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# Observation of multiply charged silver-cluster anions

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**Abstract.** Singly charged silver-cluster anions are produced in a laser vaporization source and transferred into a Penning trap. After size selection the clusters are subjected to an electron bath in the trap, which results in the attachment of further electrons. The relative abundance of dianions or trianions as a function of the clusters' size is analyzed by time-of-flight mass spectrometry. Silver-cluster dianions are observed for sizes $n \geq 24$ and trianions for $n > 100$. In addition, a detailed study of the cluster sizes $24 \leq n \leq 60$ shows a pronounced resistance to electron attachment for singly charged anions $\mathrm{Ag}_n^-$ with a closed electronic shell, in particular $\mathrm{Ag}_{29}^-$, $\mathrm{Ag}_{33}^-$, and $\mathrm{Ag}_{39}^-$. Both the threshold size for the observation of dianionic silver clusters and the shell effects in the production yield correlate favorably with previous theoretical investigations of the respective electron affinities.

**PACS.** 36.40.Wa Charged clusters – 36.40.Qv Stability and fragmentation of clusters – 36.40.Cg Electronic and magnetic properties of clusters

## 1 Introduction

The properties of metal clusters $\mathrm{M}_n^z$ change with size $n$, but also with their charge state $z$. While the removal of electrons is relatively easily accomplished, the attachment of further electrons to a negatively charged system is a challenging task. Dianionic systems have attracted much interest [1] and in particular small carbon clusters [2], fullerenes [3–5] and alkali halide clusters [6] have been observed. However, until recently only theoretical investigations had been reported for doubly charged metal cluster anions [7,8]. The discovery of gold-cluster dianions [9] has changed the situation. Within a short period of time several di- and trianionic metal clusters have been observed [10,11].

Although the production process is still being investigated in further detail, first studies on the abundance of doubly charged gold-cluster anions showed a strong size dependence [12], which can be explained in a simple classical model. Apparently, the electron affinity is a decisive parameter for the onset of metal cluster dianions. In addition, for small gold-cluster dianions structures were observed in the yield as a function of cluster size, which are due to closed electronic shells of the valence electrons in the Jellium model [13]. The experiments have stimulated further calculations for doubly charged gold cluster anions. The results are in good agreement with the structures observed and predictions have been made for silver clusters [14]. Thus, we have applied the new dianion-cluster production method to this element and in this present work we report on measurements of the abundance spectra of doubly and triply charged silver cluster anions. In analogy to the case of gold clusters the results on dianions are compared to electron affinities calculated by Yannouleas and Landman [14].

## 2 Experimental details

The experimental setup has been been reviewed recently [15,16]. The clusters are produced by laser vaporization of a metal wire in the presence of a helium gas pulse [17]. The source produces neutral as well as singly charged cationic and anionic species. The anions are transferred by ion optical elements to the Penning trap, where they are captured in flight and stored for further experiments. The last step of an experimental sequence consists of a time-of-flight (TOF) mass analysis of the reaction products.

In the following, the production and analysis of metal-cluster dianions is described in some more detail. A typical experimental sequence is illustrated in fig. 1. The singly charged metal cluster anions from the laser vaporization source are transferred into the Penning trap (fig. 1(a)), where the captured bunch of particles is a distribution of several cluster sizes. If the number of trapped ions is not sufficient for the experiment, the capture process can be repeated several times (fig. 1(b)). In order to accumulate the cluster bunches, it is necessary to prevent the ions from escaping from the trap during the repeated capturing. To this end buffer gas pulses are applied and in addition, the clusters of interest are centered by quadrupole excitation [18]. In the next step all unwanted ions are removed from the trap by radial ejection (fig. 1(c)). The following reactions are thus performed with size selected clusters.

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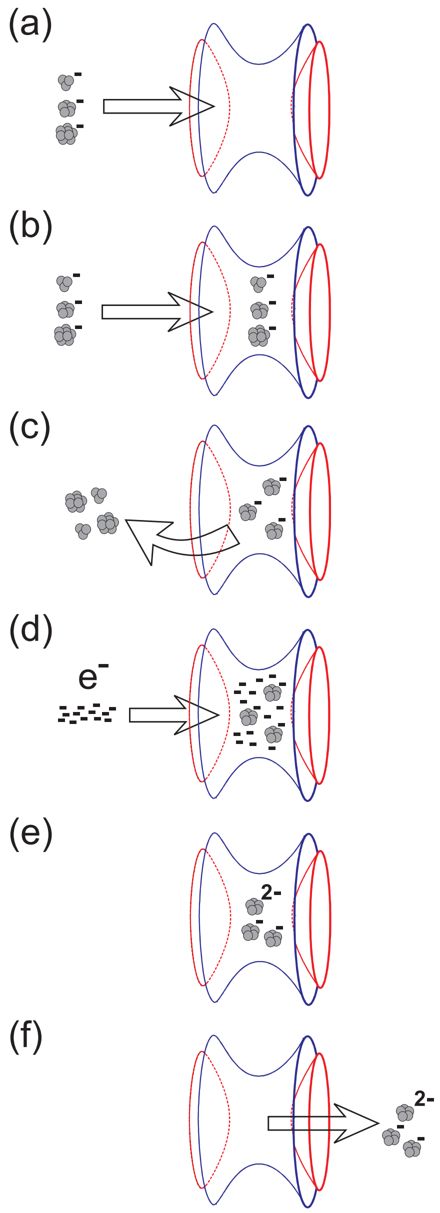

**Fig. 1.** Experimental sequence of the dianion production: (a) ion transfer and capture, (b) accumulation of several cluster ion bunches, (c) size selection, (d) application of electron beam, (e) electron attachment and (f) mass analysis. For details see text.

An electron beam is guided through the trap, while simultaneously argon gas pulses are applied to the trap region. Some argon atoms are ionized and secondary low-energy electrons are produced, which stay trapped due to their negative charge (fig. 1(d)). This leads to an electron bath for the captured cluster anions and eventually electrons may attach producing doubly charged cluster anions (fig. 1(e)). Finally, the resulting cluster ensemble is analyzed by ejecting the ions from the trap into the TOF spectrometer (fig. 1(f)). In order to reduce statistical fluctuations in the cluster production and the dianion formation, the experimental cycle described above is repeated up to several hundred times.

## 3 Results and discussion

In case of the silver clusters, the reaction of stored anions in the size range $24 \leq n \leq 60$ with an electron bath has been investigated in more detail. As an example, three typical TOF spectra after electron attachment are shown in fig. 2. Note, that no fragmentation has been observed after the electron bombardment and only the precursor cluster size and the doubly charged cluster anions appear in the TOF spectra. The comparison of the spectra in fig. 2 shows that the attachment of a second surplus electron is much less likely in the case of $\mathrm{Ag}_{39}^{1-}$ than in the case of its neighbors. This behavior can be explained with a shell closing effect within the Jellium model [13]. With $n_e = 39 + 1 = 40$ atomic valence electrons, $\mathrm{Ag}_{39}^{-}$ already has 40 delocalized electrons, *i.e.* a closed electronic shell configuration. Therefore, $\mathrm{Ag}_{39}^{-}$ has (almost) no intention to attach a further electron.

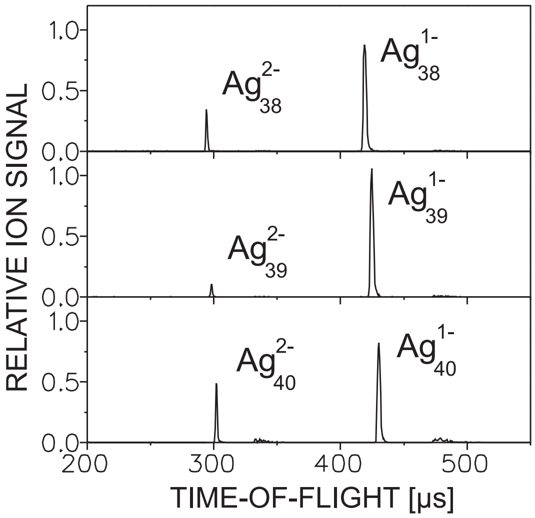

**Fig. 2.** TOF spectra after electron attachment to size selected cluster anions $\mathrm{Ag}_n^{1-}$, $n = 38, 39, 40$. For comparison, each of the TOF spectra has been normalized by dividing with the summed area of the anion and dianion signal peaks.

As already observed for the production of gold cluster dianions [12], the abundance of dianions relative to the number of anions prior to the attachment process gives a qualitative measure for the stability of the doubly charged species. For the present measurements, the electron beam was operated for a period of one second at an energy of $E = 38\,\mathrm{eV}$ and within that time 5 short argon gas pulses were injected into the trap region. After the electron beam had been turned off, the cluster ions remained stored for a reaction time of one second before being analyzed in the TOF spectrometer. With these parameters, silver-cluster dianions $\mathrm{Ag}_n^{2-}$ have been produced in the trap and the resulting relative abundance is plotted as a function of the clusters' size in fig. 3

Note, that these kind of measurements require that the experimental parameters are kept constant throughout the experimental series. Different conditions can lead to

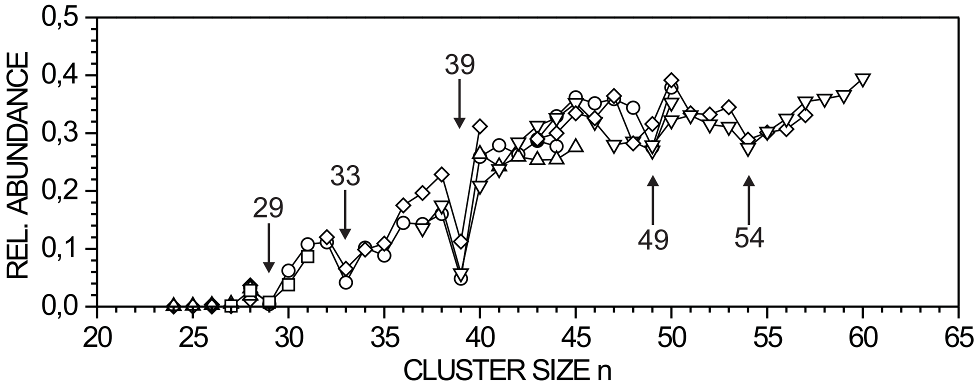

**Fig. 3.** Relative abundance of silver cluster dianions as a function of cluster size $n$. Data points of the same experimental series are connected and have the same symbol. An upper limit of the statistical uncertainty is indicated by the symbol size.

respective deviating yields of dianions. The measurements have been performed mostly twice and sometimes even four times for a given cluster size. The variation of data taken at the same cluster size reflects the systematic error due to the limited control of the experimental parameters.

While dianionic silver clusters have been observed down to the size $n = 24$ the production yield starts rising significantly at $n = 28$. On the average, a linear increase as a function of cluster size is observed up to about $n = 45$. For larger clusters the dianion yield stays constant. Superimposed on these general trends are several pronounced dips in dianion intensity, in particular at $n = 29, 33$, and 39. As already discussed for the latter case, these clusters have filled electronic shells or subshells and are thus inert with respect to further electron attachment. The observed structures have been predicted in electron-affinity calculations by Yannouleas and Landman [14]. For sizes $n > 45$ where the measured relative abundance is almost constant, some further structures seem to show up, one dip at or just below $n > 49$ and another one around $n = 54$.

In addition to the size-by-size investigation of the small clusters, the abundance of larger silver-cluster dianions $60 \leq n \leq 135$ has been measured in larger steps of $\Delta n = 5$. The resulting yields are plotted together with the previously discussed data in the top diagram of fig. 4. The relative abundance of dianions stays roughly constant, but for sizes of about $n > 100$ a new signal appears in the TOF spectra, namely silver cluster trianions. (Fig. 5 shows a TOF spectrum for the case of $n = 125$.) Similar to the case of dianions, the yield of triply charged silver clusters rises linearly as a function of cluster size, starting from a threshold size of about $n = 100$ to $n = 120$ from where on it seems to stay constant with possible exceptions for some further structure (fig. 4, lower part).

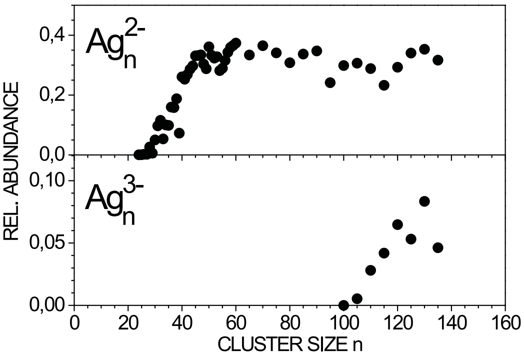

**Fig. 4.** Abundance of doubly (top) and triply (bottom) charged silver cluster anions, as compared to the total number of clusters and the number of the corresponding doubly charged clusters, respectively.

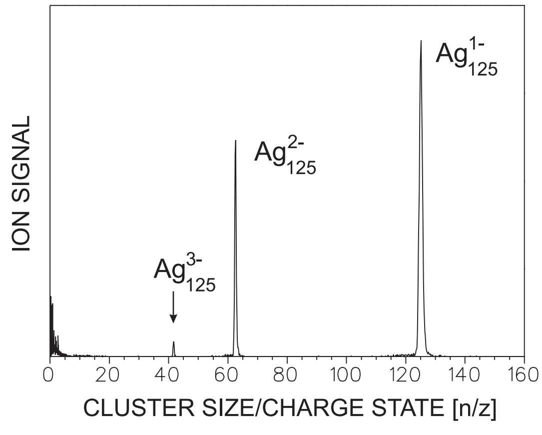

**Fig. 5.** TOF spectrum of size selected $\mathrm{Ag}_{125}^{1-}$ after electron attachment. The ion signal of doubly and triply charged cluster anions appear at $n/z = 125/2$ and $n/z = 125/3$, respectively.

## 4 Conclusion and outlook

With the technique described above, *i.e.* by use of an ion trap to attach further electrons to the negatively charged systems, highly charged silver-cluster anions have been studied. As an extension to previous experiments on gold cluster dianions [12], the abundance of dianionic silver clusters has been measured as a function of the clusters' size. While the steep rise of the abundance seems to follow the electron affinity as in a simple classical model of a charged sphere, the onset of dianions and certain dips in the production yield as a function of cluster size are likely the result of the electronic properties of small metal clusters. The observed structures for gold and silver cluster dianions are in good agreement with theoretical predictions [14].

In order to complete the group of noble metals, detailed measurements on the production of copper cluster dianions are in preparation. Furthermore, we plan to further study the properties of dianionic noble metal clusters by collisional activation as already applied to singly [19, 20] and multiply charged cations [21,22], and by time-resolved laser measurements, which may lead to a study of a delayed response in analogy to the observation of delayed photodissociation [23–25]. First steps to this end have already been taken in the case of dianionic titanium clusters [10]. These investigations will shed further light on the structure of small metal clusters.

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