UNIVERSITY OF GOTHENBURG

THESIS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY IN NATURAL SCIENCE, SPECIALISING IN CHEMISTRY

Experimental Studies of Cluster Ions Containing Water, Ammonia, Pyridine and Bisulphate

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at 10:15 in the seminar hall 10-an, Chemistry Building of Chalmers University of
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ABSTRACT

Molecular cluster ions are fascinating subjects of study. Bridging the size gap between molecules and bulk, they often display non-trivial size dependent behaviour and properties. As an example, for some cluster types there are certain sizes that are found in unusually high abundance in a produced cluster distribution, these are referred to as “magic numbers”. Apart from being interesting in their own right and serving as useful model systems in a number of applications, molecular clusters have a very real and important role in the vast and dynamic system we refer to as the atmosphere. Molecular clusters act as precursors for the formation of atmospheric particles. As such, it is necessary to learn as much as possible about the formation, growth, physical properties and chemistry of these clusters, because the particles they form will ultimately have a large effect on the global climate.

This work investigates the properties of some ionic molecular clusters and their gas phase reactions with heavy water and ammonia, and also the effects of collision induced dissociation on air. This is done in cluster beam experiments, using two different experimental setups.

The first instrument is a quadrupole-time-of-flight instrument, consisting of an electrospray ion source, a quadrupole mass filter, a collision cell and a time-of-flight mass spectrometer. In this instrument, relative reaction cross sections were measured for $H^+(H_2O)_n$, $H^+(NH_3)_1(H_2O)_n$ and $H^+(\mathrm{pyridine})_{1–3}(H_2O)_n$ colliding with D_2O; and for $H^+(H_2O)_n$, $H^+(\mathrm{pyridine})_{1–2}(H_2O)_n$ and $H^+(NH_3)_1(\mathrm{pyridine})_1(H_2O)_n$ colliding with NH_3. The results for the reaction $H^+(\mathrm{pyridine})_1(H_2O)_n + NH_3$ were used to improve a kinetic model of the atmospheric positive ion composition. Abundance spectra and evaporation patterns were recorded for all clusters. It was found that protonated clusters containing water and pyridine do not have magic numbers in the investigated size range (≤ 1500 u), unlike clusters consisting of water, pyridine and ammonia. Furthermore the magic numbers of $H^+(NH_3)_1(\mathrm{pyridine})_1(H_2O)_n$ were the same as those recorded for $H^+(NH_3)_1(H_2O)_n$. Cluster reactions with D_2O proceed through a short-lived reaction complex. The clusters add the heavy water molecule and subsequently lose a D_2O, HDO or H_2O molecule; the latter two reaction channels are associated with a cluster mass increase of one or two atomic mass units, respectively. The formation of a HDO species in a cluster requires proton mobility, and is known to occur in $H^+(H_2O)_n$ clusters. The reaction channel leading to formation of HDO was not observed for protonated water clusters containing an ammonia or pyridine molecule, which is attributed to the proton being bound in place by the Brønsted base. However, the experiments indicate proton mobility in clusters with two or three pyridine molecules, $H^+(\mathrm{pyridine})_{2–3}(H_2O)_n$. Quantum chemical calculations suggest that this may be due to transfer of the proton to a water molecule, forming H_3O^+, or due to proton transfer between the two pyridine molecules along a wire of hydrogen bonds.

The second instrument is a double sector instrument, having a magnetic sector, a collision cell and an electrostatic sector. Collision induced dissociation of $H^+(NH_3)_m(H_2O)_n$ clusters (m = 4–6) indicate that clusters having six NH_3 prefer to lose NH_3, while clusters with four or five NH_3 prefer to lose H_2O.

Keywords: clusters, ions, water, ammonia, pyridine, bisulphate, cross sections, collision induced dissociation (CID), kinetic modelling, electrospray ionization (ESI), time-of-flight (TOF), mass spectrometry.

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