Answers (**in bold**) to anonymous referee #2

M. Ryding et al have conducted an experimental study on protonated water-ammonium-pyridine clusters, and related their results to atmospheric field measurements. While the comments of reviewer 1, especially on the atmospheric relevance of the results, should definitely be addressed, I find the study both well-written and interesting, and well worth publishing in Atmos. Chem. Phys.

Some comments, suggestions and questions:

- I would (like reviewer 1) also be interested in the approximate RH (or RH ranges) which the cluster distributions and reactions measured here correspond to. If the RH is not directly measurable, could it somehow be obtained by reverse-calculating from experimental or computational equilibrium constants? (For example, if the most abundant peak measured for NH+4 - H2O clusters corresponds to (NH+4)(H2O)n, then given equilibrium constants for all (NH+4)(H2O)x + H2O reactions up to x = n+2 or so, and assuming a steady-state cluster distribution, the water partial pressure can be approximately and numerically solved - though this of course disregards fragmentation in the instrument.)

Answer: As mentioned in the reply to reviewer 1, the distribution of clusters produced by the electrospray ion source cannot be said to result from a particular RH in the experiment. In addition, all experimental data presented are for single cluster sizes; they are “taken out of the context” of a distribution. Although not included in this work, the actual distribution produced by the instrument can of course be measured, and examples can be found in the referenced papers Andersson et al. 2008 and Ryding et al. 2011. The produced distribution of protonated water clusters usually peaks at between 20 and 30 H_2O, and it might be possible to calculate which RH is required in order to produce such a distribution in the atmosphere (if at all possible), as suggested by the reviewer. While this is an intriguing suggestion; firstly, the overall shape of such a distribution is generally resulting from the particular operating parameters of the instrument, and have little to do with the atmosphere. Secondly, it is not really relevant since we only sample a small part of the distribution. Again, the data given are given without the context of a distribution and we feel the suggested calculation to be beyond the scope of this paper.

- If I understand correctly, the gain and loss of water molecules are not explicitly included in the dynamic model. This may be a reasonable assumption, but I wonder how large the variation in the average reaction rates (and the ultimate results) with RH is likely to be? Can the experimental data, e.g. the relative rates shown in Fig 6, be used to constrain this?

The reviewer is correct in this assumption, as a single rate coefficient is used regardless of cluster size. For pure water clusters, the rate coefficient used is the thermal rate coefficient determined by Viggiano et al. for $H^+(H_2O)_4$. Rate coefficients for reaction with NH_3 for pure water clusters $H^+(H_2O)_n$ in the range n = 5 to 15 are approximately the same, and

about 20% higher than the one used (Fig. 6). For the pyridine containing clusters, the rate coefficient of $H^+(pyridine)_1(H_2O)_4$ was used as representative for all clusters, also here the size dependence is weak except for the smallest clusters. In order to fully estimate the effect of varying RH on the total (average) rate coefficient, one would need to know the atmospheric size distribution of clusters at the relevant RH, and then average the rate coefficients in Fig. 6 with these distributions. In absence of this, we consider the rate coefficients used to be representative, especially since the size dependence is weak; arguably, a 20% higher rate for pure water clusters could be justified if one suspects that the main part of the cluster distribution are found above n = 4. This should only have minor effects on the outcome of the modelling.

- The cluster ion + aerosol coagulation rate constant k16 presumably corresponds to an aerosol concentration of 1000 cm^{-3}, as given in Table 2. Perhaps sensitivity tests should be performed to test whether the main conclusions about the cluster distribution hold in both clean (lower k16) and polluted (higher k16) air.

We would like to thank the reviewer for this suggestion. We have now used different aerosol concentrations to test the sensitivity of the model on this concentration. Five different concentrations where used, from 100 cm^{-3} (clean) to 10 000 cm^{-3} (polluted). A figure on the results is now included in the paper and as a supplement to this answer. The main findings are that a very clean air would give slightly higher ion concentrations (a factor of 2) but the relation between the different cluster ion intensities does not change significantly. A very high concentration of aerosols will decrease the ion concentration significantly (a factor of 10). In addition the relation between the cluster-ion intensities are now changed. This is now described and discussed in the manuscript.

- Despite repeated readings, I was unable to completely follow the discussion in the second paragraph of page 24543 ("Due to..."). Could the authors please try to clarify a bit, e.g. by giving a specific example, or a schematic illustration?

A more thorough description of the model employed to a specific example in now included in the supplementary material (see attachment no1 in the end of this reply).

- Why does the number of water molecules leaving the cluster after a base uptake or base-exchange increase with cluster size? Energy non-accommodation effects would act in the opposite direction (larger clusters have *more* degrees of freedom to accommodate the excess energy liberated by the binding), so this must presumably be related to the decrease in the average binding energy of water molecules as the cluster size increases (and the ion-molecule attraction weakens). This could be mentioned.

This is not a trivial question. On one hand, the dissociation energy of H_2O decreases with increasing cluster size, as pointed out by the referee. On the other hand, the energy rereleased when NH_3 adds to the clusters also decreases with increasing cluster size. Overall, the thermochemistry data indicate that the latter effect is slightly larger than the former, as discussed in the paper on page 24549, i.e. the binding energy of NH_3 decrease more rapidly than the binding energy of water with size. The increased number of degrees

of freedom certainly means that larger clusters should be able to cope with excess energy in a more efficient manner. However, this is offset by a larger energy reservoir available for evaporation. RRKM calculations in the referenced paper Andersson et al. 2008 indicate that the reaction complex lifetime increases rapidly up to n = 5 for pure water clusters, but then level off to a plateau. We prefer to leave the manuscript as is, but could include our above given discussion if suggested.

- Related to the discussion on page 24548: the difference in ordering of the gas-phase and liquid-phase basicities of ammonia and pyridine presumably has to do with the fact that the ammonium ion can form H-bonds to four water molecules, while the pyridium ion can form only one H-bond. This could be mentioned. Also the acid dissociation constants reported are presumably those for the conjugate acids (i.e. ammonium and pyridium ions), not the neutral bases.

The suggested comments and modifications have been incorporated at the relevant place in the manuscript.

- Like referee 1, I also found the claim that positively charged clusters in the atmosphere likely contain multiple pyridine molecules to be somewhat premature. In the atmosphere, there are many other potentially condensable (i.e. cluster-forming) compounds than water, pyridine and ammonia, and clustering is a competition between all these species. It might well be that positively charged clusters in a pure N2-O2-H2O-NH3- acetone-pyridine/pyridine derivative atmosphere contain multiple pyridines (or pyridine derivatives) - and the results presented in this study do indicate this - but the situation may change when other bases (such as non-cyclic alkylamines) as well as inorganic and organic acids are added to the mixture. The evaporation of bases also likely increases with the number of base molecules - pyridine may not evaporate from a protonated two-pyridine cluster (as indicated in the authors' results), but this very likely does not hold for a four-pyridine cluster. These issues should be better acknowledged, and the discussion on atmospheric clusters revised accordingly.

We agree with the referee and have therefore studied the influence of evaporation of pyridine on the outcome of the model. We have also studied experimentally the evaporation of pyridine from clusters containing more than one pyridine molecule. The results from these studies are now included in the manuscript and the part of the discussion and conclusions related to the above question have been modified. (A figure showing the importance of evaporation of pyridine in Model B is included as a supplement to this answer. The experimental results are attached as attachment no2 in the end of this reply.)

I look forward to seeing the future studies reporting results of measurements on amine-containing clusters (discussed by the authors at the end of the manuscript).

Attachment no 1

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 $H^+(H_2O)_{15}$ clusters (> 90%) remains un-reacted because of the low NH_3 pressure in the collision cell.

$$
\begin{aligned}
H^+(H_2O)_{15} + NH_3 &\rightarrow H^+(NH_3)_1(H_2O)_{14} + 1H_2O \quad -1\text{ u relative PI (RA)}\\
&\rightarrow H^+(NH_3)_1(H_2O)_{13} + 2H_2O \quad -19\text{ u relative PI (RB)}\\
&\rightarrow H^+(NH_3)_1(H_2O)_{12} + 3H_2O \quad -37\text{ u relative PI (RC)}
\end{aligned}
$$

We define the reaction where the cluster lose $1H_2O$ as a type-A reaction; a reaction where the ion lose $2H_2O$ is a type-B reaction; and, if the ion lose $3H_2O$, type-C reaction.

Due to an unavoidable evaporation of H_2O from the parent ion (PI) $H^+(H_2O)_{15}$ after selection but before reaction, there will also be $H^+(H_2O)_{14}$ and $H^+(H_2O)_{13}$ (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 $H^+(H_2O)_{14}$, i.e. adding NH_3 and losing $1H_2O$ 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 $H^+(NH_3)_1(H_2O)_{14}$ 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 $H^+(NH_3)_1(H_2O)_{14}$ product relative the total ion intensity will tell how large fraction of the inbound reactant clusters that reacted through this reaction channel (RA).

$H^+(NH_3)_1(H_2O)_{13}$ can be formed in two ways, namely the ordinary way

$$H^+(H_2O)_{15} + NH_3 \rightarrow H^+(NH_3)_1(H_2O)_{13} + 2H_2O \quad \text{(RB)}$$

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

$$
\begin{aligned}
&H^+(H_2O)_{15} \rightarrow H^+(H_2O)_{14} + 1H_2O\\
&H^+(H_2O)_{14} + NH_3 \rightarrow H^+(NH_3)_1(H_2O)_{13} + 1H_2O\,\text{(RBF).}
\end{aligned}
$$

The abundance of $H^+(H_2O)_{14}$ 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 $H^+(NH_3)_1(H_2O)_{13}$ we do the following. A separate measurement is performed with $H^+(H_2O)_{14}$ as the parent ion, and the frequency of the type-A reaction $H^+(H_2O)_{14} + NH_3 \rightarrow H^+(NH_3)_1(H_2O)_{13}$

+ $1H_2O$ relative to the reactant abundance is calculated as described above. We now assume that the frequency of the $H^+(H_2O)_{14} + NH_3 \rightarrow H^+(NH_3)_1(H_2O)_{13} + 1H_2O$ reaction when $H^+(H_2O)_{14}$ was the parent ion can be used also when $H^+(H_2O)_{14}$ was formed by evaporation of H_2O from $H^+(H_2O)_{15}$ in the original measurement. Thus, the contribution of Reaction (RBF) is calculated using this relative frequency and the intensity of $H^+(H_2O)_{14}$ as formed from evaporation. The remaining abundance of $H^+(NH_3)_1(H_2O)_{13}$ is then attributed to the reaction (RB), i.e. to the PI $H^+(H_2O)_{15}$.

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

Attachment no2

Evaporation of pyridine—additional experiments

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 $H^+(\text{pyridine})_m(H_2O)_5$ and $H^+(NH_3)_1(\text{pyridine})_m(H_2O)_5$ ($m = 1–4$) 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 $H^+(\text{pyridine})_1(H_2O)_5$, for which no such peaks where 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 $H^+(\text{pyridine})_m(H_2O)_5$ ($m = 3–4$) and $H^+(NH_3)_1(\text{pyridine})_m(H_2O)_5$ ($m = 1–4$), 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 $H^+(\text{pyridine})_2(H_2O)_{11}$ in Fig. 3. The cluster $H^+(\text{pyridine})_2(H_2O)_5$ 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 $H^+(\text{pyridine})_1(H_2O)_1$ 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 though 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.

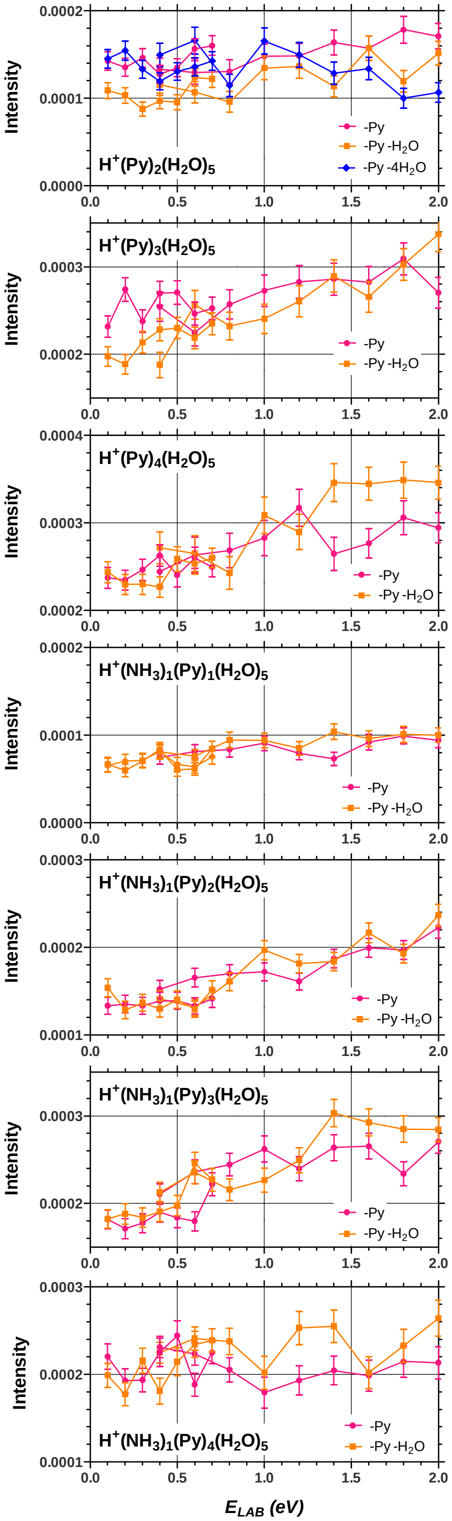

Figure S1. The main reaction channels for loss of pyridine (Py) as the clusters $H^+(pyridine)_m(H_2O)_n$ ($m = 2…4$) and $H^+(NH_3)_1(pyridine)_m(H_2O)_n$ ($m = 1…4$) pass through an empty collision cell at various collision energies in the lab frame (E_{LAB}). $H^+(pyridine)_1(H_2O)_5$ is not included as no loss of pyridine was detected.