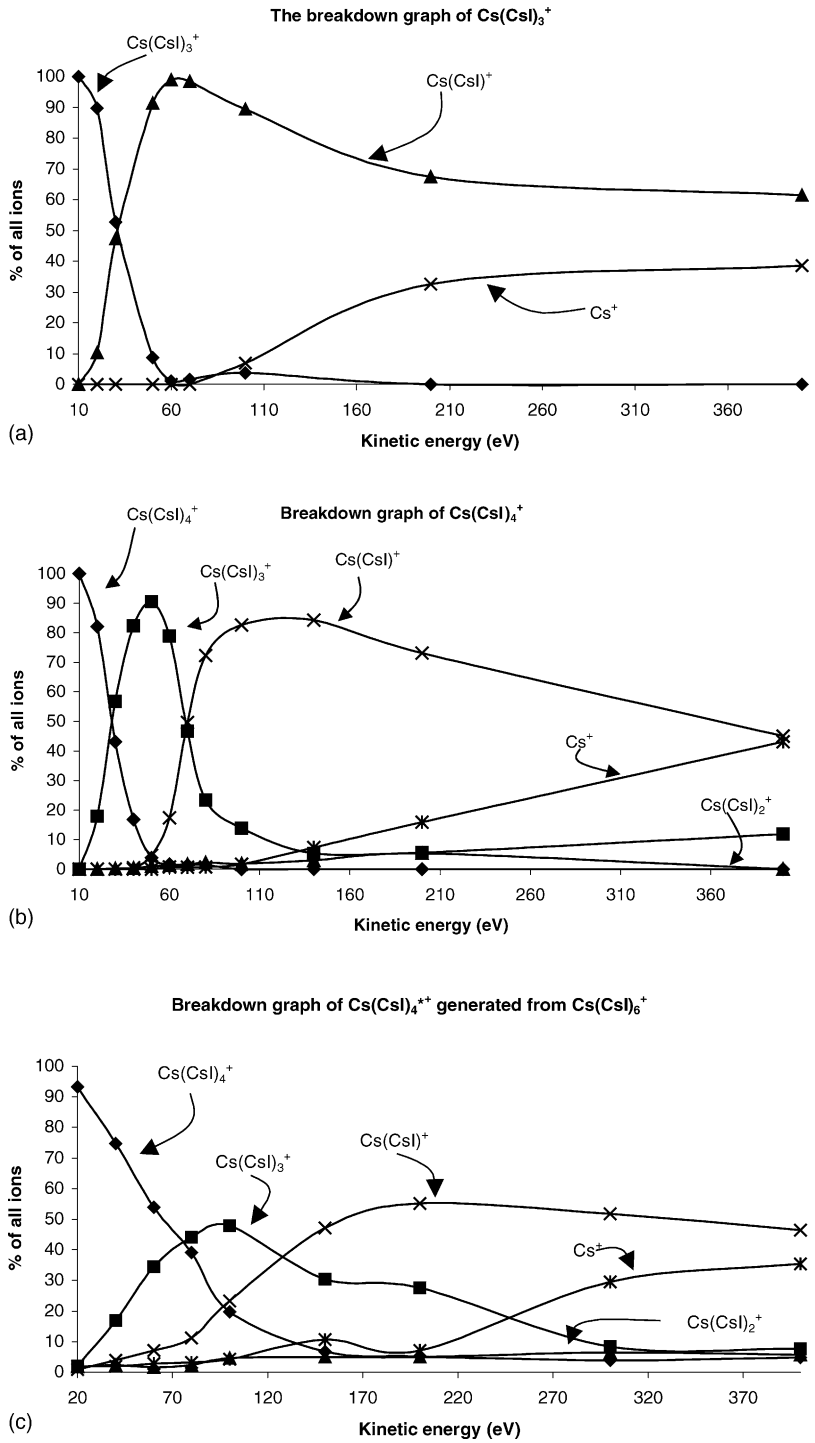

Fig. 1. (a) Breakdown graph of $Cs(CsI)_3^+$, (b) $Cs(CsI)_4^+$ and (c) $Cs(CsI)_4^+$ produced unimolecularly from $Cs(CsI)_6^+$.

Considering the successful re-ionisation of larger intact $(CsI)_n$ units with up to $n = 4$ being expelled from caesium cluster cations in high-energy (keV) collisions [16], it is reasonable to assume that the latter reaction also proceeds via the loss of an intact $(CsI)_4$ neutral. As the $Cs(CsI)_3^+$ abundance goes through a maximum and declines, the $Cs(CsI)^+$ signal rises even further, which is now the consequence of the aforementioned dimer loss from the $Cs(CsI)_3^+$ intermediate.

The energy dependent decay of $Cs(CsI)_6^+$ (Fig. 2b) is essentially consistent with a decomposition pattern that can be deduced from the well-known unimolecular decay behaviour of the parent and resulting fragment ions. At low collision energies $Cs(CsI)_n^+$ with $n = 4$ and 5 are formed, both of which continue to decompose predominantly into $Cs(CsI)_3^+$ as the collision energy increases. The latter ion is besides $Cs(CsI)_n^+$ with $n = 4$ and 5 the main intermediate towards

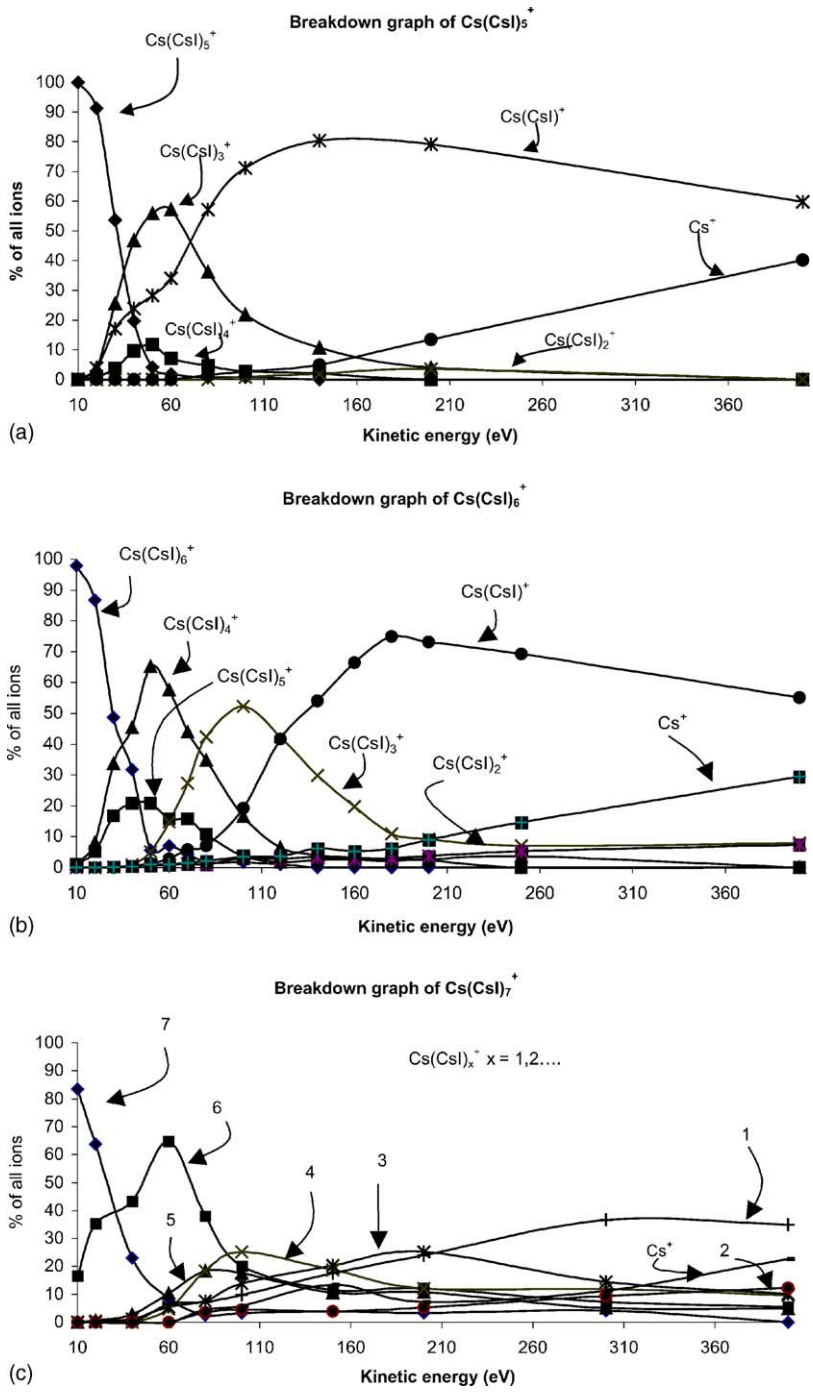

Fig. 2. (a) Breakdown graph of $Cs(CsI)_5^+$, (b) $Cs(CsI)_6^+$ and (c) $Cs(CsI)_7^+$.

production of $Cs(CsI)^+$ from which it is formed presumably via $(CsI)_2$ loss. The $Cs(CsI)_6^+$ precursor ions is also the largest cluster which under the applied conditions allowed a meaningful interpretation of the fragmentation dynamics. Fig. 2c provides the breakdown graph of $Cs(CsI)_7^+$. The loss of one CsI unit is the least energy demanding reaction pathway. With increasing energies the $Cs(CsI)_6^+$ production is accompanied by an almost simultaneous formation of all other feasible fragment ions, preventing a further assignment of the energy-dependent daughter ion formation. Upon entering the collision quadrupole at relative moderate collision energies, all fragment ions commonly observed by high-energy CID are readily formed from the $Cs(CsI)_7^+$ precursor ion under the applied conditions. This behaviour is in line with earlier findings, indicating a more pronounced dissociation efficiency with increasing size of these clusters [7].

4. Conclusion

In summary, low-energy collisions have been performed under multiple collision conditions with a "classic" amongst the salt-like clusters. The breakdown graphs obtained represent the missing link between the well-known unimolecular decomposition behaviour and the equally well-established dissociations following high-energy collision. The collision energy-dependent fragmentation dynamics follows predominantly a succession of events that can be predicted from the metastable ion dissociations, comprising the loss of one and/or two CsI units (the later presumably as dimer). However, the breakdown graphs also reveal the occurrence of daughter ions of lower mass than detected unimolecularly, which is tentatively interpreted as collision-induced loss of larger intact neutrals of $(CsI)_n$ with $n > 2$, as observed in earlier high-energy CID experiments [16]. Despite the fact that the present experiments cannot provide more clarifying insight into the nature of the neutrals lost in these dissociations, the energy-dependent breakdown graph offers additional new insight into the fragmentation dynamics of caesium iodide cluster ions, bridging the gap between the dissociation behaviour at threshold and following highly energetic collisions.

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