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Short communication

# Loss of $Ag_3$ moiety from clusters $Ag_n^+$ ($n = 4, 6, 8, 10, 12$) upon collision induced dissociation

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ABSTRACT

The positively charged silver clusters ($Ag_n^+$ ions) were generated in the gas phase by using laser desorption ionization. On the basis of collision induced dissociation MS/MS spectra of the clusters obtained, it has been found that small even clusters (ions $Ag_4^+$, $Ag_6^+$, $Ag_8^+$, $Ag_{10}^+$, $Ag_{12}^+$) lose $Ag_3$ moiety (trimer evaporation). This unexpected result has not been observed in previous studies devoted to the gas phase fragmentation of silver clusters. Loss of an odd-electron fragment $Ag_3$ from odd-electron parent clusters $Ag_4^+$, $Ag_6^+$, $Ag_8^+$, $Ag_{10}^+$, $Ag_{12}^+$, results in the formation of even-electron daughter cluster that are relatively more stable than the parent ions.

## 1. Introduction

Clusters are groups of a small number of atoms with sizes from ~1 to 2 nm, which may be regarded as a bridge between atoms and nanoparticles. Some of the properties of clusters may be size-dependent [1–5]. Size dependence of the cluster properties reflects the transition from the isolated atom to the bulk state. Among metal clusters, the silver ones have attracted considerable attention [6–10]. EPR spectroscopy of silver clusters formed within metal–organic frameworks has shown the presence of paramagnetic $Ag_3$ clusters, as reported very recently by Allendorf et al. [11].

Investigation of the metal clusters in the gas phase is important from the fundamental science point of view [12], for example, it provides valuable information on the stability of clusters of different sizes. There are many reports on the gas phase generation of charged silver clusters, $Ag_n^+$ and $Ag_n^-$ ions, from silver salts by using laser desorption/ionization (LDI). In most of the reports the clusters were generated with the use of a matrix [13–16] (matrix assisted laser/desorption ionization, MALDI), but the clusters can be also obtained without a matrix [17]. Clusters being even-electron ions (containing an odd number of silver atoms) were more abundant (more stable) than those being odd-electron ions (containing an even number of silver atoms). There is also a number of reports devoted to the gas phase fragmentation of silver clusters [18–23]. It was found that their fragmentation pattern displays odd–even alteration, as well as size dependence. Small odd clusters ($Ag_3^+$, $Ag_5^+$, $Ag_7^+$ and $Ag_{11}^+$) lose $Ag_2$ moiety (dimer evaporation). Ion $Ag_9^+$ and odd clusters with $n \geq 13$ lose one Ag atom and $Ag_2$ moiety (both monomer evaporation and dimer evaporation were observed). Decomposition of even clusters consists in the loss of one Ag atom, only monomer evaporation was observed. Our studies have confirmed the above briefly described results. On the other hand, we have found that small even clusters may also lose $Ag_3$ moiety (trimer evaporation). This finding is reported in this short communication. It is worth adding that neutral $Ag_3$ moiety in the gas phase has already been a subject of a few interesting works [24–28], besides some theoretical works concerned with neutral $Ag_3$ moiety are also worth mentioning [29,30].

## 2. Experimental

The LDI full scan mass spectra and collision induced dissociation (CID) MS/MS spectra were obtained on a Waters/Micromass (Manchester, UK) Q-tof Premier mass spectrometer (software MassLynx V4.1, Manchester, UK) fitted with a 200 Hz repetition rate Nd/YAG laser ($\lambda = 355$ nm, power density $10^7$ W/cm$^2$). For MS/MS experiments, argon was used as a collision gas at the flow-rate 0.5 ml/min in the collision cell (T-wave, pressure $6.5 \times 10^{-3}$ mbar) unless indicated otherwise. Collision energy given in the laboratory frame (CE – the most important parameter for MS/MS experiments) is indicated in each MS/MS spectrum presented further. The so-called $m/z$ window for MS/MS experiments was three; therefore, the selected precursor ion beams contained some isotopes, one and two mass units higher than the mass of the ion selected for MS/MS.

In order to prepare the target spots, 1 μl of methanol solution containing silver salt was used (the concentration was of about

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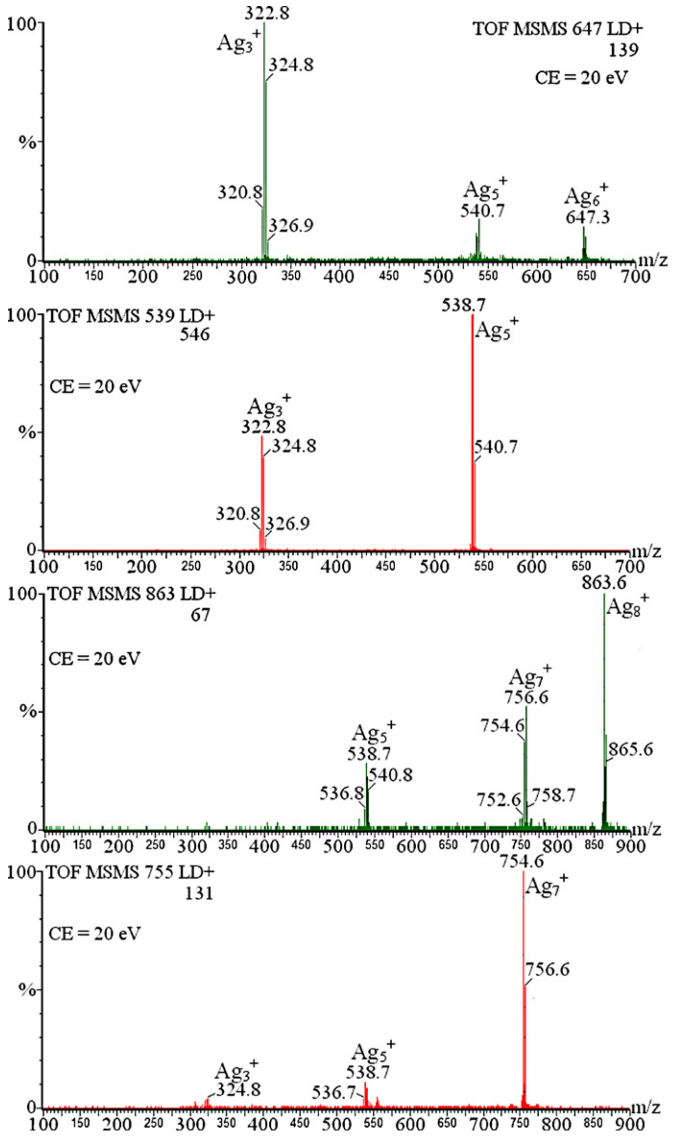

**Fig. 1.** Collision induced dissociation (CID) MS/MS spectra of ions (from the top) $Ag_6^+$, $Ag_5^+$ $Ag_8^+$, $Ag_7^+$.

0.1 mol/dm$^3$). After a few minutes at room temperature the spot was dry and LDI mass spectra could be recorded. Choi et al. have tried to generate silver clusters ($Ag_n^+$ ions) without a matrix from silver benzoate, silver trifluoroacetate, silver nitrate and silver *p*-toluenesulfonate, the clusters have been successfully generated only from silver benzoate [17]. We used four organic salts, namely silver acetylacetonate, silver trifluoroacetate, silver salicylate and silver benzoate (see supplemental material for preparation procedure). The most abundant clusters ($Ag_n^+$ ions) were obtained from silver acetylacetonate. Silver trifluoroacetate and silver salicylate gave clusters as well. From silver benzoate no clusters were obtained. Thus our results are in contrast to those obtained by Choi et al. [17] but it will not be discussed here. We also tested three inorganic salts ($AgNO_3$, $Ag_2SO_4$, $AgClO_4$) but $Ag_n^+$ ions were not detected. Presentation and discussion of all the LDI full scan mass spectra obtained seems not to be necessary, in supplemental material the LDI full scan mass spectrum of silver acetylacetonate is shown as an example.

## 3. Results and discussion

Among the even clusters, $Ag_6^+$ and $Ag_8^+$ were characterized by the highest abundances (have the highest signal to noise ratio). Thus the results for these two clusters seem to be the most reliable. Fig. 1 shows the collision induced dissociation (CID) MS/MS spectra of ions $Ag_6^+$ and $Ag_8^+$, and for comparison the spectra of ions $Ag_5^+$ and $Ag_7^+$.

The spectrum of ion $Ag_6^+$ shows fragment ions $Ag_3^+$ and $Ag_5^+$ and the spectrum of ion $Ag_8^+$ shows fragment ions $Ag_5^+$ and $Ag_7^+$. It can be assumed that the fragment ions $Ag_3^+$ and $Ag_5^+$ are formed from the fragment ions $Ag_5^+$ and $Ag_7^+$, respectively, as a result of

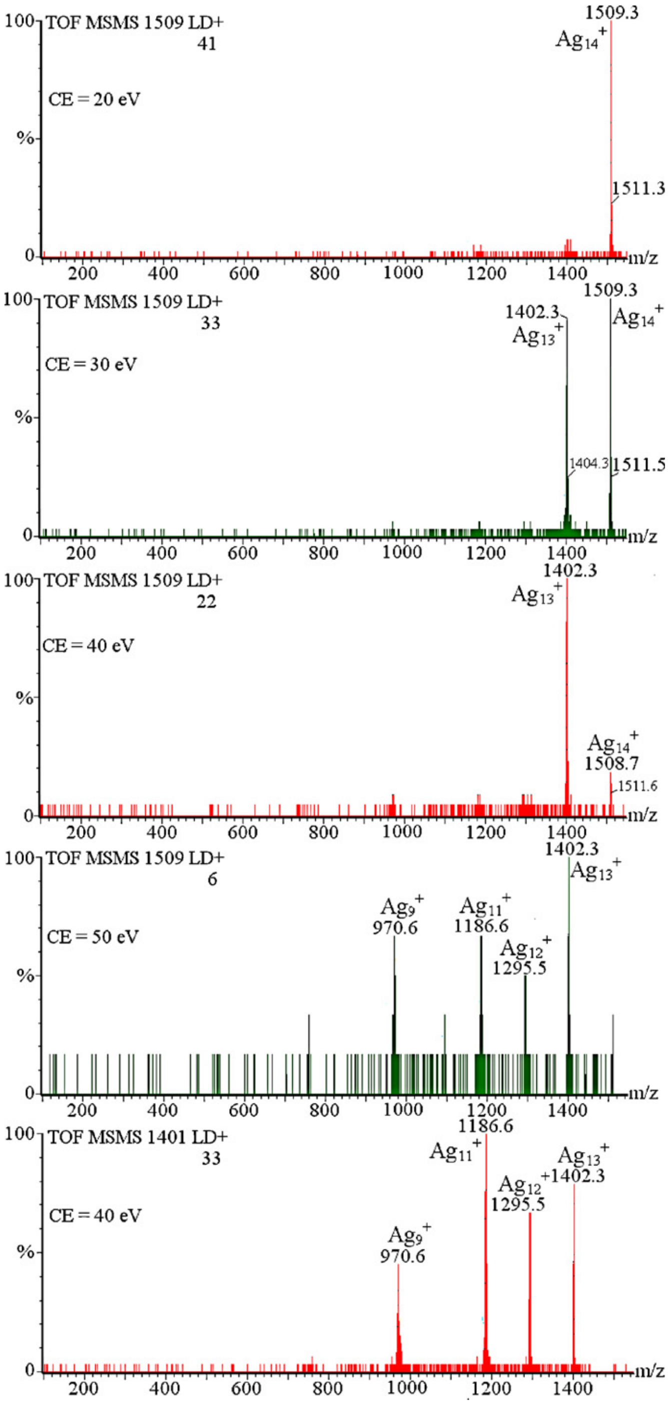

**Fig. 2.** CID MS/MS spectra of $Ag_{14}^+$ ion and CID MS/MS spectrum of $Ag_{13}^+$ ion (bottom).

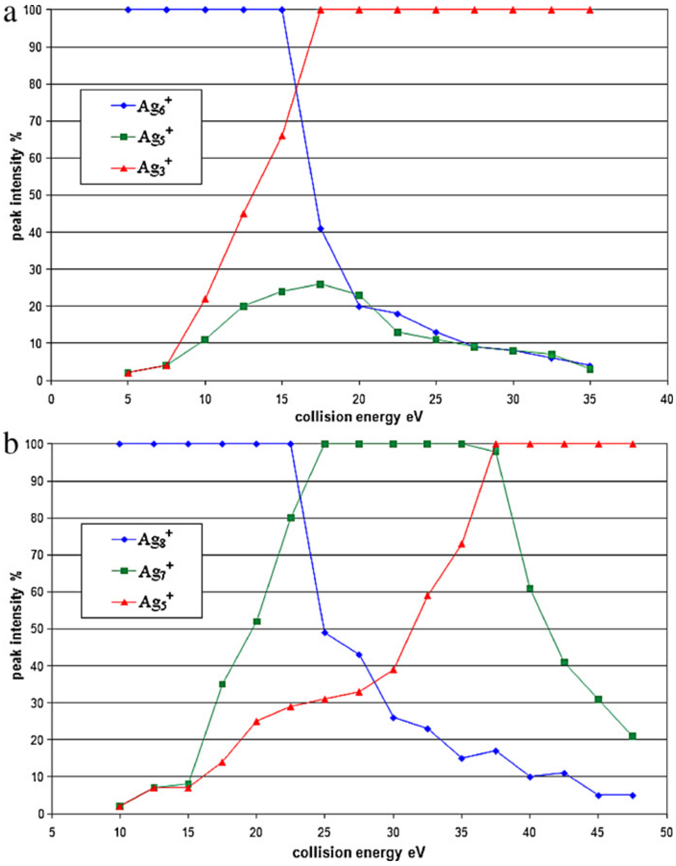

**Fig. 3.** The plot of the normalized signal intensities taken from CID MS/MS spectra of ions $Ag_6^+$ (a) and $Ag_8^+$ (b) versus the collision energy.

dimer evaporation. However, comparison of the spectra of ions $Ag_6^+$ and $Ag_8^+$ with those of ions $Ag_5^+$ and $Ag_7^+$, respectively, strongly suggest trimer evaporation from ions $Ag_6^+$ and $Ag_8^+$. In the mass spectrum of ion $Ag_5^+$ the fragment ion $Ag_3^+$ was obtained, but its abundance was about half of that of ion $Ag_5^+$. In the mass spectrum of ion $Ag_6^+$ the fragment ion $Ag_3^+$ was much more abundant than fragment ion $Ag_5^+$. In the mass spectrum of ion $Ag_7^+$ the fragment ion $Ag_5^+$ was obtained, but its abundance was much lower than that ion $Ag_7^+$. In the mass spectrum of ion $Ag_8^+$ the abundance of fragment ion $Ag_5^+$ was about half of that of fragment ion $Ag_7^+$. Therefore, it can be concluded that fragment ions $Ag_3^+$ and $Ag_5^+$ are formed as a result of $Ag_3$ moiety loss (trimer evaporation) from ions $Ag_6^+$ and $Ag_8^+$, respectively.

The loss of $Ag_3$ moiety (trimer evaporation) was also observed for ions $Ag_4^+$, $Ag_{10}^+$ and $Ag_{12}^+$. It may be concluded from the respective CID MS/MS spectra, although there are low signal to noise ratios, in an analogous way as above for ions $Ag_6^+$ and $Ag_8^+$. The spectra are shown in the supplemental material.

Fig. 2 shows the CID MS/MS spectra of $Ag_{14}^+$ ion obtained at collision energies 20, 30, 40 and 50 eV and the CID mass spectrum of $Ag_{13}^+$ ion and obtained at the collision energy 40 eV.

At collision energies 20, 30, 40 eV, fragmentation of $Ag_{14}^+$ ion involves monomer evaporation, the only fragment ion formed is $Ag_{13}^+$. Trimer evaporation does not proceed. At collision energy 50 eV, the dissociation of formed fragment ion $Ag_{13}^+$ proceeds. Therefore the CID MS/MS spectrum of ion $Ag_{14}^+$ obtained at collision energy 50 eV is similar to the CID mass spectrum of ion $Ag_{13}^+$ obtained at collision energy 40 eV (Fig. 2).

In order to confirm the hypothesis that we deal with trimer evaporation for even clusters, the CID MS/MS spectra were taken for more collision energies. Fig. 3 shows the plot of the normalized signal intensities taken from CID MS/MS spectra of ions $Ag_6^+$ (Fig. 3a) and $Ag_8^+$ (Fig. 3b) versus the collision energy. The collision energy changed with a step of 2.5 eV.

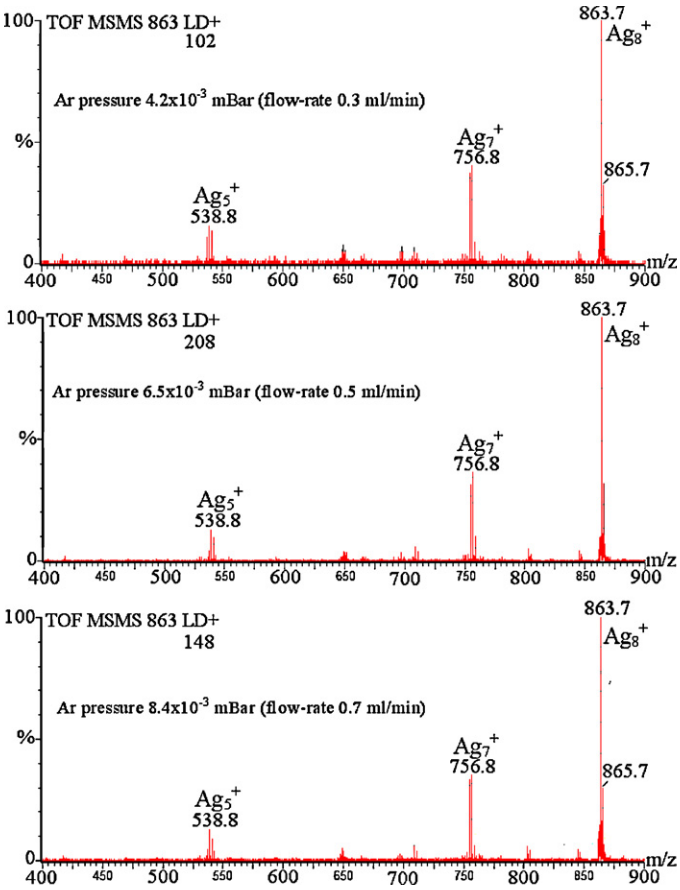

**Fig. 4.** CID MS/MS spectra of ion $Ag_8^+$ obtained at the collision energy 17.5 eV at different argon pressure.

As shown in Fig. 3a, the effective losses of $Ag_3$ and Ag (formation of ions $Ag_3^+$ and $Ag_5^+$, respectively) from ion $Ag_6^+$ begin at collision energy 10 eV. The loss of $Ag_3$ is much more efficient than loss of Ag. For collision energies higher than 20 eV the signal of ion $Ag_5^+$ decreases as a result of its decomposition ($Ag_2$ loss).

For ion $Ag_8^+$ we deal with a different situation (Fig. 3b). The loss of Ag (formation of ion $Ag_7^+$) is more efficient than that of $Ag_3$ (formation of ion $Ag_5^+$); both processes begin at the collision energy of 17.5 eV. For collision energies higher than 30 eV, the formation of ion $Ag_5^+$ became more efficient as a result of $Ag_2$ loss from ion $Ag_7^+$. At higher collision energies an efficient formation of ion $Ag_3^+$ proceeded (loss of $Ag_2$ from $Ag_5^+$), but for clarity this ion was not included in Fig. 3b.

If the even clusters (ions $Ag_4^+$, $Ag_6^+$, $Ag_8^+$, $Ag_{10}^+$ and $Ag_{12}^+$) really lose $Ag_3$ moiety, the relative yield of these processes should be independent of the argon pressure in the collision cell. Therefore a number of CID MS/MS spectra at different collision energies and different argon pressure were obtained. Fig. 4 shows the three CID MS/MS spectra of ion $Ag_8^+$ obtained at the collision energy 17.5 eV at different argon pressure as representative example. The spectra are very similar, confirming the hypothesis that we deal with trimer evaporation from selected parent ion.

The $Ag_n^+$ ions with an even n number, are odd-electron ions (radical cations), the neutral Ag and $Ag_3$ are radicals. Therefore, the loss of Ag or $Ag_3$ from $Ag_n^+$ ions with an even n number leads to the formation of even-electron ions. As mentioned in the introduction, clusters being even-electron ions are more stable than those being odd-electron ions. Thus, the loss of $Ag_3$ described here, analogically as the loss of Ag, leads to the formation of more stable ionic clusters.

As mentioned in the introduction, $Ag_3$ clusters have been recently found in silver clusters formed within metal–organic frameworks, thus in the condensed phase [11]. The loss of $Ag_3$ moiety under CID conditions occurs strictly in the gas phase. Taking into account this work and previous studies of neutral $Ag_3$ moiety in the gas phase [24–28], it is reasonable to assume that the existence of $Ag_3$ moieties is quite a common feature of silver clusters.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2011.04.010.

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