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# Observation of electronic and geometric shell structures of small silver clusters

## Electron impact ionization/dissociation of size selected silver clusters

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**Abstract.** Singly charged silver clusters $\mathrm{Ag}_n^+$ in the size range $n = 17$ to $n = 78$ have been captured and stored in a Penning trap, size selected and subjected to an electron beam which leads to further ionization as well as dissociation. The resulting abundance spectra of doubly and triply charged clusters show several features: (1) A critical size for the production of doubly charged clusters which can be understood in terms of the decay pathways as previously investigated by collision induced dissociation, (2) an odd-even alternation in the abundance of singly and doubly charged clusters which inverses sign with change of charge state, (3) prominent signals for particular doubly and triply charged species that indicate both electronic and geometric influences on the clusters' stability.

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

## 1 Introduction

The significance and interplay of electronic and geometric structure and stability is a fascinating facet of the science of metal clusters. Electronic shells have been observed first in abundance spectra of alkali and noble metal clusters [1, 2]. Enhanced stabilities occur at cluster sizes where 'magic' numbers of atomic valence electrons, $n_\mathrm{e}$, happen to fill an energetic shell in the average potential due to the ionic core of the cluster atoms, e.g. in the spherical case at $n_\mathrm{e} = 8, 20, 34, 58, \ldots$ [2]. An additional beat pattern, the supershells, can be observed for larger metal clusters [3]. However the electronic shells dissapear with incrasing cluster size in favor of geometrically stabilized configurations [4]. Such geometrical shells of atoms have been found for small noble gas clusters ($n = 13, 55, 147$) [5], clusters of fullerenes $(\mathrm{C}_{60})_{55}$ [6] but also for ligand stabilized gold clusters $\mathrm{Au}_{55}$ in solution [7, 8] and their sputter products $(\mathrm{Au}_{13})_{55}$ [9].

The comparison of experimental abundance spectra with calculated stabilities allows the determination of the clusters' structure. However, even the experimental results themselves can give model independant information about electronic or geometric effects, if the investigations include a variation of both the cluster size, $n$, and the charge state, $z$. As for silver clusters sputter experiments have provided abundance spectra for singly charged cations and anions [10, 11] while laser- and electron-induced ionization of neutral precursors [12, 13] led to spectra of doubly and triply charged cations. In the latter case the broad initial size distribution resulted in significant overlap of clusters of different charge states and hence complicated the analysis.

We have developed a technique for electron induced ionization/dissociation of size selected singly charged metal clusters stored in a Penning trap [14]. After presenting the experimental setup and procedure (Sect. 2) we give an overview of the abundance spectra in the size range up to $n = 78$ (Sect. 3). Then the results are compared with previous experiments and discussed with respect to the cluster structure (Sect. 4).

## 2 Experimental setup and procedure

Detailed descriptions of the Penning trap system have been published recently [15–17]. Singly charged metal cluster

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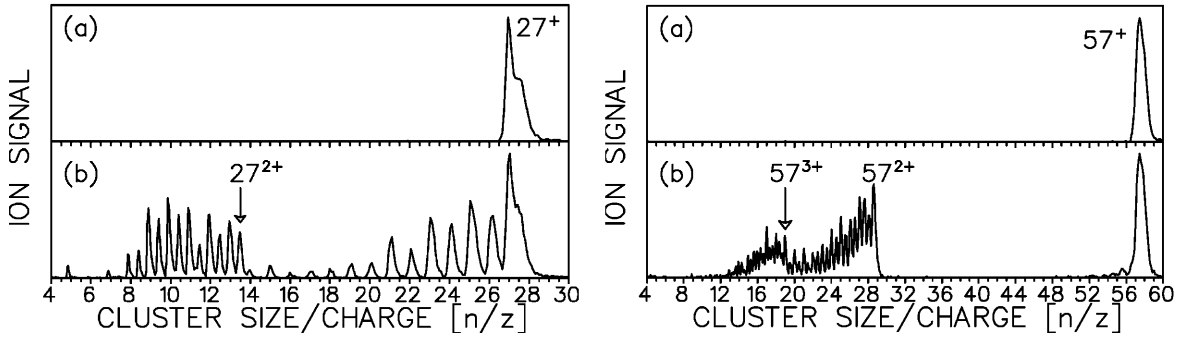

**Fig. 1.** Abundance spectra of $\mathrm{Ag}_{27}^{+}$ (left) and $\mathrm{Ag}_{57}^{+}$ (right) before (top) and after (bottom) the application of the electron beam. For details see text.

ions produced by a laser vaporization source are transferred to, accumulated and centered in a Penning trap. One cluster size is selected by radial ejection of all other ions. The clusters are subsequently bombarded for 600 ms with electrons (150–200 eV). Thus the clusters may be transferred to higher charge states [14, 18]. The charged reaction products remain stored in the trap until the surviving precursor and the fragment ions are axially ejected and analyzed by time-of-flight (TOF) mass spectrometry. Single ion detection is performed by use of a conversion dynode detector. During the electron bombardment the residual gases, including pumping liquids from diffusion pumps, are ionized and result in large background intensities in the mass range up to $400u$. Therefore, only the fragmentation pattern for $n/z \geq 4$ is analyzed.

**Table 1.** Summary of clusters with high abundance.

| Cluster $\mathrm{Ag}_{n}^{z+}$ | $n$ | $z$ | $n_\mathrm{e} = n - z$ |
|---|---|---|---|
| $\mathrm{Ag}_{21}^{+}$ | 21 | 1 | **20** |
| $\mathrm{Ag}_{22}^{2+}$ | 22 | 2 | |
| $\mathrm{Ag}_{28}^{2+}$ | 28 | 2 | **26** |
| $\mathrm{Ag}_{50}^{2+}$ | 50 | 2 | **48** |
| $\mathrm{Ag}_{51}^{3+}$ | 51 | 3 | |
| $\mathrm{Ag}_{55}^{2+}$ | **55** | 2 | 53 |
| $\mathrm{Ag}_{55}^{3+}$ | | 3 | 52 |
| $\mathrm{Ag}_{60}^{2+}$ | 60 | 2 | **58** |
| $\mathrm{Ag}_{61}^{3+}$ | 61 | 3 | |

## 3 Results

As an example, Fig. 1 shows the spectra of $\mathrm{Ag}_{27}^{+}$ (left) and of $\mathrm{Ag}_{57}^{+}$ (right) before (top) and after (bottom) the application of the electron beam. In the case of $\mathrm{Ag}_{27}^{+}$, singly charged clusters with $n \leq 27$ and doubly charged clusters in the size range $n = 16 - 27$ can be observed. The singly charged clusters show an odd-even staggering with odd-$n$ clusters displaying a higher abundance than their even-$n$ neighbours. For the doubly charged systems the odd-even staggering is reversed: here, even-$n$ clusters are more prominent than odd-$n$ clusters.

In the case of $\mathrm{Ag}_{57}^{+}$ the production of singly charged fragments is very much reduced. In addition to the doubly charged clusters triply charged ones appear as well. There is no odd-even pattern at these clusters sizes, but some peaks show a special prominence (see below).

The investigations have been conducted for several cluster sizes ranging from $n = 17$ to 78. All spectra are shown in Fig. 2. In the case of small clusters ($n = 17 - 31$), the chain of doubly charged clusters is limited towards small sizes: There are no doubly charged clusters below $n = 16$ and only small amounts for $n = 17$. The odd-even staggering mentioned above in the case of $\mathrm{Ag}_{27}^{+}$ is found in all spectra for the singly charged systems and in reversed order for the doubly charged systems. In addition, $\mathrm{Ag}_{22}^{2+}$ shows a high relative abundance, especially in comparison to the next larger cluster.

With increasing cluster size ($n = 33$ to $n = 52$) the amount of singly charged fragments decreases. In addition to doubly charged clusters, triply charged systems can be observed. Though the regions of $z = 2$ and $z = 3$ partly overlap in the TOF spectra some signals ($\mathrm{Ag}_{21}^{+}$, $\mathrm{Ag}_{22}^{2+}$, $\mathrm{Ag}_{28}^{2+}$) can be identified, where either the signals themselves are very intense or those of the next-larger clusters have a particularly low intensity.

For even larger precursor clusters ($n = 55$ to $n = 78$) the regions of doubly and triply charged clusters become better separated and the relative amount of triply charged clusters increases. Prominent signals (or exceptionally low signals at the following cluster size) occur for $\mathrm{Ag}_{50}^{2+}$, $\mathrm{Ag}_{55}^{2+}$ and $\mathrm{Ag}_{60}^{2+}$ as well as for $\mathrm{Ag}_{51}^{3+}$, $\mathrm{Ag}_{55}^{3+}$ and $\mathrm{Ag}_{61}^{3+}$. A summary of all observed pronounced cluster signals is given in Table 1.

## 4 Discussion

Most of the observations can be explained in terms of the fragmentation pathways as previously investigated by collision induced dissociation [19] and by electronic

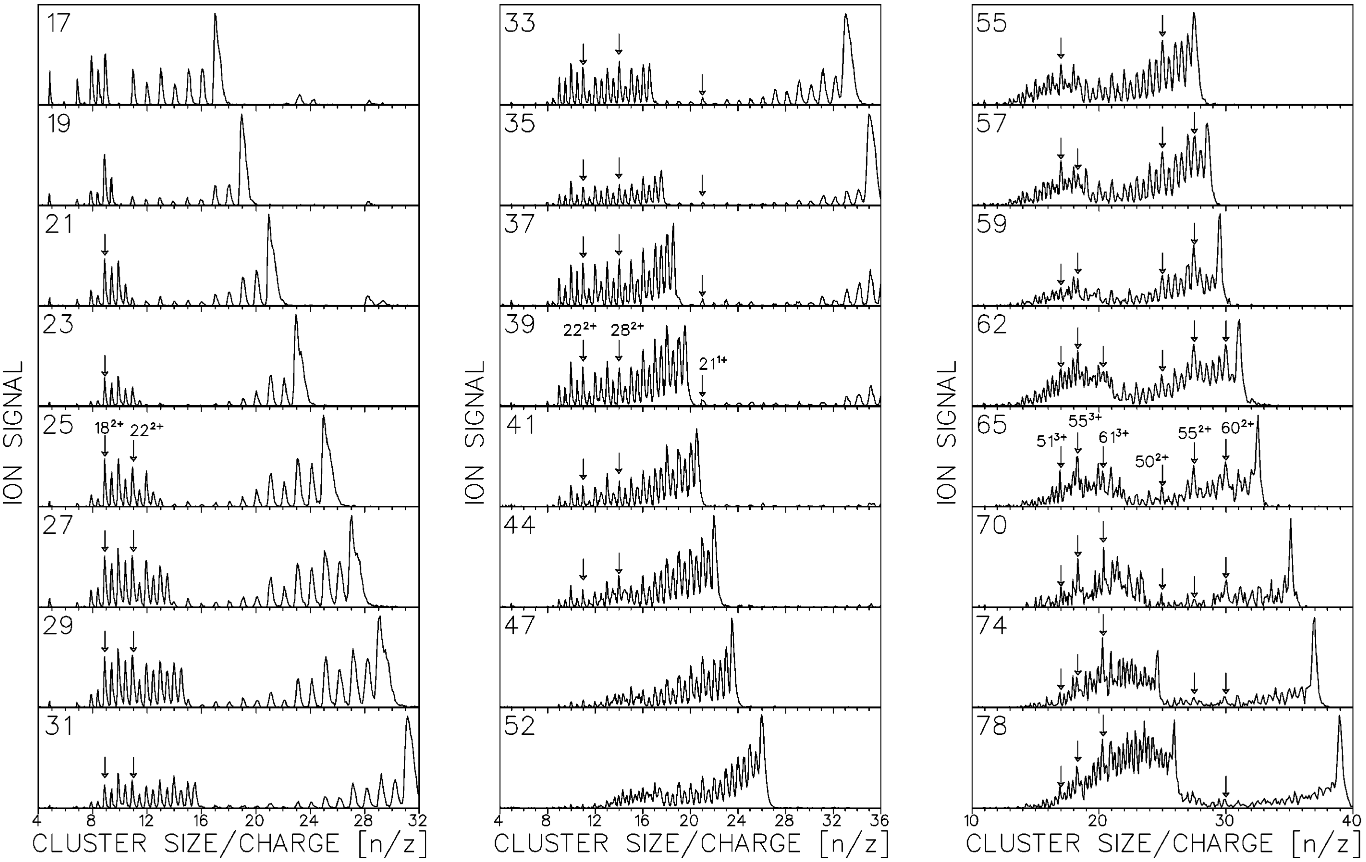

**Fig. 2.** Abundance spectra of size selected silver clusters after application of electron impact ionization/dissociation. Left: Small clusters ($n = 17 - 31$). Middle: Medium-size clusters ($n = 33 - 52$). Right: Larger clusters ($n = 55 - 78$).

shell structure. Doubly charged clusters of size $n \geq 19$ and $n = 17$ are known to decay by neutral monomer evaporation ($\mathrm{Ag}_n^{2+} \rightarrow \mathrm{Ag}_{n-1}^{2+} + \mathrm{Ag}_1$), while clusters of size $n \leq 16$ decay by trimer fission into two singly charged fragments ($\mathrm{Ag}_n^{2+} \rightarrow \mathrm{Ag}_{n-3}^{+} + \mathrm{Ag}_3^{+}$) [19]. For $n = 18$ a competition between these channels occurs. Therefore, no doubly charged clusters are found in the spectra below $n \leq 15$ and a reduced abundance is found for $\mathrm{Ag}_{17}^{2+}$. Dissociation energies have been determined by CID for singly and doubly charged silver clusters in the size range $n \leq 25$ [20]. They show for both charge states an odd-even pattern with even-$n_\mathrm{e}$ clusters having higher dissociation energies than odd-$n_\mathrm{e}$ ones. In addition, the dissociation energies are outstandingly large for particular numbers of valence electrons $n_\mathrm{e}$, where $n_\mathrm{e} = n - z$ in the present case of the monovalent element silver: $n_\mathrm{e} = 8$ ($\mathrm{Ag}_9^{+}$, $\mathrm{Ag}_{10}^{2+}$, outside the scope of this paper) and $n_\mathrm{e} = 20$ ($\mathrm{Ag}_{21}^{+}$, $\mathrm{Ag}_{22}^{2+}$). Both effects reappear in the abundance spectra.

Electronic shells and subshells are expected for the valence electron numbers $n_\mathrm{e} = 20, 28, 34, 58$, which explains some of the dominant signals, e.g. $\mathrm{Ag}_{21}^{+}$ and $\mathrm{Ag}_{22}^{2+}$, or $\mathrm{Ag}_{60}^{2+}$ and $\mathrm{Ag}_{61}^{3+}$. However, we do not observe the numbers $n_\mathrm{e} = 28, 34$ but instead the numbers $n_\mathrm{e} = 26, 58$. Finally, both doubly and triply charged clusters show a prominent signal at $n = 55$. A cluster stability at a given size independent of the charge state indicates a geometric rather than an electronic effect. The size $n = 55$ known from noble gas clusters can be attributed to an icosahedral as well as to a cuboctahedral geometry [4]. Recent calculations for the geometric structure of large neutral silver clusters predict an icosahedral structure for $n = 55$ [21, 22].

Previous electron impact investigations with non-mass-selected neutral silver clusters have shown decreasing abundances at $\mathrm{Ag}_{21/23}^{2+}$, $\mathrm{Ag}_{35/37}^{2+}$, $\mathrm{Ag}_{59/61}^{2+}$ and maxima for triply charged systems at $n = 37, 43, 61, 71$ [12]. Though valuable information is lost due to the strong overlap of different charge states, shell closures at $n_\mathrm{e} = 20, 34, 40, 58, 68$ have been postulated. Overlapping distributions of different charge states have also been produced by irradiation of neutral silver clusters with a laser beam [13]. In this case 'magic' numbers of $n_\mathrm{e} = 20, 58, 92$ have been found from doubly and triply charged clusters. Note that in contrast to the earlier experiments our method of electron induced ionization/dissociation of mass selected precursors drastically reduces the problem of overlapping charge state distributions.

Abundance spectra of singly charged sputtered clusters have been previously analysed in a double focussing mass spectrometer [10] and in a FTICR cell [11]: The first experiment has yielded abundance spectra of both cations and anions and led to magic numbers $n_\mathrm{e} = 20, 34, \sim 57/58$. In the second example, intensity drops were observed at $n = 9, 21, 27, 36, 50, 55$. Thus it indicates that the stability of $Ag_{28}^{2+}$ in our spectra is indeed due to an electronic effect at $n_e = 26$.

Measurements of the photoionization potentials of neutral silver clusters led to a strong decrease of the IP after the cluster sizes $n = 8, 20, 34, 48, 58$ [23]. Experiments with photoelectron spectroscopy gave an especially small electron affinity for the neutral systems $n = 8, 20, 34, 58$ [24].

Finally, the observed plasmon resonances of small silver clusters show a similar behaviour with respect to magic numbers [25].

In summary, the electron shells measured in the Penning trap agree with those measured previously (except for $n_e = 34$). In addition a geometrical shell at $n = 55$ was found, located between electronic shell closures at $n_e = 48$ and $n_e = 58$.

## 5 Conclusion

Electron impact ionization/dissociation of mass selected silver clusters has been used to produce abundance pattern of doubly and triply charged clusters. From the spectra, electronic stabilities at $n_e = 20, 26, 48, 58$ have been infered. A new geometric shell closure has been observed at $n = 55$ between electronic shell closures. The electron impact investigations are currently extended to other metals. In addition we plan the extension to higher charge states [18].

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