

Thermospray Mass Spectrometry, a New Technique for Studying the Relative Stability of Cluster Ions of Salts

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Thermospray (TSP) mass spectrometry provides a means of studying stability effects in the frequency distribution of cluster ions of salts under conditions of heat transfer to the cluster ions via thermal collisions in a gas. This is demonstrated for the cluster ions of ammonium chloride. The TSP mass spectrum is compared with that obtained by sputtering of the salt in secondary ion mass spectrometry.

Cluster ions of salts are easily generated by particle impact in secondary ion mass spectrometry (SIMS) [1, 2]. Therefore SIMS has been extensively used for studying the relative stability of cluster ions of alkali halides [2–10] and some other salts [11–13]. As shown in Fig. 1 for ammonium chloride differences in the stability give rise to anomalies in the intensity distribution of cluster ions whose envelope typically decreases exponentially with increasing number of salt molecules forming the clusters. It has been shown for CsI that the frequency distribution of cluster ions when leaving the bombarded surface is nearly structureless and that the anomalies mainly result from unimolecular decomposition of cluster ions of different stability [6]. The unimolecular decompositions may cause considerable adiabatic cooling of cluster ions.

In this note we show that cluster ions of salts can also be generated by a new technique called thermospray (TSP) mass spectrometry [14, 15]. This technique provides an interesting means of studying the stability of cluster ions under conditions of thermal stress, i.e. heat transfer via thermal collisions in a gas.

In the TSP technique, which was developed for on-line coupling of liquid chromatography and mass spectrometry, an electrolytic solution is sprayed into vacuum by passing the solution through a heated capillary, thus forming a jet of randomly

charged droplets. These droplets decompose in a heated jet chamber in which a pressure of several mbar is maintained, and desolvated ions enter the mass analyser via a small orifice. Typically quadrupole mass filters are employed. For the production of salt cluster ions the temperatures of the jet and in the jet chamber must be high enough to allow the decomposition of charged small solid particles. For the ammonium halide this condition is easily achieved.

The ammonium chloride cluster ion distribution as obtained by the new TSP technique is shown in Figure 2. The TSP mass spectrum was obtained with the experimental arrangement described in [16]. A quadrupole mass filter with a mass range 1–420 was utilized. A 0.1 molar aqueous solution of NH_4Cl was applied. The temperature at the end of the capillary was 250 °C and the temperature of the jet chamber was 180 °C.

A comparison of Fig. 1 with Fig. 2 shows that the variation in the relative intensities of cluster ions formed by different numbers of NH_4Cl molecules is essentially the same for both techniques. However, some differences are observed. For example in Fig. 1 the intensity ordering is $I(n=4) > I(5) > I(6)$ whereas in Fig. 2 the reverse order is observed. The intensity differences in the spectra are attributed to the effect of adiabatic cooling during unimolecular decomposition of cluster ions in SIMS, Fig. 1, and to a thermally induced decay of cluster ions in TSP, Figure 2. This conclusion is supported by an observed increase in the intensity difference between $I(4)$, $I(5)$ and $I(6)$ when raising the pressure in the jet chamber at constant temperature.

The anomalies in the frequency distribution of cluster ions of ammonium halides can be explained by the same structure effects as previously discussed for alkali halides [17]. However, when comparing SIMS spectra of the cluster ion distribution of ammonium and alkali salts the relative instability of the $(\text{NH}_4\text{X})_2\text{NH}_4^+$ ions with $\text{X} = \text{Cl}, \text{Br}, \text{I}$ is striking and not observed for alkali halides.

Further work is required by utilizing a mass spectrometer with a higher mass range to explore the potential of the TSP technique for the study of cluster ion phenomena.

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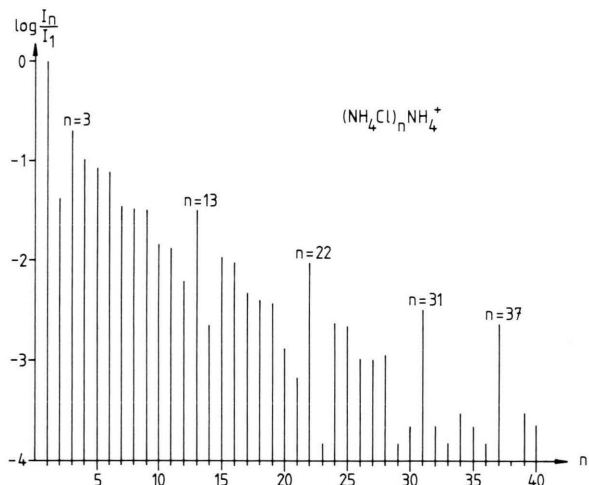


Fig. 1. Secondary ion mass spectrum of ammonium chloride cluster ions obtained by bombardment with 5 keV Xe atoms. A double focusing mass spectrometer (MS9) was used.

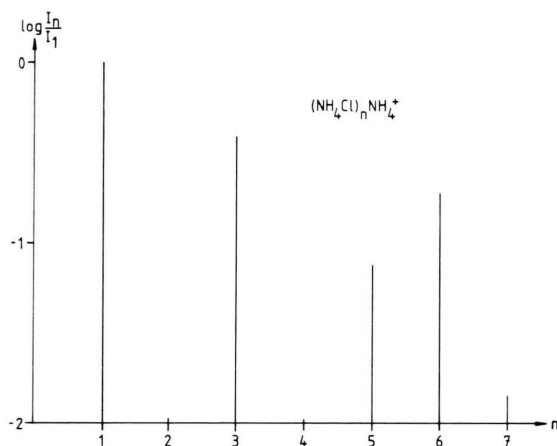


Fig. 2. Thermospray mass spectrum of ammonium chloride cluster ions. The mass range of the quadrupole mass filter utilized was limited to 420 amu.

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