

Stability of hydrated Ca^{2+} clusters studied by energy and pressure resolved collision-induced decomposition

Dear Sir,

Solvated ions provide a connection between gas-phase and condensed-phase systems; therefore, these are in the focus of intensive interest. Investigation of structure and energetics of cluster ions can provide data on the intrinsic physico-chemical behavior of specific species, including thermodynamic data on ion–ligand interactions, reactivity, or coordination spheres. Mass spectrometry is one of the most powerful analytical techniques in cluster chemistry because it provides a possibility to study individual clusters.

Information on cluster ions studied by mass spectrometry may be derived from the mass spectrum itself. Often, clusters of particular stability are observed in the mass spectrum (when a given cluster has a much higher abundance than that containing one more, or one less monomer unit), these are often referred to as ‘magic’ clusters.^[1,2] Such experiments are easy to perform but difficult to reproduce, as they depend on a number of experimental parameters (e.g. on pressure profile along the atmospheric interface, which is difficult to control). Another disadvantage is that differences in cluster intensity yield at most qualitative information on cluster stability.

Hydration of metal ions is studied using mass spectrometry since the 1960s. Kobarle and co-workers were the first to obtain thermodynamic information on hydrated alkali ions generated in a high-pressure mass spectrometer containing a thermionic alkali ion source attached to a reaction chamber.^[3,4] Ion formation in a mass spectrometer involves complex desolvation–solvation processes. A given cluster may be formed either by partially desolvating a larger cluster, or by sequential solvation of an originally naked ion. Distinction between these processes is often not straightforward; in most cases, solvation and desolvation processes both contribute to the appearance of a mass spectrum. Uncertainties of the mechanism of cluster ion formation in electrospray are unlikely to influence conclusions on ion stabilities derived from mass spectrometric studies.

Recently, we developed a new mass spectrometric technique to generate solvated ions in a simple triple quadrupole instrument.^[5,6] The method is based on electrospray ionization of a metal salt solution and a subsequent solvation of these gas phase ions in the atmospheric interface of the instrument. Note that vapors introduced into the atmospheric interface region may be different from the original solvent. In this way, cluster ions of various compositions can be formed in an unusually wide mass range. The aim of the present work was the production of gas-phase hydrated calcium ions in the mass spectrometer using ion-molecule reactions and investigation of the stability of these clusters by tandem mass spectrometry.

Experimental investigation of doubly charged metal ion hydrates is complicated by a possible charge separation reaction leading to $\text{MOH}^+(\text{H}_2\text{O})_n$ instead of $\text{M}^{2+}(\text{H}_2\text{O})_n$ species.^[7] In part,

this has been overcome by using electrospray ionization to transfer ions from solution to the gas phase.^[7,8] The structure and energetics of doubly charged calcium-water clusters was studied by equilibrium determinations performed in a reaction chamber attached to a mass spectrometer,^[9,10] as well as by using blackbody infrared radiative dissociation (BIRD).^[11–13] These results indicate that the first six water molecules go into the inner shell of the Ca^{2+} ion, whereas the additional water molecules go into the outer solvation shell. These results are in a good agreement with a Car–Parrinello molecular dynamics simulation of the hydrated calcium ion, in which a well-defined octahedral arrangement of six water molecules was demonstrated in the first shell around the calcium ion.^[14] Interestingly, production of low molecular weight, doubly charged hydrated Ca^{2+} clusters was observed by means of low-temperature fast atom bombardment technique as well.^[15] Most recently, the sequential bond energies of Ca^{2+} -water clusters were determined by collision-induced dissociation (CID) using a guided ion beam tandem mass spectrometer equipped with a lab-made electrospray ionization source.^[16] These suggest that six water molecules can bind directly to the central calcium ion.

In this work, a series of calcium-water cluster was produced, and their gas-phase stability was investigated by MS/MS to obtain information on their coordination structure. In the experiments, a commercial Perkin-Elmer SCIEX API-2000 triple quadrupole instrument equipped with electrospray ion source was used in positive mode. Ions were formed by electrospraying 1 mM aqueous $\text{Ca}(\text{NO}_3)_2$ solution in a flow rate of 50 $\mu\text{L}/\text{min}$. A minor modification was carried out on the curtain gas introduction system to allow the introduction of water vapors into the curtain gas, as described previously.^[6] The primary ions formed in electrospray reacted in the atmospheric interface with introduced water vapor, forming $\text{Ca}\cdot\text{H}_2\text{O}$ clusters. A minor modification was carried out on the collision gas introduction line as well to allow pressure control externally (to allow lower pressure in the collision cell than conventionally used). CID experiments were performed varying the collision voltage in the range of 6–14 V. Note that 6 V was the minimum voltage needed to observe ions; at a lower value, the ion transfer efficiency through the collision cell was negligible. Above 14 V, typically, complete fragmentation of the precursor ion was observed.

With this resolving method, doubly charged, hydrated Ca^{2+} clusters were produced in a wide mass range (Fig. 1). Increasing the partial pressure of water vapor in the curtain gas shifts the cluster distributions to higher m/z values. Depending on the flow rate, $\text{Ca}(\text{H}_2\text{O})_n^{2+}$ clusters could be detected in the full mass range

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of the instrument (up to m/z 1800). In the experiments, aqueous $\text{Ca}(\text{NO}_3)_2$ solution were electrosprayed. The mass spectra show superposition of two ion series: One is doubly charged $\text{Ca}(\text{H}_2\text{O})_n^{2+}$ type ions, n starting from 6 ($n=4$ and 5 being a minor component) and reaching $n > 150$. The other series is singly charged $\text{Ca}(\text{NO}_3)(\text{H}_2\text{O})_n^+$ clusters.

An important feature of the $\text{Ca}^{2+}/\text{H}_2\text{O}$ system is that the smallest cluster of significant abundance in the spectra is $\text{Ca}(\text{H}_2\text{O})_6^{2+}$. It has approximately 15 times higher intensity than that containing five or four ligands. The latter are most likely due to CID in the interface region, which is difficult to avoid. The $\text{Ca}(\text{H}_2\text{O})_7^{2+}$ cluster has a similar intensity as $\text{Ca}(\text{H}_2\text{O})_6^{2+}$, larger clusters ($n=8, 9$, etc.) are significantly less intense in the spectra. We can see a gradual decrease in the ion intensities when $n=7-9$. Note that this behavior is independent of water pressure in the interface region. Partial pressure of water vapors influences how fast is the decay of cluster abundance with cluster size, but the first abundant cluster peak is always $\text{Ca}(\text{H}_2\text{O})_6^{2+}$. The most straightforward explanation of this behavior is that the binding (solvation) energy of the first 6 H_2O molecules to Ca^{2+} is very high compared with the binding energy of H_2O in larger clusters ($\text{Ca}(\text{H}_2\text{O})_n^{2+}$, $n > 6$).

More detailed information on solvation and the structure of the cluster ions can be derived from tandem mass spectrometric studies. The amount of energy imported to an ion in CID can be influenced by two experimental parameters, the center of mass collision energy (which in turn depends on the laboratory frame collision energy, the mass of the ion and that of collision gas) and the gas pressure of the collision gas (determining the average number of collisions). In most cases, the pressure is kept constant while varying the collision energy yields structural and thermochemical information (energy-resolved mass spectrometry). In the experiments, energy-resolved mass spectra were measured for $\text{Ca}(\text{H}_2\text{O})_n^{2+}$ clusters using the lowest selectable collision gas pressure ($\sim 10^{-2}$ Pa). A convenient way to evaluate the results is depicting survival ion yield (intensity ratio of the present ion divided by the sum of all ions observed in the spectra) as a function of the collision energy.^[17,18] Such experiments were performed for various $\text{Ca}(\text{H}_2\text{O})_n^{2+}$ clusters. The result is shown in Fig. 2 in the $n=4-9$ range. Note that the increase in internal energy of a

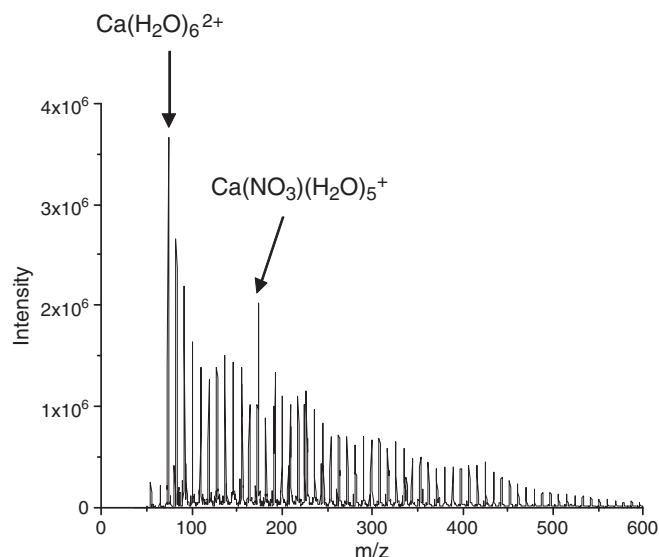


Figure 1. Formation of hydrated calcium ions by electrospraying aqueous $\text{Ca}(\text{NO}_3)_2$ solution and after ion-molecule reactions of the ions with water vapors in the atmospheric interface of the mass spectrometer.

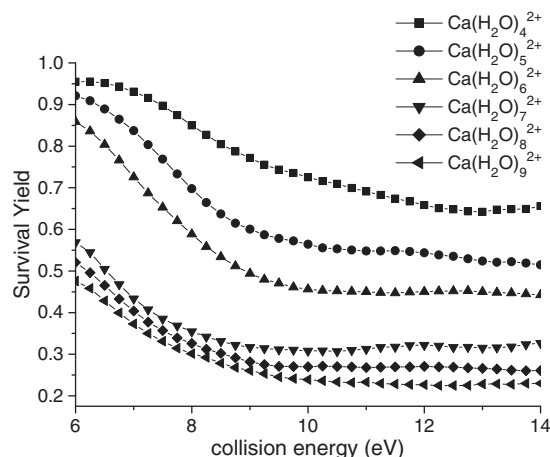


Figure 2. Measurement of the survival yield of hydrated calcium ions as a function of the collision energy.

selected ion is proportional to collision energy. The amount of internal energy necessary to obtain a given degree of survival yield is proportional to the dissociation (binding) energy of a given cluster. (Note that this is subject to the condition that the respective activation entropies are the same, but this condition is most likely valid in this case). There is one more factor that should be considered, and this is the change in the collisional cross-section of the ion. However, this is a relatively minor effect and has been neglected in the present qualitative treatment. Small clusters ($n=4,5,6$) fragment at relatively large collision energy, and a certain fraction of the ions does not fragment even at high collision energy. For example, the $\text{Ca}(\text{H}_2\text{O})_6^{2+}$ cluster reaches a minimum of $\sim 50\%$ survival yield at around 10 V, which is not decreased further at higher collision voltage. This can be explained by the low collision gas pressure used: $\sim 50\%$ of the ions do not collide at all and, in the absence of spontaneous fragmentation, will not decompose. On the other hand, larger clusters ($n=7, 8, 9$) fragment spontaneously (the survival yield is low even at the minimum collision energy). This suggests that the binding energy of H_2O in these $\text{Ca}(\text{H}_2\text{O})_n^{2+}$ clusters is low, especially when compared with the smaller clusters. The difference is particularly large between $n=6$ and 7, suggesting that there are six water molecules for the inner solvation shell around Ca^{2+} .

The main difficulty evaluating the energy resolved tandem mass spectra of $\text{Ca}(\text{H}_2\text{O})_n^{2+}$ clusters is that the binding energy of the relatively large solvated clusters is quite small. This results

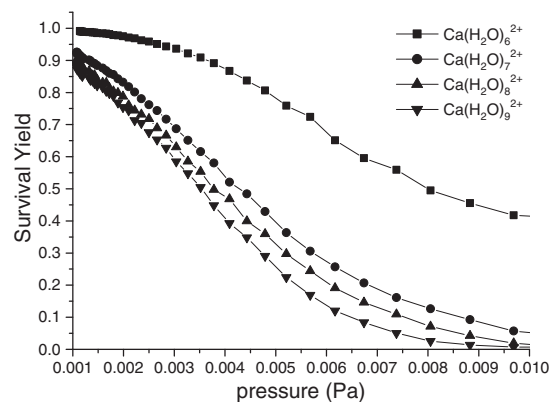


Figure 3. Measurement of the survival yield of hydrated calcium ions as a function of the collision gas pressure.

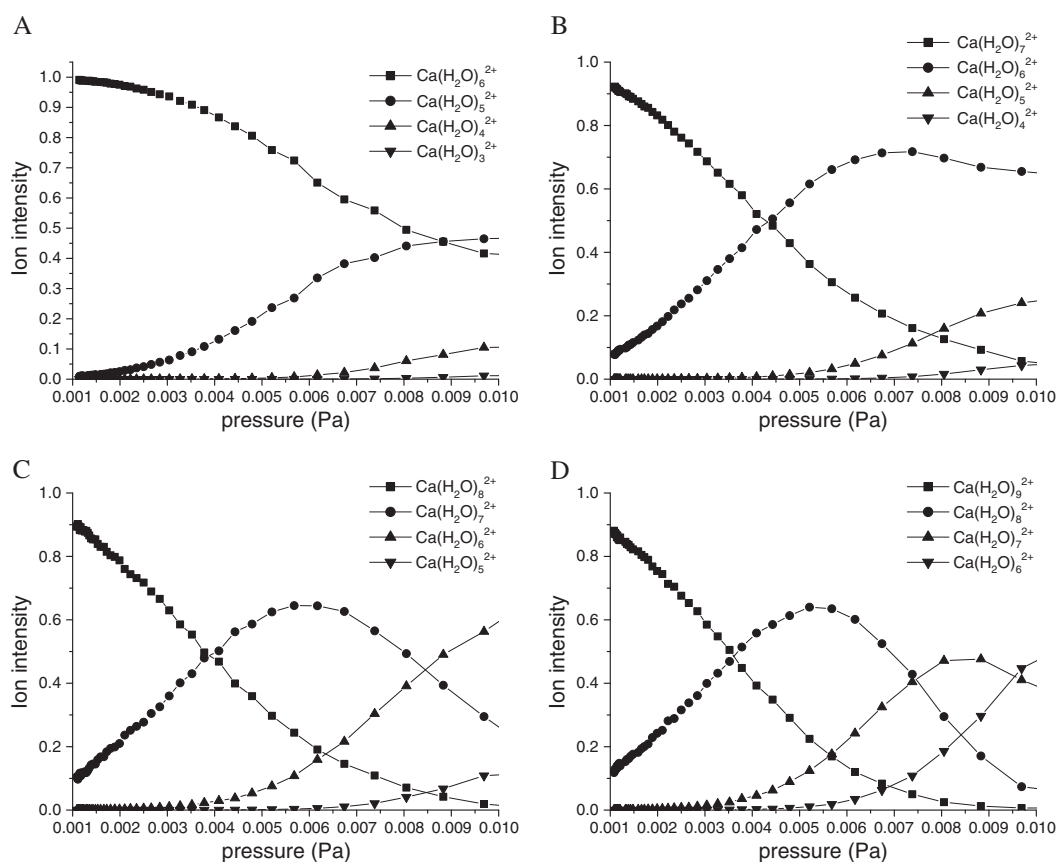


Figure 4. Collision-induced dissociation breakdown curves of hydrated calcium ions in the function of the collision gas pressure: (A) $\text{Ca}(\text{H}_2\text{O})_6^{2+}$, (B) $\text{Ca}(\text{H}_2\text{O})_7^{2+}$, (C) $\text{Ca}(\text{H}_2\text{O})_8^{2+}$, (D) $\text{Ca}(\text{H}_2\text{O})_9^{2+}$.

in a large degree of fragmentation even under much milder conditions (low collision energy, low pressure) than usual for most CID experiments. To study fragmentation of loosely bound clusters, a different type of energy-resolved tandem mass spectra were developed. In this case, the collision energy was kept constant (at 10 V), but the pressure of the collision gas was varied. This changes the number of collisions, so increasing gas pressure will result in an increase of internal energy of the cluster. In the present case, to study low-energy processes, we decreased the pressure of the collision gas. A valve was inserted into the nitrogen collision gas inlet line, and the gas flow was stopped, allowing the gas to be removed by the vacuum system. This technique yields a very reproducible, exponentially decreasing gas pressure in the collision cell. In this way, survival yield in the function of the collision gas pressure can be measured on an analogous matter (Fig. 3). In the experiments, breakdown curves of the clusters as a function of collision gas pressure were determined for selected clusters as well (Fig. 4). The pressure-dependent curves are analogous to the conventionally used collision energy-dependent curves but are much more informative for low-energy processes (such as those of $\text{Ca}(\text{H}_2\text{O})_n^{2+}$, $n = 7, 8, 9$). Figures 3 and 4 clearly indicate that water loss from $\text{Ca}(\text{H}_2\text{O})_6^{2+}$ is a relatively high-energy process, and water loss from $\text{Ca}(\text{H}_2\text{O})_7^{2+}$, $\text{Ca}(\text{H}_2\text{O})_8^{2+}$, $\text{Ca}(\text{H}_2\text{O})_9^{2+}$ is a relatively low-energy process. This, in turn suggests that the inner solvation shell of Ca^{2+} consists of six water molecules.

In the present letter, we have shown that collision gas pressure-dependent CID studies yield analogous information to those obtained more commonly by collision energy dependence.

Pressure-dependent studies have an advantage for studying loosely bound clusters. These provide a simple alternative to determine structure and relative energetics of metal solvation but could be useful for studying solvation phenomena in general.

Yours,

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