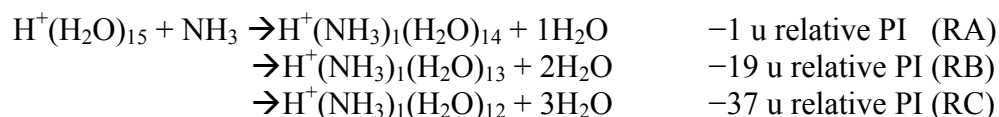


Reactions of $H^+(\text{pyridine})_m(\text{H}_2\text{O})_n$ and $H^+(\text{NH}_3)_1(\text{pyridine})_m(\text{H}_2\text{O})_n$ with NH_3 : experiments and kinetic modelling

Supplementary Material

Description of peak attribution model

Consider for example the reaction of the protonated water cluster having 15 water molecules with ammonia. The cluster in question has been selected in the quadrupole and is the largest cluster in our measurement. Incorporation of ammonia is followed by loss of water molecules. Change in mass occur relative the parent ion (PI). Note that the majority of the inbound $H^+(\text{H}_2\text{O})_{15}$ clusters ($> 90\%$) remains un-reacted because of the low NH_3 pressure in the collision cell.

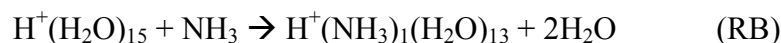


We define the reaction where the cluster lose $1\text{H}_2\text{O}$ as a type-A reaction; a reaction where the ion lose $2\text{H}_2\text{O}$ is a type-B reaction; and, if the ion lose $3\text{H}_2\text{O}$, type-C reaction.

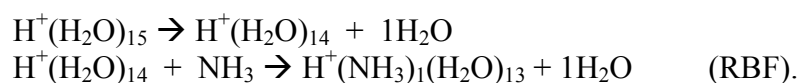
Due to an unavoidable evaporation of H_2O from the parent ion (PI) $H^+(\text{H}_2\text{O})_{15}$ after selection but before reaction, there will also be $H^+(\text{H}_2\text{O})_{14}$ and $H^+(\text{H}_2\text{O})_{13}$ (and perhaps even smaller clusters) among the reactant clusters. Reactions of these evaporation products with NH_3 can form products that overlap with those of the parent ion. For instance, the type-A reaction of $H^+(\text{H}_2\text{O})_{14}$, i.e. adding NH_3 and losing $1\text{H}_2\text{O}$ will give the same result as the type-B reaction of the parent ion (RB). In order to separate these “contaminations” from the reactions of the parent ion, a simple model was devised.

Firstly, in our example measurement, the product $H^+(\text{NH}_3)_1(\text{H}_2\text{O})_{14}$ can only be formed in one way: the reaction (RA), so this product can safely be attributed as originating from the parent ion. The intensity of the $H^+(\text{NH}_3)_1(\text{H}_2\text{O})_{14}$ product relative the total ion intensity will tell how large fraction of the inbound reactant clusters that reacted through this reaction channel (RA).

$H^+(\text{NH}_3)_1(\text{H}_2\text{O})_{13}$ can be formed in two ways, namely the ordinary way



and by prior loss of H_2O followed by a type-A reaction, A false (RB) reaction (RBF),



The abundance of $H^+(\text{H}_2\text{O})_{14}$ formed from evaporation is known from the measurements; furthermore, the abundance is approximately the same whether NH_3 is present in the collision cell or not.

In order to estimate the contribution of the second reaction to the formation of $\text{H}^+(\text{NH}_3)_1(\text{H}_2\text{O})_{13}$ we do the following. A separate measurement is performed with $\text{H}^+(\text{H}_2\text{O})_{14}$ as the parent ion, and the frequency of the type-A reaction $\text{H}^+(\text{H}_2\text{O})_{14} + \text{NH}_3 \rightarrow \text{H}^+(\text{NH}_3)_1(\text{H}_2\text{O})_{13} + \text{H}_2\text{O}$ relative to the reactant abundance is calculated as described above. We now assume that the frequency of the $\text{H}^+(\text{H}_2\text{O})_{14} + \text{NH}_3 \rightarrow \text{H}^+(\text{NH}_3)_1(\text{H}_2\text{O})_{13} + \text{H}_2\text{O}$ reaction when $\text{H}^+(\text{H}_2\text{O})_{14}$ was the parent ion can be used also when $\text{H}^+(\text{H}_2\text{O})_{14}$ was formed by evaporation of H_2O from $\text{H}^+(\text{H}_2\text{O})_{15}$ in the original measurement. Thus, the contribution of Reaction (RBF) is calculated using this relative frequency and the intensity of $\text{H}^+(\text{H}_2\text{O})_{14}$ as formed from evaporation. The remaining abundance of $\text{H}^+(\text{NH}_3)_1(\text{H}_2\text{O})_{13}$ is then attributed to the reaction (RB), i.e. to the PI $\text{H}^+(\text{H}_2\text{O})_{15}$.

The procedure is then extended to the third product formed, i.e. Reaction (RC).

Evaporation of pyridine

Separate measurements were performed in order to estimate the evaporation of pyridine from clusters containing between one and four pyridine molecules and up to one ammonia molecule. The clusters $\text{H}^+(\text{pyridine})_m(\text{H}_2\text{O})_5$ and $\text{H}^+(\text{NH}_3)_1(\text{pyridine})_m(\text{H}_2\text{O})_5$ ($m = 1-4$) passed through the empty collision cell at various collision energies: first varying the energy (in the lab frame) from 39 to 193 kJmol^{-1} (0.4 to 2 eV), and then, in a second experiment, from 10 to 68 kJmol^{-1} (0.1 to 0.7 eV). Loss of pyridine was observed for all clusters with the exception of $\text{H}^+(\text{pyridine})_1(\text{H}_2\text{O})_5$, for which no such peaks were detected in either experiment. This is in agreement with the results in Fig. 3. Figure S1 in the supplementary material shows the intensity of the main peaks resulting from loss of pyridine as a function of the collision energy in the lab frame, for both sets of measurements. For the clusters $\text{H}^+(\text{pyridine})_m(\text{H}_2\text{O})_5$ ($m = 3-4$) and $\text{H}^+(\text{NH}_3)_1(\text{pyridine})_m(\text{H}_2\text{O})_5$ ($m = 1-4$), the pyridine loss was dominated by two peaks of approximately equal intensity, namely loss of a single pyridine molecule and loss of a pyridine molecule and a H_2O . This is the same behaviour as seen for $\text{H}^+(\text{pyridine})_2(\text{H}_2\text{O})_{11}$ in Fig. 3. The cluster $\text{H}^+(\text{pyridine})_2(\text{H}_2\text{O})_5$ had in addition to the above mentioned peaks another peak of equal magnitude corresponding to loss of pyridine and four water molecules. The reason is likely that formation of $\text{H}^+(\text{pyridine})_1(\text{H}_2\text{O})_1$ is favourable, as noted in earlier work (Ryding et al. 2011). The dominating peaks varied in relative intensity from approximately 0.6×10^{-4} to 3.5×10^{-4} depending on the cluster. For each cluster, the loss of pyridine was almost independent on the kinetic energy used; however, an increase in loss of pyridine with increasing energy could be seen for some clusters. Loss of pyridine from clusters, without first reacting with ammonia, can in the QTOF be attributed to three processes: collision induced dissociation (CID) in the collision cell, CID in other parts of the instrument, and spontaneous evaporation. The collision induced dissociation in the collision cell is expected to be minor in the absence of a collision gas; however, it can still occur on account of restgas molecules. If it occurs, the loss should increase rather noticeably with increasing collision energy. In this case, the increase was minor compared to the total intensity of the peaks, indicating comparably small contributions from this process. Collision induced dissociation might also take place in other parts of the instrument, i.e. in the ion optics etc. The relevant kinetic energy is in this case the same for all measurements, and the resulting CID is for a particular cluster a constant contribution to the total loss of pyridine. Given that the abundances of the peaks resulting from loss of pyridine contains a large contribution that appear to be constant with varying kinetic energy, the major contribution to these peaks can be traced to CID occurring outside of the collision cell. After the size selected

clusters have exited the quadrupole, passage through the collision cell constitutes the majority of the flight time (a few hundred microseconds) until the clusters are detected. Evaporation of pyridine is therefore expected to vary as the inverse square root of the collision energy in the lab frame, i.e. linearly with the residence time in the collision cell. No trends corresponding to the kinetic energy dependence of spontaneous evaporation could be recognized in the loss of pyridine for any of the clusters investigated. To summarise, we were unable to determine the evaporation rate coefficients for loss of pyridine from neither of the clusters since the signal could not be separated from the CID losses. However, we conclude that the evaporation rate coefficient is of the order 0.1 s^{-1} or lower under the experimental conditions since a higher evaporation rate coefficient would have given a noticeable evaporation.

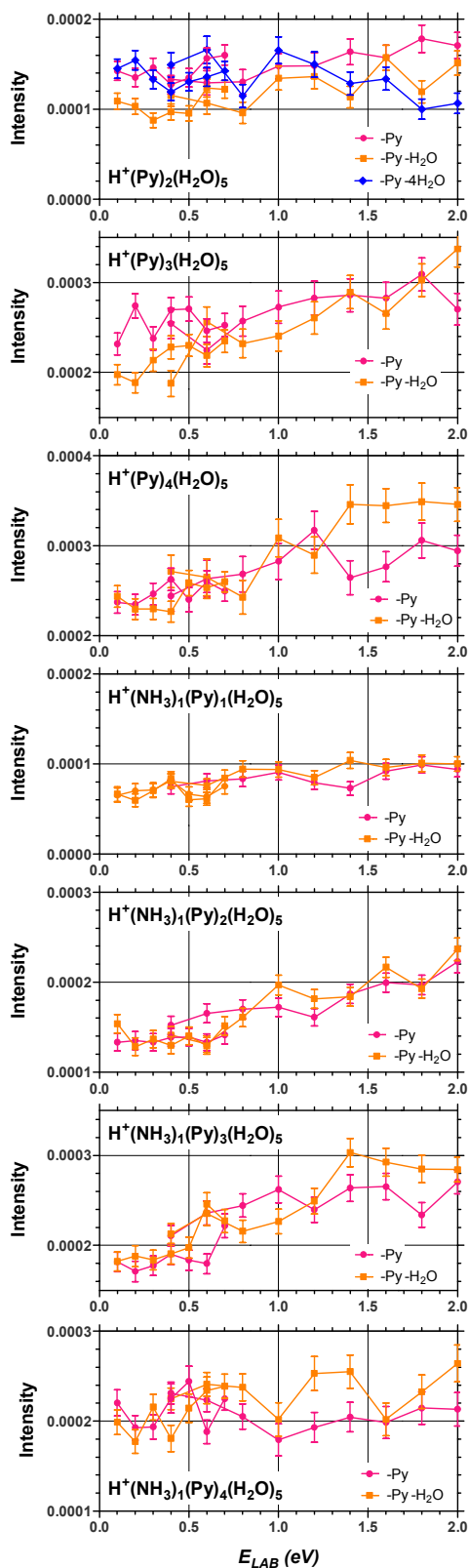


Figure S1. The main reaction channels for loss of pyridine (Py) as the clusters $\text{H}^+(\text{pyridine})_m(\text{H}_2\text{O})_n$ ($m = 2 \dots 4$) and $\text{H}^+(\text{NH}_3)_1(\text{pyridine})_m(\text{H}_2\text{O})_n$ ($m = 1 \dots 4$) pass through an empty collision cell at various collision energies in the lab frame (E_{LAB}). $\text{H}^+(\text{pyridine})_1(\text{H}_2\text{O})_n$ is not included as no loss of pyridine was detected.

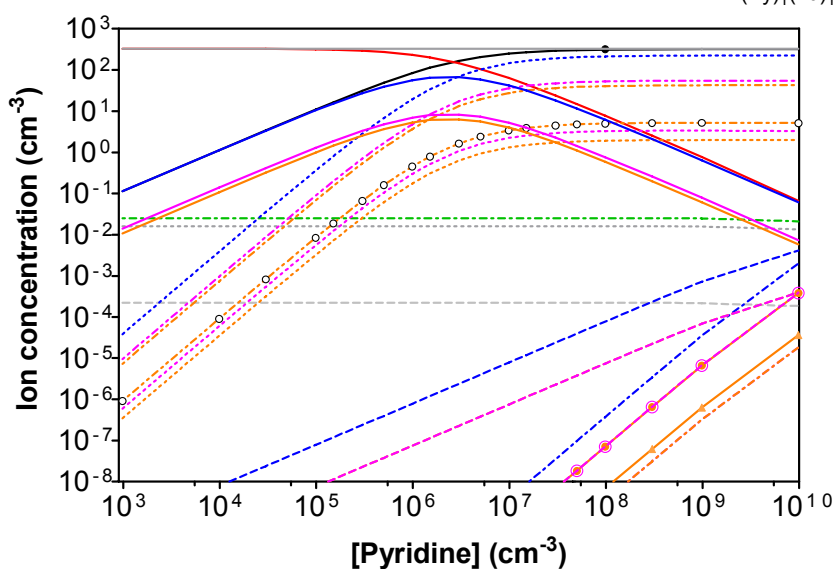
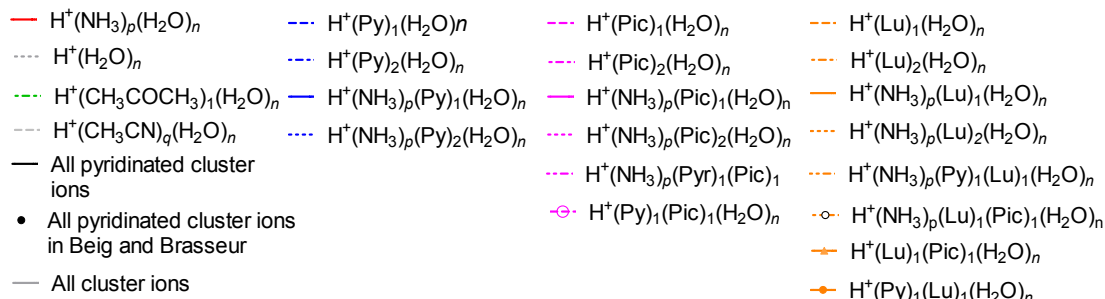


Figure S2. Concentration of cluster ions as a function of pyridine concentration. The values were calculated using Model A and the initial concentrations are given in Table 2. The total concentration of pyridinated cluster ions in the model by Beig and Brasseur (2000) is also indicated. The graph is identical to Fig. 7 except that the concentration is shown on a logarithmic axis to illustrate the concentration of cluster ions with low concentration.