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Chemical Physics 262 (2000) 105–113

Chemical Physics

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Decay pathway determination of even-size dicationic silver clusters: Ag_{16}^{2+} and Ag_{18}^{2+} revisited by pre-precursor selection and sequential decay ☆

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Received 24 March 2000

Abstract

It is demonstrated how by selection of pre-precursor cluster ions Ag_{2n+1}^{2+} and collision-induced dissociation an ensemble of Ag_{2n}^{2+} can be produced, which is not contaminated by Ag_n^+ clusters of the same size-to-charge state ratio, n/z. By use of this technique, Ag_{16}^{2+} and Ag_{18}^{2+} precursor ensembles have been prepared for further investigations. They are observed to decay by neutral monomer evaporation, $Ag_{2n}^{2+} \rightarrow Ag_{2n-1}^{2+} + Ag$, and trimer fission, $Ag_{2n}^{2+} \rightarrow Ag_{2n-3}^{+} + Ag_3^+$, and show no sign of symmetric fission. © 2000 Elsevier Science B.V. All rights reserved.

PACS: 36.40.Qv
Keywords: Stability and fragmentation of clusters

1. Introduction

The variation of their charge state adds another dimension to the "table of atomic clusters" in addition to the range of elements and the number of constituent atoms [1]. In particular, for metal clusters M_n^{z+} [2] (with the element's symbol, M, the number of atoms, n, and the charge state, z), the clusters' property are expected to be influenced by the number of atomic valence electrons n_e (where $n_e = n - z$ in the case of simple metals). In contrast, clusters that are dominated by geometric effects, i.e. by the spatial arrangement of the atoms, should show properties that depend directly on n, regardless of their charge state. In addition, there are further phenomena, which are observed for multiply charged clusters only, like fission, i.e.

☆ This article comprises part of the dissertation of S. Krückeberg.

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PII: S0301-0104(00)00213-5

the breakup into two or more charged fragments. Thus, there have been several attempts to investigate multiply charged clusters, as recently reviewed by Näher et al. [2].

The preparation and experimental study of multiply charged clusters, however, is a particular challenge: In general, clusters are produced as ensembles with a range of various sizes. Therefore, even for most studies that are not charge state sensitive, a size selection by some form of mass spectrometry (MS) is a necessary pre-requisite for detailed investigations. When the scope is expanded and the size and charge state dependence are to be studied simultaneously, again MS techniques have to be employed. However, these methods are, in general, only sensitive to the mass-over-charge (m/z) ratio, i.e. for our field of interest the n/z ratio. Therefore, many ambiguities may still remain. This paper shows, for particularly interesting cases, how the challenge of the preparation of cluster ensembles with defined size and charge state can be confronted.

After a short review of previous experiments of fragmentation pathways of doubly charged metal clusters (Sections 2.1), the advantages of ion trapping devices in cluster research are discussed (Section 2.2) and the setup of the present experiments described (Section 3). The results of the studies in two cases of particular interest, Ag_{16}^{2+} and Ag_{18}^{2+}, are presented and discussed (Section 4) before an outlook onto possible further investigations is given (Section 5).

2. Multiply charged metal clusters and mass spectrometry

2.1. Previous experiments

Most experiments on the properties of multiply charged metallic systems have focused on doubly charged clusters. In general, these have been found either to decay by evaporation of neutral particles or to fragment into two products that are both charged. The latter process is referred to as fission [2]. Since there are only two excess charges, fission is always charge-symmetric for a doubly charged cluster, but the mass asymmetry between the two products can vary. Experiments on this subject have to rely on mass spectrometric methods for the selection of a precursor as well as for the determination of the fragments. As mentioned above, MS techniques are sensitive to the mass-to-charge ratio only. Now, a doubly charged cluster of even size has the same mass-to-charge ratio as a singly charged cluster of half that size. Hence, the selected ensemble of integer n/z ratio may contain both singly and doubly charged clusters. Furthermore, the signals in the fragmentation spectra are ambiguous as well. This is especially problematic in the case of mass-symmetric charge-symmetric fission: the precursor ion and the fragment ions have the same n/z ratio.

One of the pioneering experiments on multiply charged metal systems was carried out by Saunders [3,4] who used a triple-quadrupole arrangement. Doubly charged gold clusters were produced in a liquid metal ion source (LMIS), mass selected in the first quadrupole (QP) section, subsequently excited in the second QP by collision-induced dissociation (CID) and eventually mass-analyzed in the third QP. Although single-collision conditions were used, sequential decays were observed, as the clusters emerging from the LMIS are very hot. However, it was possible to deduce dominant neutral monomer evaporation for $n = 15$–18 and trimer fission (i.e. the decay $Au_n^{2+} \rightarrow Au_{n-3}^{+} + Au_3^{+}$) for $n = 14, 12, 10, 9$. The sizes $n = 11, 13$ could not be investigated. These findings are consistent with the later Penning trap investigations at low excitation energies [5]. In a parallel effort, Brechignac et al. investigated doubly charged alkali metal clusters. Neutral clusters were charged by photoionization without prior mass selection and the resulting metastable decay was investigated. For small systems, mass-asymmetric fission with preference of trimer fission was observed, while for larger systems a competition of this fragmentation scheme with neutral monomer evaporation occurred. The transition sizes for Li, Na, and K were $n \approx 24$–26 [6]. Due to its recoil momentum, the light fission fragments were not visible in the spectrum. In addition, mass-selected singly charged K_n^{+} ($n = 5$–12) were photoionized and their fragmentation investigated, where trimer fission prevailed [7].

At about the same time, Katakuse et al. investigated doubly charged silver clusters [8,9]. The clusters were sputtered, accelerated and brought into a double focussing mass spectrometer consisting of an electric and subsequently a magnetic sector. Metastable decays in the field-free region between the acceleration section and the entrance of the first sector can be detected in the following way: The instrument is set to detect one specific fragment; its abundance as a function of the acceleration voltage indicates possible precursors. This method can identify singly charged fragments stemming from doubly charged precursors, but cannot give any information on doubly charged clusters decaying by emitting a neutral particle. In this arrangement, the clusters emerge from the sputter source at a very high internal energy which results in (multiple) sequential decay. The fragment–precursor correlations were interpreted to show a tendency of near mass-symmetric fission for the larger, and rather mass-asymmetric fission for the smaller clusters in the investigated size range $n = 12$–22 [8,9].

Experiments performed with low energy CID in a Penning trap on mass-selected, doubly charged silver clusters ($n = 9$–25) gave a different picture [10,11]: The sizes $n = 9$, 10, 12–14, and 16 showed trimer fission, and for the remaining sizes, neutral monomer evaporation was observed. No signs for more mass-symmetric channels were found, though the question of exactly mass-symmetric fission of even-size doubly charged clusters, $Ag_{2n}^{2+} \rightarrow 2Ag_n^+$, was not addressed explicitly. Penning trap experiments have also been extended to gold and copper clusters [5,12].

After the existence of higher charge states of metal clusters was observed in mass spectra [13,14], their decay modes have also been addressed experimentally. Although they are not central to the current investigations, we mention briefly two examples. Chandezon et al. carried out collision of highly charged ions with neutral precursor clusters. The analysis of the resulting fragments showed that the clusters were ionized to charge states of up to $z = 6$ before decaying [15]. Extensive work on alkali and alkaline-earth cluster performed by Heinebrodt et al. provided appearance sizes of systems with up to $z = 7$ as well as information on their decay pathways [16].

On the theoretical side, fragmentation of multiply charged clusters can be addressed in the framework of a liquid drop model [2]. In the first approach, the latter is only used to calculate the difference in energy between the initial cluster and the fragments, each taken as a sphere. The Coulombic repulsion of the fission products is then introduced as the electrostatic interaction of two touching spheres. This model already explained the preference for fission and especially for mass-asymmetric fission for smaller clusters. Other approaches calculate the energies of deformed droplets that eventually split up into the fragments [3,14,17]. Also finite-size effects can be included [18,19], i.e. shell and odd–even effects. It has been demonstrated that a liquid drop model, combined with finite-size information as measured for singly charged clusters, can successfully predict the dissociation energies of doubly charged silver clusters [20].

Still, one may ask whether mass-symmetric fission occurs for special cluster sizes. For example, Ag_{18}^{2+} could favor the decay into $Ag_9^+ + Ag_9^+$ over trimer fission, since both fragments would have closed electron shells for the closed shell structure of the two fragments, similar to the decay of Li_{30}^{2+} to $Li_{21}^+ + Li_9^+$ as observed by Brechignac et al. [21].

2.2. Ion trapping of (multiply charged) clusters

Since the discovery of "magic numbers", i.e. pronounced abundance signals at particular cluster sizes, of noble gas [22] and metal clusters [23], many important investigations in the field of cluster research have been made by use of particle beam setups where the clusters are studied in flight from a source to a detector. However, there are severe shortcomings of these systems, in particular the following two: (a) Since the functions are separated in space, each additional step in the preparation or investigation of a particular cluster species requires a dedicated piece of hardware along the path of the cluster beam. (b) Even heavy clusters of low kinetic energy have a limited flight

duration on their way from production in the source to extinction in the detector.

Ion traps, on the other hand, are wall-less containers that allow an interaction-free storage of clusters for long periods. If desired, various interactions may be introduced at will to modify the clusters and investigate their properties. Once such an interaction step has been established, it can be repeated without any additional hardware, since the experimental events are separated in time rather than in space.

One of the most important of such experimental steps is the selection of a particular precursor species of interest. As mentioned above, methods of MS only allow a selection of specific mass-overcharge state ratios (m/z). Sequential selection(s) and analysis is often denoted by "MS/MS" or "MS^n" [24]. In particular, in ion cyclotron resonance (ICR) trap experiments, the combination of selection(s) and CID reactions has a long tradition and may include many steps (as in Ref. [25]). Some of the many applications of traps in the field of cluster physics are the study of ion molecule reactions (e.g. Refs. [26–28]) and the application of electron diffraction [29].

The experiments presented in the following make use of extended MS^n techniques to answer particular questions on the fragmentation pathways of doubly charged clusters. By use of unequivocal selection of an appropriate "pre-precursor", the clusters Ag_{16}^{2+} and Ag_{18}^{2+} are selected without contamination by the singly charged clusters of the same n/z ratio, Ag_8^+ and Ag_9^+, respectively. In addition, by monitoring the total number of ions and the fragmentation spectrum as a function of excitation energy, the products are further identified. Thus, it is demonstrated how complex event sequences allow to address the question of symmetric versus asymmetric fission.

3. Experimental setup and procedure

The various aspects of the Mainz cluster trap have been described recently [30–32]. The setup includes a Penning (ICR) trap with an external cluster-ion source and transfer section on one and a time-of-flight (TOF) drift section with conversion-electrode ion detector on the other end of a superconducting magnet.

For cluster production, a Smalley-type source [33] further developed at Konstanz is used [34]. A Nd:YAG laser vaporizes a silver wire. A plasma is formed in the process and thus ions as well as neutral atoms are produced. In a helium gas pulse applied into the source body, the material condenses and small silver clusters are formed before they are carried by the helium through a nozzle into the differentially pumped transfer section to the Penning trap. The transfer is aided by electrostatic ion optical elements (lenses and deflectors). The clusters are captured in flight [35] by appropriate gate pulses applied to the entrance endcap of the Penning trap. There is some selection of the size of clusters transferred due to their kinetic energy and the appropriate choice of potential difference between source and trap [31].

The trap is composed of a superposition of a homogeneous magnetic field of 5 T and a axial quadrupolar electric potential which confines the ions along the magnetic field lines (well depth of 8.5 V). Both magnetic and electric fields are static as opposed to the radiofrequency (Paul) "ion traps" [36]. The physics of Penning traps (also called "ICR cells") has been described in detail by Brown and Gabrielse [37]. Some limitations with regard to heavy particles such as large clusters have been discussed elsewhere [38]. The Penning trap is the heart of the setup: Various kinds of interaction of the stored clusters with neutral atoms or molecules (chemically reactive or not), photons and electrons have been introduced over the recent years [30–32]. In order to apply collision gas pulses, a gated piezo valve has been installed in the vicinity of the trap [39]. An electron beam is produced by use of heated filaments halfway between the cluster source and the Penning trap. The filaments are positioned somewhat off-axis to allow the passage of the cluster ions from the source to the trap. Following the fringe magnetic field lines, the electrons are guided axially through the trap.

Reaction product analysis is performed by axial ejection of the ions from the trap and conventional TOF MS [30]. While this leads to a limited mass resolution (see the spectra shown later), highest sensitivity can be reached by use of a conversion-

electrode detector for single ion counting: Similar to a Daly detector, the cluster ions are collided at high energy (15 keV) onto the conversion electrode which leads to the emission of secondary electrons. The latter are detected by a tandem microchannelplate (MCP) detector. This detector arrangement allows free axial line of sight into the center of the trap which facilitates the application of laser beams and allows, e.g., time-resolved photo dissociation studies [40,41].

The source produces only singly charged (and neutral) clusters. Thus, for the present investigations, the following experimental event sequence has been used (Fig. 1): Several cluster ion pulses are accumulated [39] by repeated production, transfer and capture, typically 30 times, at a repetition rate of 10 Hz. When a cluster ensemble of sufficient amount has been reached, it is irradiated by the electron beam (of an energy of about 150 eV for 600 ms) for the production of multiply charged clusters [42]. The clusters of n/z ratio of interest are selected by radial ejection of all other species via the excitation of their cyclotron motion. After these preparatory measures, the cyclotron radius of the selected cluster ions is increased by single-frequency ICR excitation and argon gas is pulsed into the trap. In a multi-collision process [43], kinetic energy is converted into internal energy of the clusters which leads to their dissociation. This is demonstrated in Fig. 2 for the accumulation of Ag_{16}^{+} (Fig. 2a), electron bombardment (Fig. 2b), selection of $n/z = 8$ (Fig. 2c), and CID of the selected species (Fig. 2d). For this presentation, the

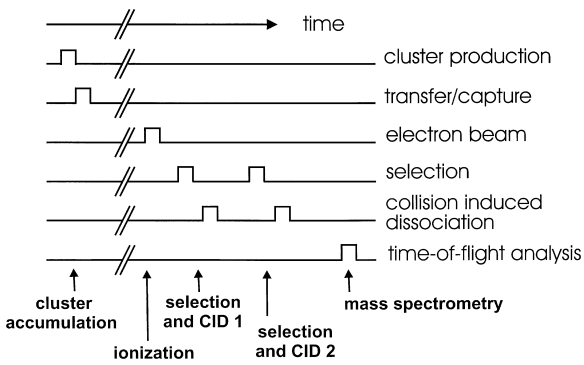

Fig. 1. Experimental event sequence.

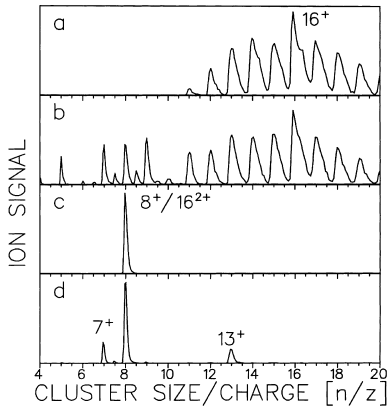

Fig. 2. CID of a mixture Ag_{16}^{2+} and Ag_{8}^{+}: TOF spectra after (a) accumulation, (b) electron impact ionization, (c) selection of $n/z = 8$, and (d) CID of the selected $n/z = 8$ clusters.

experimental event sequence has been terminated in each case after the respective event of interest and the stored clusters have been analyzed by TOF MS as described above. During the electron bombardment, residual gas molecules are ionized and lead to a background signal which extends up to about $m/z = 450$ amu per electron. In order not to saturate the MCPs, the TOF drift tube potential is gated to only let the higher-mass ions pass, and consequently, the spectra are shown for the range $n/z = 4$–20.

Typically 10 ions are registered for each experimental sequence. The sequence is repeated to improve the statistical significance of the data, and 100 spectra are added for a given set of experimental parameters. For the present study, the ICR excitation amplitude for CID is adjusted such that while a significant part of the clusters have decayed, not too many have undergone sequential decays.

The event sequences with CID are alternated with sequences where no ICR excitation has been applied. This procedure leads to quasi-simultaneous reference spectra which allow various checks such as on the performance of the cluster source and the selection steps [30].

As indicated in Fig. 1, the present measurements involve in general two pairs of selection/CID events. The first is a preparatory measure ("pre-precursor selection") for the production of a pure precursor ensemble, in this example Ag_{16}^{2+}.

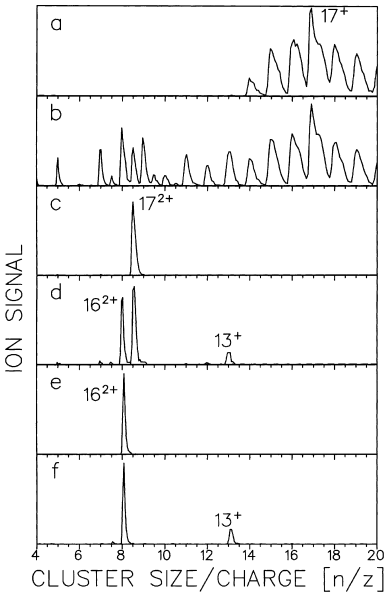

Fig. 3. CID of Ag_{16}^{2+} produced by CID of Ag_{17}^{2+}: TOF spectra after (a) accumulation, (b) electron impact ionization, (c) selection of Ag_{17}^{2+}, (d) CID of Ag_{17}^{2+}, (e) selection of Ag_{16}^{2+} and (f) CID of Ag_{16}^{2+}.

Thus, the full sequence looks as shown in Fig. 3: Ag_{17}^{+} is accumulated (Fig. 3a) to first produce Ag_{17}^{2+} by electron impact ionization (Fig. 3b) which is selected (Fig. 3c). Note, that only the signals of even-size clusters can be contaminated by singly charged species. In contrast, the odd-sized Ag_{n}^{2+} appear at half-integer n/z values. Thus, we now have a pure sample of Ag_{17}^{2+} (Fig. 3c). CID converts these clusters into Ag_{16}^{2+}. Since sequential decay leads to further decay products (Fig. 3d), a pure Ag_{16}^{2+} sample has to be produced by another selection step (Fig. 3e). Finally, CID can be performed on an Ag_{16}^{2+} ensemble which is not contaminated by Ag_{8}^{+} (Fig. 3f), which has an identical n/z ratio.

The nature of Ag_{16}^{2+} decay will be discussed in Section 4. At this point, it is worthwhile, however, to complete the story of precursor selection by a look at the decay of a pure Ag_{8}^{+} ensemble (Fig. 4). Ag_{n}^{+} clusters around $n = 8$ may be captured (Fig. 4a) by an appropriate shift of the potential of source or trap [31]. No electron beam is applied, and Ag_{8}^{+} is selected (Fig. 4b). CID leads to monomer evaporation to Ag_{7}^{+} (Fig. 4c), which

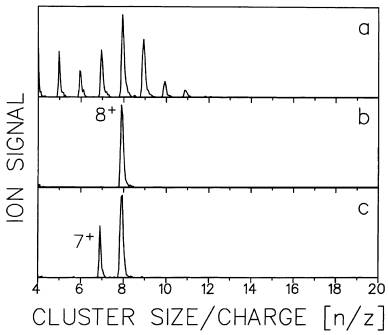

Fig. 4. TOF spectra of Ag_{8}^{+} after (a) capture, (b) selection, and (c) CID.

explains the $n/z = 7$ signal in the spectrum of Fig. 2d.

4. Results and discussion

The CID spectrum of Fig. 2 shows fragment signals at $n/z = 7$ and 13 and a very small signal at $n/z = 7.5$. The latter two signals can only be due to the decay of Ag_{16}^{2+}. It is evident from Section 3 that the $n/z = 7$ signal stems from the singly charged precursor Ag_{8}^{+}, since this is the only decay channel observed in Fig. 4 while it is absent in the case of Ag_{16}^{2+} selection (Fig. 3). Thus, it can be concluded that the main Ag_{16}^{2+} dissociation pathway is trimer fission, $Ag_{16}^{2+} \rightarrow Ag_{13}^{+} + Ag_{3}^{+}$, with a small probability of neutral monomer evaporation, $Ag_{16}^{2+} \rightarrow Ag_{15}^{2+} + Ag$.

The situation is similar in the case of Ag_{18}^{2+}. Fig. 5 shows spectra for increasing CID energies of an Ag_{18}^{2+}/Ag_{9}^{+} mixture (Fig. 5, top) and of a Ag_{18}^{2+} ensemble (Fig. 5, bottom). The latter is produced by pre-precursor selection of Ag_{19}^{2+}, its CID decay to Ag_{18}^{2+} and renewed selection. For the mixture, signals appear at $n/z = 8.5$, 8, 15, and for higher energy at 7. The pure Ag_{18}^{2+} shows fragments at $n/z = 8.5$, 8, 15, and for higher energy also at 13 and 14.

The $n/z = 8.5$, and 15 signals can only be explained by trimer fission and neutral monomer evaporation, respectively, of Ag_{16}^{2+}. A direct fission of the form $Ag_{18}^{2+} \rightarrow Ag_{10}^{+} + Ag_{8}^{+}$ to explain the peak at $n/z = 8$ is excluded since there is no corresponding signal at $n/z = 10$.

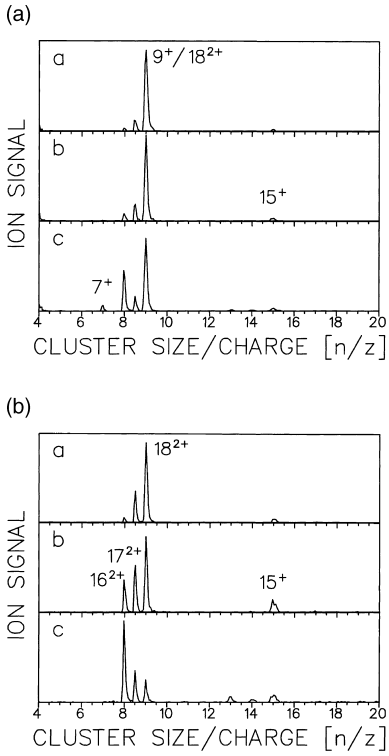

Fig. 5. Top: CID TOF spectra of mixture of Ag_{18}^{2+} and Ag_9^+; bottom: CID of Ag_{18}^{2+} produced by CID of Ag_{19}^{2+}. In both cases, the CID excitation amplitude increases from spectrum a to spectrum c.

The decay pathways of singly charged silver clusters have been discussed in detail elsewhere [44]: Ag_9^+ decays into Ag_8^+ which continues to Ag_7^+. Ag_{15}^+ shows neutral monomer evaporation to Ag_{14}^+ which, in turn, decays to Ag_{13}^+. However, the decay chain $Ag_{15}^+ \rightarrow Ag_{14}^+ \rightarrow Ag_{13}^+$ cannot explain the observed intensity ratios, where Ag_{13}^+ and Ag_{15}^+ are strong with respect to Ag_{14}^+. Thus, Ag_{13}^+ has to be fed through another channel, too. There is a natural explanation: At higher CID energies, the Ag_{17}^{2+} fragments continue to decay to Ag_{16}^{2+} [10,11] and it is the latter that contributes to the Ag_{13}^+ signal to lift it to higher intensity than expected from a sequential decay via Ag_{15}^+. A competing Ag_{14}^+ contribution from a potential fission $Ag_{17}^{2+} \rightarrow Ag_{14}^+ + Ag_3^+$ is not expected, since this reaction has not been observed in earlier investigations [10,11].

It can be concluded for Ag_{18}^{2+} that there is mainly neutral monomer evaporation, $Ag_{18}^{2+} \rightarrow Ag_{17}^{2+} + Ag$, and also competition of trimer fission, $Ag_{18}^{2+} \rightarrow Ag_{15}^+ + Ag_3^+$. But there is no indication of a more symmetric fission reaction. In principle, there could still be some contribution of $Ag_{18}^{2+} \rightarrow Ag_9^+ + Ag_9^+$. However, Ag_9^+ would further decay to Ag_8^+ and the latter continues to Ag_7^+, which is not observed. In addition, a symmetric breakup of Ag_{18}^{2+} into $Ag_9^+ + Ag_9^+$ would result in an increase of the cluster ion signal at $n/z = 9$, since the detection proceeds via single ion counting. Fig. 6 shows the intensity of that signal as a function of the CID excitation amplitude. To avoid any possible bias by drifts of experimental parameters, the intensity has been normalized with respect to a quasi-simultaneous measurement of the Ag_{18}^{2+} reference signal in the absence of CID excitation. No increase of the signal at $n/z = 9$ is observed. Indeed, the decrease of the signal at $n/z = 9$ is just compensated by the increase of the sum of all fragment ion signals (also shown in Fig. 6). Thus, there is no indication of any kind of symmetric fission.

More generally, any fission into two fragments with $n \geqslant 4$ would lead to an increase of the total ion signal. No indication of such an increase is given by the total ion intensity. However, some indication of another "fission pathway" even more asymmetric than trimer fission has been observed: 1% of the fragment ions (relative to all fragments)

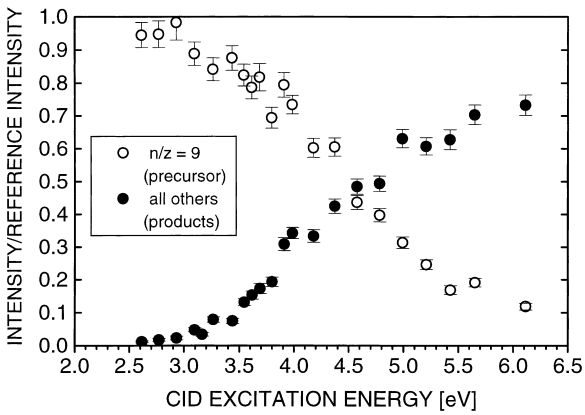

Fig. 6. Relative intensities for the signals of the precursor and the fragments after CID of Ag_{18}^{2+} ($n/z = 9$), as a function of the excitation amplitude. The signals have been normalized with respect to the signal intensity of Ag_{18}^{2+} in reference measurements without the application of a CID excitation.

appear at $n/z = 17$. Therefore, in addition to neutral monomer evaporation, "monomer fission" is observed for about every one out of 100 decays.

5. Conclusion and outlook

Doubly charged cluster ions have been investigated in a Penning trap. It has been shown how by use of several sequential MS events a selection of a particular cluster size (mass) and simultaneously a particular charge state of interest can be selected for further investigation. Thus, it has been possible to prepare defined samples of pure Ag_{16}^{2+} and Ag_{18}^{2+}. Upon further collisional excitation, these clusters show mainly neutral monomer evaporation and trimer fission. In addition, the breakup of Ag_{18}^{2+} into Ag_{17}^{+} and Ag^{+}, i.e. monomer fission has been observed on a level of two orders below the main pathways. No indication for mass-symmetric fission is found.

The present experiments were performed at relatively low activation energy. This may explain the discrepancy with respect to earlier reports of more symmetric fission channels [8,9]. The decay pathway probabilities of multiply charged clusters may well depend on the activation energy, in analogy to recent observations with regard to the evaporation of monomers and dimers [45]. Thus, it will be interesting to extend the measurements on selected multiply charged metal clusters by the application of pulsed laser excitation to reach higher activation energies before the breakup of the clusters.

It should be noted that there is a second and even more direct way to select a contamination-free sample of Ag_n^{2+}. If the resolving power is sufficient (in the present case of the order of 10 000), appropriate isotopomers may be selected. However, this alternative method is based on the ejection of lots of precious ions. And in all cases where there is only one isotope readily available, say e.g. for gold clusters, there is also only one single isotopomer. The present experiments show a way how to deal with this situation.

Finally, note that, in addition to multiply charged cations, also multiply negatively charged clusters have recently been discovered [46,47]. Thus, the stage is set for further exciting experiments on the various modes of reactions of activated metal clusters.

Acknowledgements

This work was financed in part by the Deutsche Forschungsgemeinschaft (Schw 401/13). We further thank the Materials Science Research Center at Mainz and the Fonds der Chemischen Industrie. S.K. has been supported by the Studienstiftung des deutschen Volkes, C.W. by the Graduiertenkolleg Physik und Chemie Supramolekularer Systeme.

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