STABILITY OF HYDRATED Ca^{2+} CLUSTERS STUDIED BY ENERGY AND PRESSURE RESOLVED COLLISION INDUCED DECOMPOSITION

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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, that differences in cluster intensity yield at most qualitative information on cluster stability.

Hydration of metal ions are studied using mass spectrometry since the 1960s. Kebarle 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 clusters 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 formation of a mass spectrum. Uncertainties of the mechanism of cluster ion formation in electrospray is unlikely to influence conclusions on ion stabilities derived from mass spectrometric studies. Egy altalanos kerdes: Eddig ugy volt, hogy idodalmi ellentet van, 6 vagy 7 ligandumos a belso szolvatacios kor. ???? Igen, ezt mondták Pálinkásék, de én csak az itt is említett cikkeket találtam a témában.

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 subsequent solvation of these gas phase ions in the atmospheric interface of the instrument. Note, vapors introduced into the atmospheric interface region may be different from the original solvent. 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 $MOH^+(H_2O)_n$ instead of $M^{2+}(H_2O)$ species [7]. In part, this has been overcome using electrospray ionization [7, 8] to transfer ions from solution to the gas phase. 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 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, while 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 $Ca(NO_3)_2$ solution in a flow rate of 50 µl/min. A minor modification was done 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 Ca-H_2O clusters. A minor modification was done on the collision gas introduction line as well in order to allow pressure control externally (to allow lower pressure in the collision cell than conventionally used). CID experiments were performed variying the collision voltage in the range of 6-14 eV. Note that 6 eV was the minimum voltage needed to observe ions, at a lower value the ion transfer efficiency through the collision cell was negligible). Above 14 eV, typically, complete fragmentation of the precursor ion was observed.

Using this re-solvating method, doubly charged, hydrated Ca^{2+} clusters were produced in a wide mass range (Figure 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, $Ca(H_2O)_n^{2+}$ clusters could be detected in the full mass range of the instrument (up to m/z 1800). In the experiments aqueous $Ca(NO_3)_2$ solution were electrosprayed. The mass spectra show superposition of two ion series: One is doubly charged $Ca(H_2O)_n^{2+}$ type ions, n starting from 6 (n=4 and 5 being a minor component) and reaching n>150. The other series is singly charged $Ca(NO_3)(H_2O)_n^{+}$ clusters containing a counter anion.

An important feature of the Ca^{2+}/H_2O system is that the smallest cluster of significant abundance in the spectra is $Ca(H_2O)_6^{2+}$. It has approximately 15 times higher intensity than that containing 5 or 4 ligands. The latter are most likely due to collision induced dissociation (CID) in the interface region, which is difficult to avoid. The $Ca(H_2O)_7^{2+}$ cluster has a similar intensity as $Ca(H_2O)_6^{2+}$, larger clusters (n=8, 9, etc) are significantly less intense in the spectra. 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 $Ca(H_2O)_6^{2+}$. 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 to the binding energy of H_2O in larger clusters ($Ca(H_2O)_n^{2+}$, $n>6$).

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 collision induced dissociation can be influenced by two experimental parameters, the collision energy 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 $Ca(H_2O)_n^{2+}$ clusters using the lowest selectable collision gas pressure (ca. 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 $Ca(H_2O)_n^{2+}$ clusters using the lowest selectable collision gas pressure on the instrument (ca. 10^{-2} Pa). The result is shown in Figure 2 in the n=4-9 range. Note that the increase in internal energy of a 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. 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 $Ca(H_2O)_6^{2+}$ cluster reaches a minimum of ca. 50% survival yield at around 10 eV, which is not decreased further at higher collision voltage. This can be explained by the low collision gas pressure used: ca. 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 $Ca(H_2O)_n^{2+}$ clusters is low, especially compared to the smaller clusters. The difference is particularly large between n=6 and 7; suggesting that 6 water molecules for the inner salvation shell around Ca^{2+}.

The main difficulty evaluating the energy resolved tandem mass spectra of $Ca(H_2O)_n^{2+}$ clusters is that the binding energy of the relatively large solvated clusters is quite small. This results in a large degree of fragmentation even under much milder conditions (low collision energy, low pressure), than usual for most CID experiments. In order 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 eV), 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. To do so 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, breakdown curves of the clusters as a function of collision gas pressure were measured for the clusters and are shown in Figure 3. The pressure-dependent survival yield curves are analogous to those of the conventionally used collision energy dependent curves, but are much more informative for low energy processes (like those of $Ca(H_2O)_n^{2+}$, n=7,8,9). This Figure clearly indicates that, water loss from $Ca(H_2O)_6^{2+}$ is a relatively high, from $Ca(H_2O)_7^{2+}$, $Ca(H_2O)_8^{2+}$, $Ca(H_2O)_9^{2+}$ is a relatively low energy process. This, in turn suggests that the inner solvation shell of Ca^{2+} consists of 6 water molecules. This is in good agreement with recent results in the literature [14, 16]

In the present Letter we have shown that collision 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.

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Figures

Figure 1. Formation of hydrated calcium ions by electrospraying aqueous $Ca(NO_3)_2$ 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.

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.) $Ca(H_2O)_6^{2+}$, B.): $Ca(H_2O)_7^{2+}$, C.) $Ca(H_2O)_8^{2+}$, D.) $Ca(H_2O)_9^{2+}$.

FIGURES

Figure 1.

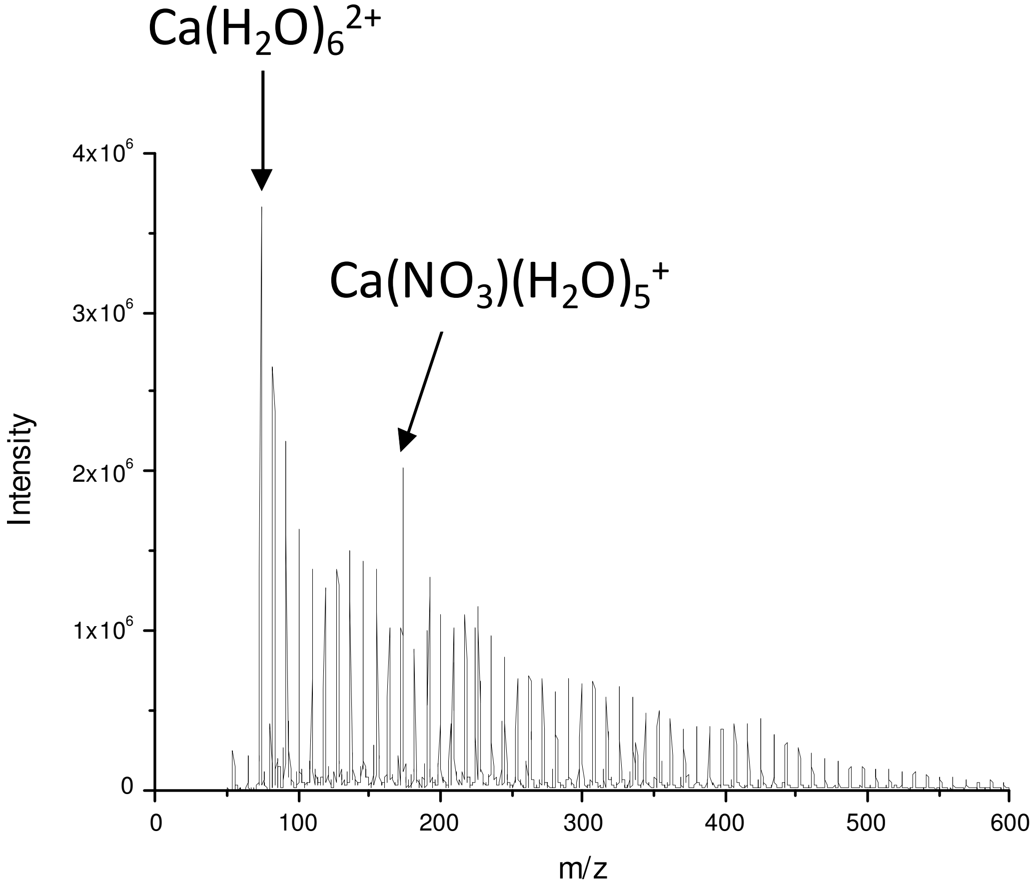


Figure 2.

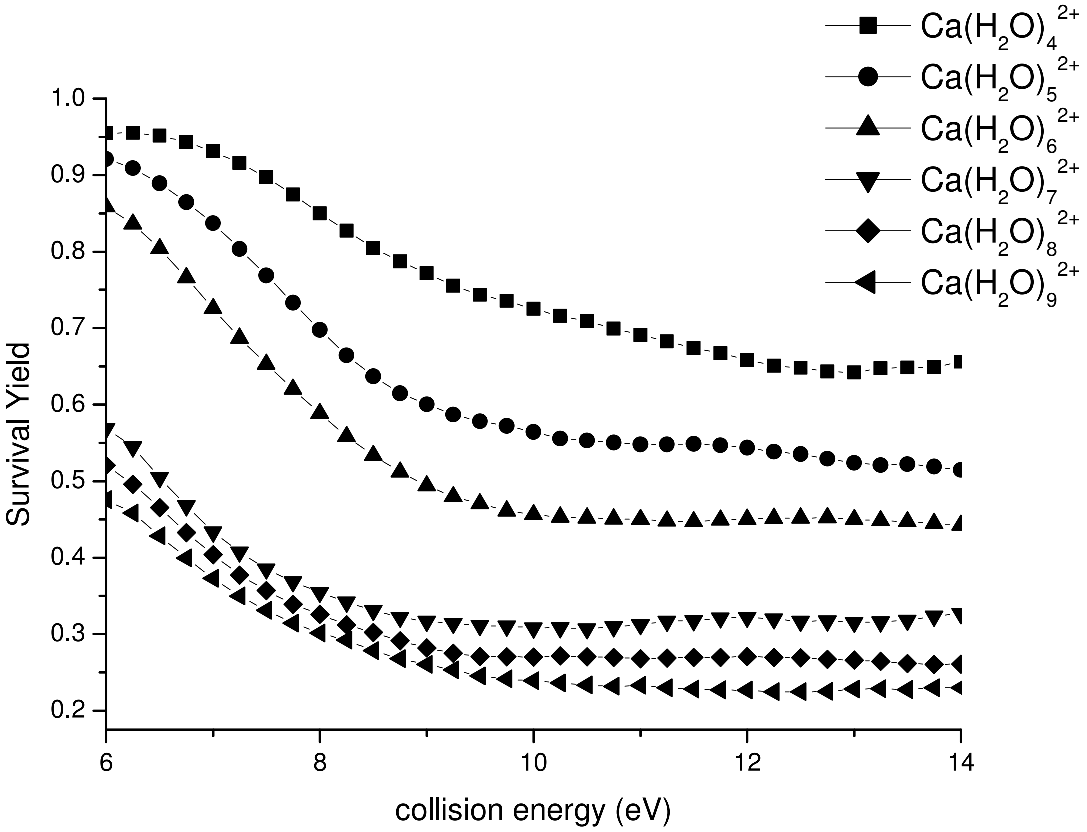

Ca(H_2O)$_4$$^{2+}$
Ca(H_2O)$_5$$^{2+}$
Ca(H_2O)$_6$$^{2+}$
Ca(H_2O)$_7$$^{2+}$
Ca(H_2O)$_8$$^{2+}$
Ca(H_2O)$_9$$^{2+}$
Survival Yield
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
6
8
10
12
14
collision energy (eV)

Figure 3.

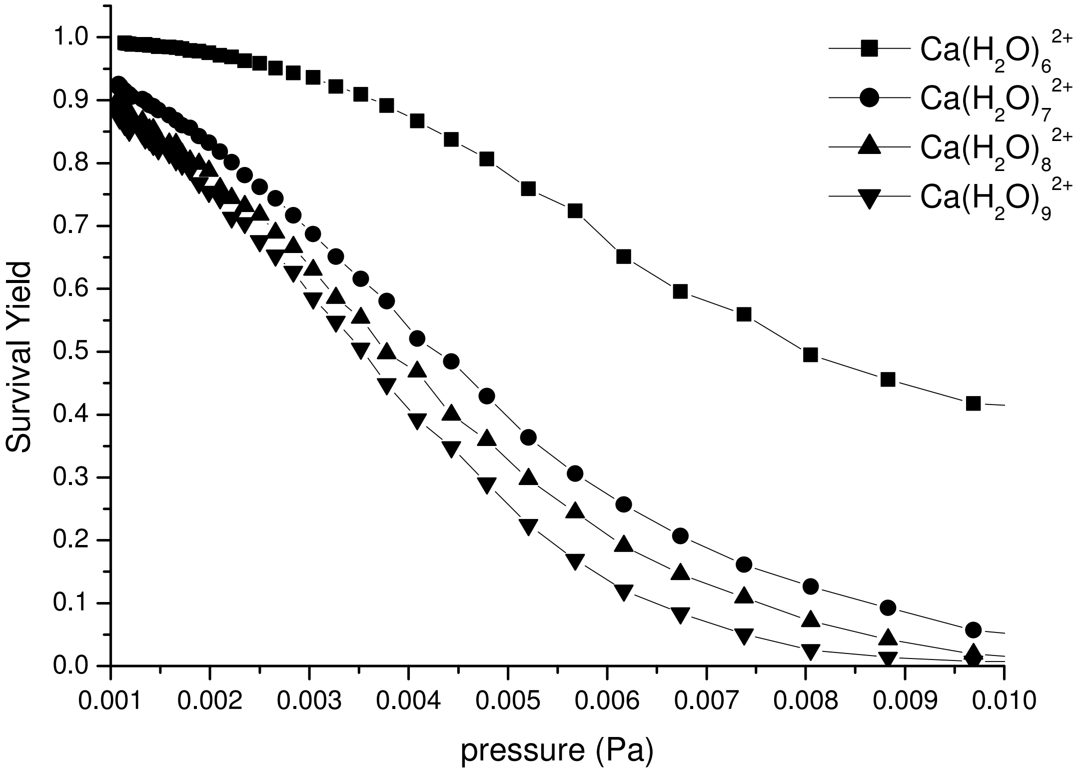
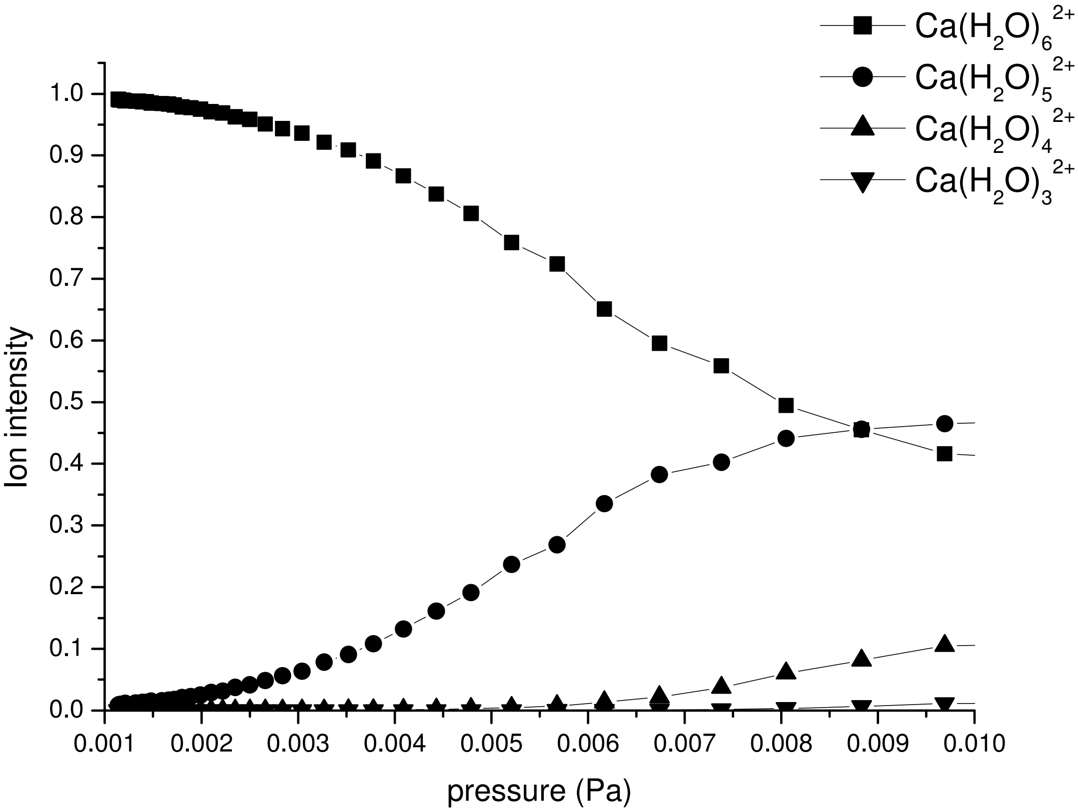
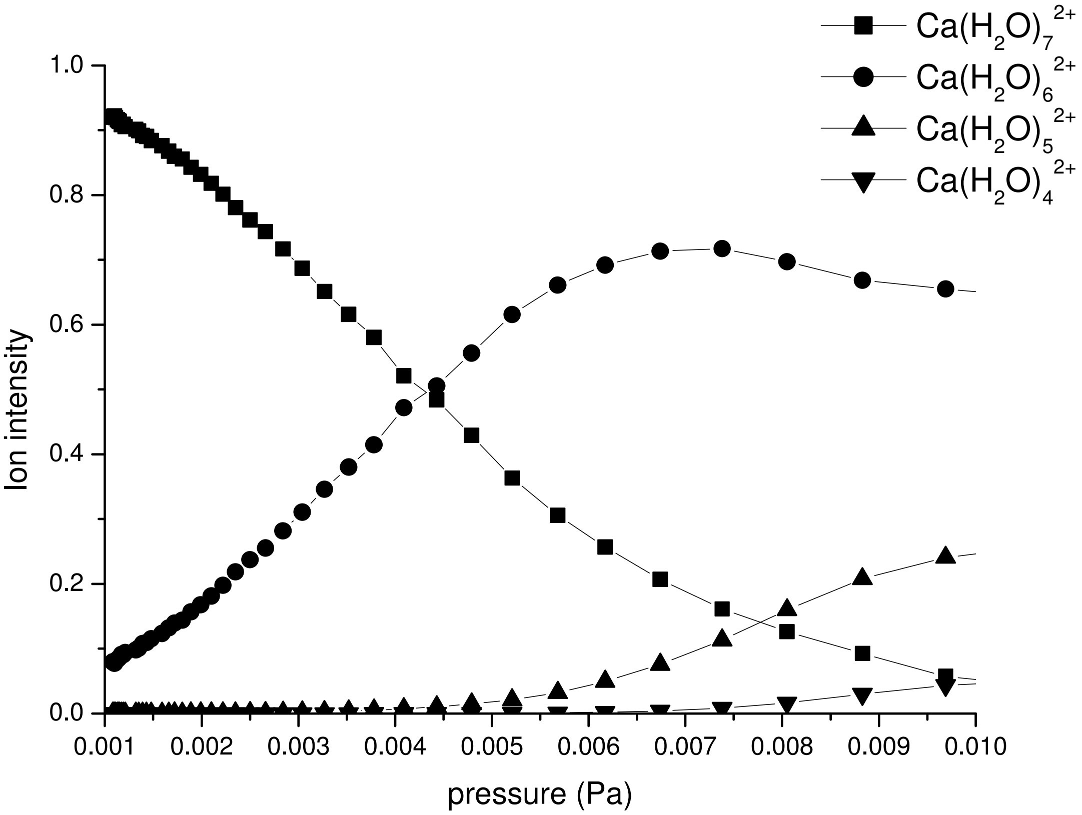

Survival Yield
pressure (Pa)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.001
0.002
0.003
0.004
0.005
0.006
0.007
0.008
0.009
0.010
■ $Ca(H_2O)_6^{2+}$
● $Ca(H_2O)_7^{2+}$
▲ $Ca(H_2O)_8^{2+}$
▼ $Ca(H_2O)_9^{2+}$

Figure 4.A.



$Ca(H_2O)_6^{2+}$
$Ca(H_2O)_5^{2+}$
$Ca(H_2O)_4^{2+}$
$Ca(H_2O)_3^{2+}$
Ion intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.001
0.002
0.003
0.004
0.005
0.006
0.007
0.008
0.009
0.010
pressure (Pa)

Figure 4.B.



$Ca(H_2O)_7^{2+}$
$Ca(H_2O)_6^{2+}$
$Ca(H_2O)_5^{2+}$
$Ca(H_2O)_4^{2+}$
Ion intensity
1.0
0.8
0.6
0.4
0.2
0.0
0.001
0.002
0.003
0.004
0.005
0.006
0.007
0.008
0.009
0.010
pressure (Pa)

Figure 4. C.

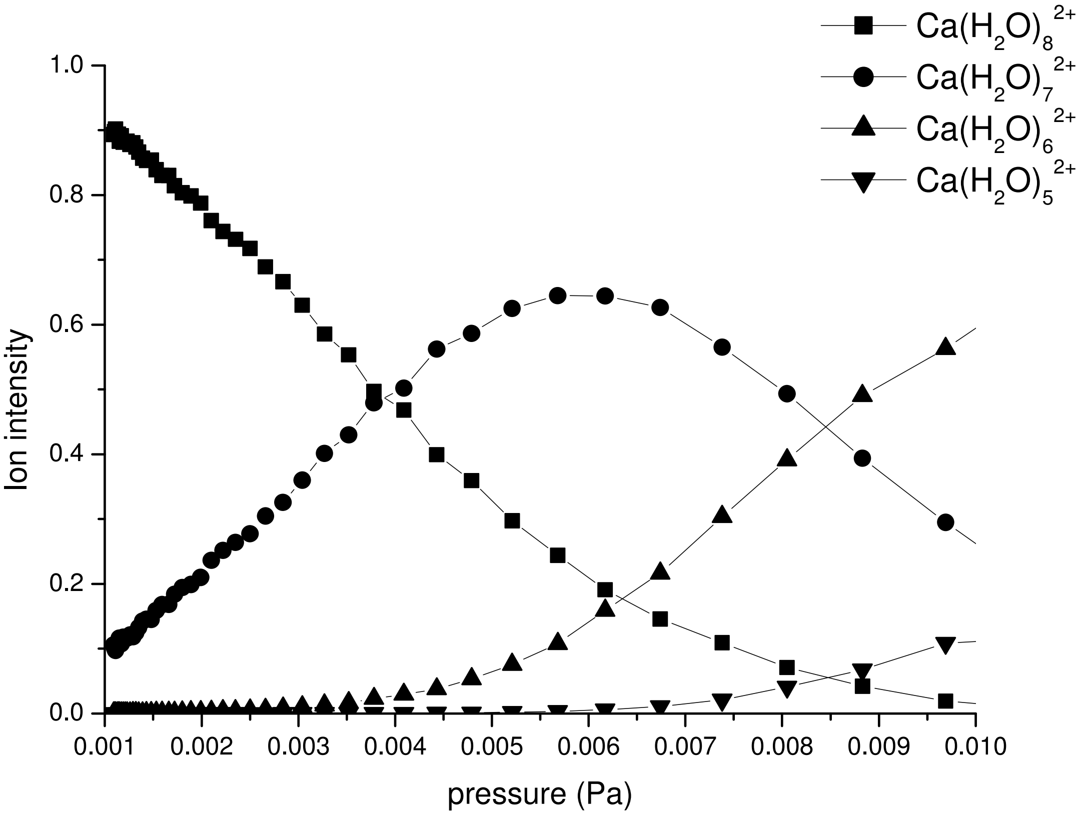
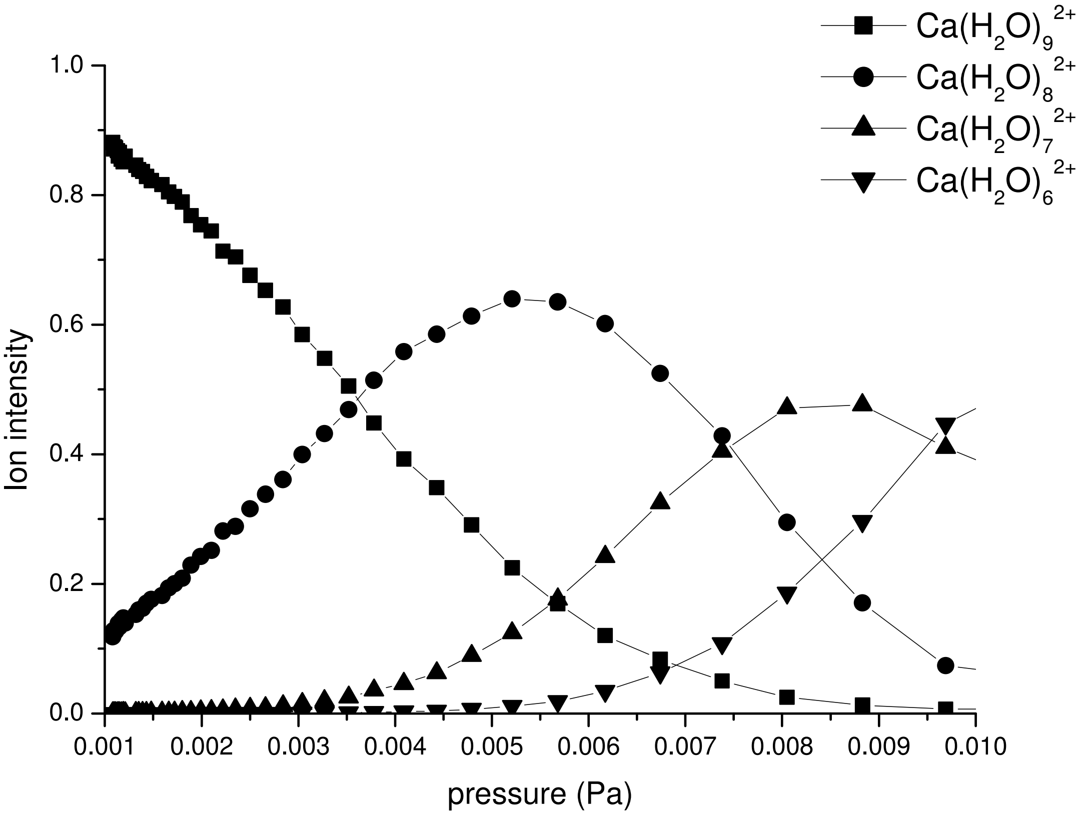

$Ca(H_2O)_8^{2+}$
$Ca(H_2O)_7^{2+}$
$Ca(H_2O)_6^{2+}$
$Ca(H_2O)_5^{2+}$
Ion intensity
1.0
0.8
0.6
0.4
0.2
0.0
0.001
0.002
0.003
0.004
0.005
0.006
0.007
0.008
0.009
0.010
pressure (Pa)

Figure 4. D.



$Ca(H_2O)_9^{2+}$
$Ca(H_2O)_8^{2+}$
$Ca(H_2O)_7^{2+}$
$Ca(H_2O)_6^{2+}$
Ion intensity
1.0
0.8
0.6
0.4
0.2
0.0
0.001
0.002
0.003
0.004
0.005
0.006
0.007
0.008
0.009
0.010
pressure (Pa)