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Facile formation of bare silver clusters in electrospray ionization multi-stage mass spectrometry

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Abstract. We report the observation of bare silver cluster cations obtained by electrospray ionization from a solution containing a metal salt and tryptophan. Multiple step collision-induced dissociation in a quadrupole ion trap of Ag_9^+ is reported.

PACS. 36.40.-c Atomic and molecular clusters – 82.80.Ms Mass spectrometry (including SIMS, multiphoton ionization and resonance ionization mass spectrometry, MALDI)

Electrospray ionization (ESI), which provides a soft ionization and an easy coupling with chromatography and mass analyzers, led to a revolution in mass spectrometry. It allows a direct transfer of molecules from solution to the gas phase and is particularly suitable for biomolecules and biomolecular complexes [1]. Surprisingly, few results are available in the literature on the use of ESI to study simple inorganic clusters. Fragmentation studies of negatively charged fullerenes have recently been performed in a Fourier transform ion cyclotron mass spectrometer on ions generated with an ESI source from a fullerene solution [2]. Several reports have demonstrated the possibility of formation of salt clusters and complex ions from salt solutions (see for example [3–6]). Complexes of silver (I) with peptides have also been produced by electrospray of mix peptide-metal salt solutions [7]. Recently, O'Hair and coll. showed the possibility to form silver clusters from multistage dissociation (MS^4) of $[(M+Ag–H)_n+Ag]^+$ argentinated complexes [6]. In the present work, using a similar approach, we managed to produce complexes where a silver cluster is bound to an amino acid. Bare metal clusters up to size 9 were produced by dissociation of these complexes. The coupling of the ESI source with a quadrupole ion trap (QIT) opens the way to the study of chemical and physical properties of bare metal clusters on long range time scales.

Experiments were performed using a commercial QIT from ThermoElectron (LCQ Duo with MS^n option) coupled with an off-axis electrospray source. The electrolyte solution was prepared by mixing (1:1) a solution of silver nitrate salt (1 mM in H_2O/CH_3OH 1:1 (v/v)) and a solution of tryptophan (200 μM in H_2O/CH_3OH 1:1 (v/v)). 3% of acetic acid was added to the final solution. The signal is sensitive to the difference in voltages between the capillary and the tube lens and little sensitive to other source and ion electrostatic conditions. Helium (purity >99.9999 vol.%) is used as collision and damping gas in the trap. In order to keep the number of ions in the trap constant, the automatic gain control mode was used.

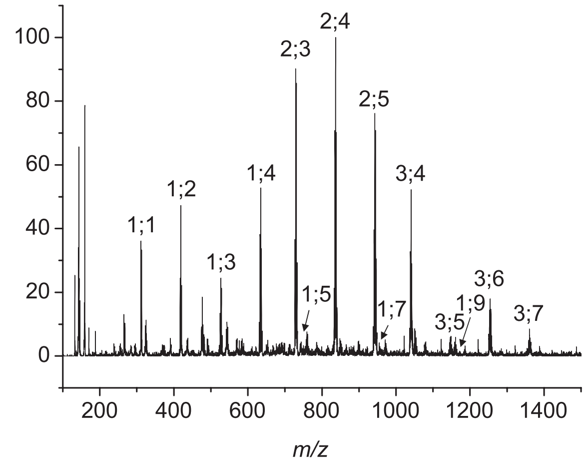

Fig. 1. Electrospray mass spectrum of $n;m$ tryptophan silver complexes (where n is the number of tryptophans and m the number of silver atoms, see text for details).

Tryptophan-silver complexes with different stochiometries of the general form $n;m$ (where n is the number of tryptophans and m the number of silver atoms) were observed in the mass spectra (Fig. 1). Here, we focus on the complexes formed of one tryptophan bound to a silver cluster, which were not observed in previous experiments. $[Trp+Ag]^+$, $[Trp+Ag_3]^+$, $[Trp–H+Ag_n]^+$ (n = 2, 4, 6, 8)

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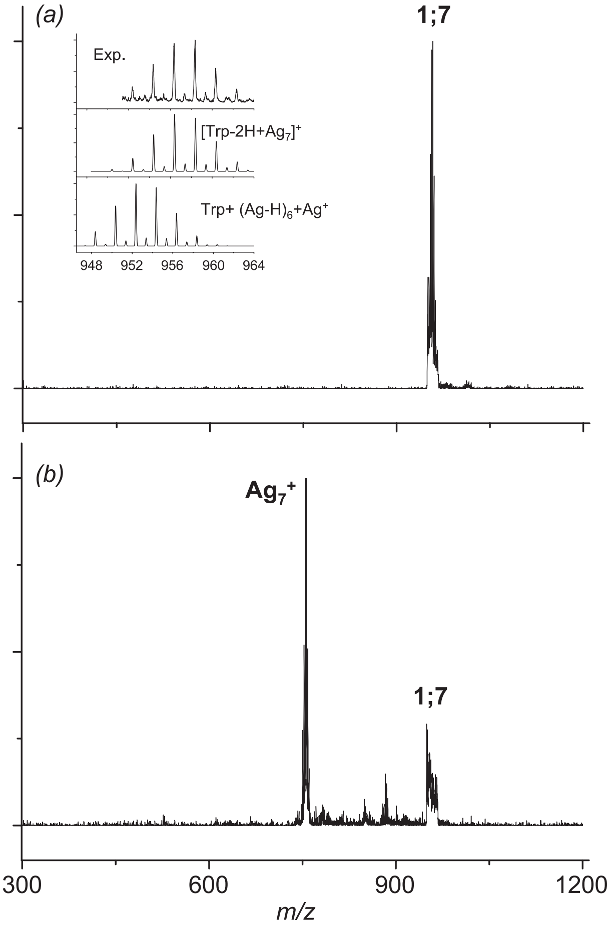

Fig. 2. (a) Isolation spectrum of the 1;7 complex. The insert compares the experimental isotopic distribution to the calculated distribution for the $[\mathrm{Trp{-}2H{+}Ag_7}]^+$ and $\mathrm{Trp{+}(Ag{-}H)_6{+}Ag^+}$ complexes. The comparison shows that the $[\mathrm{Trp{-}2H{+}Ag_7}]^+$ cation is observed. (b) CID spectrum of the 1;7 complex. The activation time for CID is 30 ms.

and $[\mathrm{Trp{-}2H{+}Ag}_n]^+$ (n = 5, 7, 9) complexes were obtained. These cations have an even number of electrons, but they do not correspond to $[\mathrm{M{+}(Ag{-}H)}_n\mathrm{{+}Ag^+}]$ structures where one silver atom systematically replaces a hydrogen atom, as previously observed [7]. Figure 2 displays isolation and collision induced dissociation (CID)spectra for the 1;7 cation. The main fragmentation channel leads to the formation of Ag_7^+. In the CID spectra of smaller 1;n complexes, the formation of a bare silver cluster cation is in competition with a neutral $\mathrm{Ag_2}$ loss. No plasmon peak was observed in the UV-Vis spectrum of the electrolyte solution indicating that there is no formation of nanoparticle in the solution prior to the ESI process. Silver clusters were not observed by electrospraying the solution of silver nitrate (without addition of Tryptophan). The formation of metal clusters occurs during the ESI process and involves the organic molecule. Reduction of silver cations in salt solutions is generally the first step in the metal aggregation [8]. The tryptophan molecule may act as the reductor agent that permits to reduce silver ions.

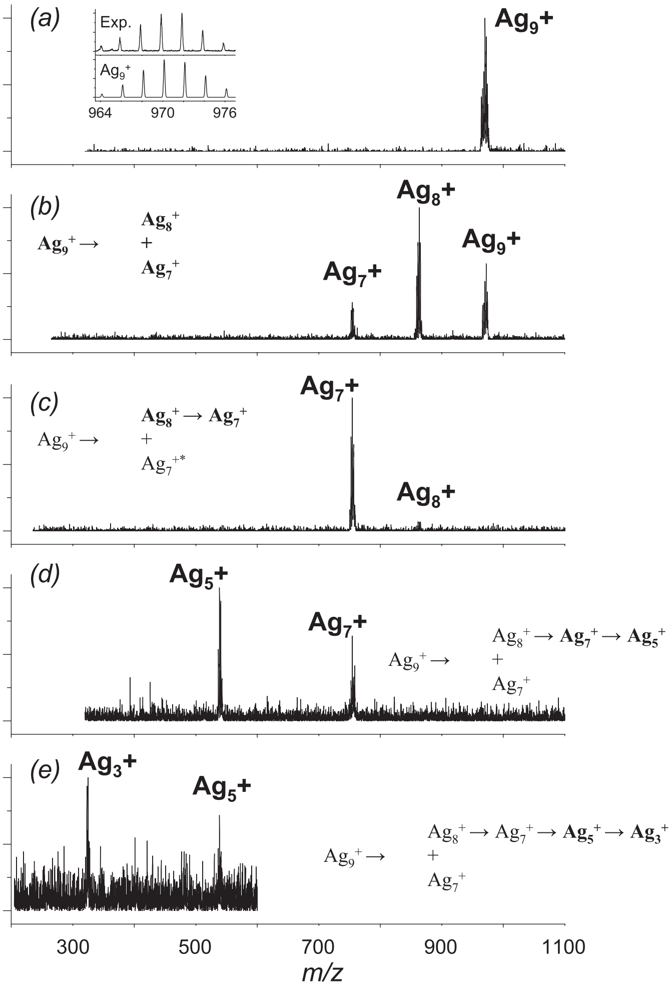

Fig. 3. Mass spectra obtained by multi step sequential CID of Ag_9^+ (produced by dissociation of $[\mathrm{Trp{-}2H{+}Ag_9}]^+$). (a) Isolation of Ag_9^+(CID–MS^2 spectrum). The insert compares the experimental isotopic distribution to the calculated one for Ag_9^+. The comparison shows that a bare silver cluster cation is observed. (b) CID spectrum of Ag_9^+(CID–MS^3 spectrum), (c) CID spectrum of Ag_8^+ (CID-MS^4 spectrum), (d) CID spectrum of Ag_7^+(CID–MS^5 spectrum), (e) CID spectrum of Ag_5^+ (CID–MS^6 spectrum). The activation time for CID is 30 ms at each step. The schemes show the fragmentation pathway that leads to each spectrum.

After reduction, there seems to be a competition between H/Ag exchange leading in particular to n;n+1 complexes and metal aggregation leading to silver clusters (1;n complexes).

After formation, the metal clusters can be isolated, trapped, and handled during several seconds. As an example, Figure 3 shows a complete fragmentation filiation of the Ag_9^+ cluster obtained by multiple-stage collision induced dissociation. Figure 3b shows that Ag_9^+ dissociates into Ag_8^+ and Ag_7^+. Then Ag_8^+ was isolated and further fragmented. The corresponding fragmentation spectrum is shown in Figure 3c. A single size, Ag_7^+, is observed. Isolation and fragmentation cycles were performed from this fragment, up to the observation of the silver trimer. The observation of the high propensity of odd-number silver cluster cations reflects the particular stability of clusters with an even number of electrons [9,10].

In conclusion, in this brief report, we have demonstrated, using an ESI source coupled to a QIT mass spectrometer, the formation of silver clusters bound to an amino acid and the facile trapping of bare silver clusters. Multiple stage mass spectrometry involving six steps of sequential isolation/fragmentation cycles was shown. The method reported could be a general method to generate metal clusters in the gas phase. The possibility to handle ions on long time windows and to perform multiple stage mass spectrometry is particularly suitable to study mechanisms of relaxation or reactivity, which is of fundamental interest to understand the remarkable chemical properties of metal nanoparticles.

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