Answers (**in bold**) to anonymous referee #1

The authors present measurements and modeling of the reactions of positively charged pyridine-containing water clusters with ammonia. The methods and results are presented clearly and the manuscript is well-structured. The presentation quality is high, but my concern lies in the scientific significance of the manuscript.

I do not feel that the authors have motivated why this research is of importance for the atmospheric research community and thus would motivate publication in ACP. The introduction mentions aerosol formation, but the authors do not relate their results to aerosols.
Rewrite the introduction to focus more on the ion question.

Answer: See question on motivation below.

Furthermore, the conclusion of the paper is that atmospheric positive ions should contain several pyridine molecules (Py) and ammonia, and then suggests that the fact that this is not in agreement with atmospheric measurements is due to problems with the atmospheric measurements. Although evaporation/fragmentation may have been of importance in the atmospheric measurements, I think a larger problem with the comparison is the overly simplified model used in this paper. Nevertheless, I will recommend publication in ACP if the authors can address the specific comments below, as the improvement of ion cluster models is of certain interest, although the manuscript only presents an incremental improvement of a previous model.

Answer: See answers below.

Specific comments

- Model limitation. The model produces water clusters that then can react with pyridines, NH3, acetone and acetonitrile. When looking at ambient positive ion spectra published by Eisele, Junninen or Ehn, there are a great number of peaks around that are not related to Py. Additionally, the authors suggest that major evaporation/fragmentation may have influenced the ambient measurements, and if correct, the real ambient spectra would be even more complex. The obvious molecules that are missing in the model are at least alkyl amines and quinolones which have been observed in most ambient measurements, but a large part of the ambient ions are still completely unidentified.

Answer: We agree that amines and quinolines have been observed in most ambient measurements. However, in the absence of experimental rate coefficients for water cluster formation including alkylamines and quinolines, we decided not to include these molecules in the reaction scheme since it would have introduced more uncertainties into the model.

- The last sentence in the abstract states "...cluster ions containing ammonia and more than one pyridine, picoline or lutidine molecule should dominate at ground level under typical conditions." I do not know if this should be interpreted as clusters with Py will contain more than one Py, or that the positive ion spectrum is typically dominated by clusters with several Py. If the former, this should be stated clearly. If the latter, ambient observations do not agree with this, and the limitations of the model should be discussed.

Answer: Due to other questions from the referees about the lack of evaporation of pyridine in the model, we now study the importance of evaporation in the model. Due to the outcome of these calculations the last sentence has now been changed.

- Overall, the limited number of molecules included in the model, and the effect of this on the results should be discussed in more detail.

Answer: We consider pyridine to be a representative for high proton affinity amines in the atmosphere. The effect of this on the results is now discussed in the discussion.

- Motivation of study. To warrant publication in ACP, the reason for conducting this research, and how this benefits atmospheric science should be made clear in the introduction. Further, if the introduction is to be started with aerosols, they should be discussed and related to the current study in more detail. If this is not possible, then the text about aerosols should be shortened and rewritten. Ions may enhance nucleation rates, but are the authors aware of papers claiming Py to be specifically important?

Answer: Parts of the introduction is now rewritten. The first two sentences about aerosol formation are removed. The end of the introduction is also rewritten to more clearly motivate the work:
"The pyridinated cluster ions, $H^+(X)_1(NH_3)_m(H_2O)_n$, which may be the dominating positive cluster ion in the atmosphere, as suggested by Beig and Brasseur, could potentially be an important source for new aerosol formation. However, these cluster ions have to date not been measured in the atmosphere. This discrepancy has motivated us to perform well controlled experiments to investigate the formation mechanisms of these clusters. The reactions of two types of cluster ions with NH_3 in a cluster beam experiment are studied; the clusters being $H^+(\text{pyridine})_m(H_2O)_n$ ($m = 1-2$, $n \leq 15$) and $H^+(NH_3)_1(\text{pyridine})_1(H_2O)_n$ (also $n \leq 15$). The results from the experiments are input to improve the present kinetic model by Beig and Brasseur for atmospheric positive ions. The importance of evaporation of pyridine from the cluster ions is also studied in the improved modelled. Finally, the atmospheric implications of the experimental results and the results from the kinetic modelling are discussed."

- Experimental conditions. The title of the manuscript suggests experiments at atmospheric conditions, but as the reactions are made in vacuum, I would not call the conditions atmospheric. The authors could consider modification of the title.

Answer: The title was never meant to suggest that the experiments were made under tropospheric conditions; only the conditions in the modelling were atmospheric. However, we agree with the referee that the title is ambiguous and can easily be misunderstood. The title of the manuscript has now been modified to "Reactions of $H^+(\text{pyridine})_m(H_2O)_n$ and

$H^+(NH_3)_1(pyridine)_m(H_2O)_n$ with NH_3: experiments and kinetic modelling" in order to avoid misunderstandings.

- Another concern I have relates to the large water clusters used in this study. Do the authors suggest that water cluster ions with 10 or more water molecules are abundant in the atmosphere? The amount of water molecules attached to cluster ions should also be a function of RH. What was the RH of the sample entering the QTOF? If the ESI does not produce atmospherically relevant clusters to begin with, the reaction rate coefficients derived from the experiments are also not relevant.

Answer: The paper makes no claims regarding the number of water molecules found or not found in clusters in the atmosphere per se. The question of relative humidity is also not really applicable to the electrospray ionization source. In the spray plume, RH is likely close to 100%; however, at this stage the particles are droplets. During the transition to high vacuum, the RH drops and the droplets shrink. As the actual clusters enter the instrument interior they experience a RH that is for practical purposes nil. As such, the clusters are meta-stable, but they generally survive passage through the instrument without evaporation of H_2O.

The distributions of clusters produced by the ESI are not necessarily representative of the distribution in the atmosphere (indeed, this is unlikely). Therefore, each cluster has been studied individually, and a relative rate coefficient is given for each cluster (in Fig. 6) as opposed to a rate coefficient for the total cluster distribution. When it comes to the modelling we--like the original model by Beig and Brasseur--do however neglect the size dependent effects and have taken the thermal rate coefficient for $H^+(H_2O)_4$ as representative for all pure water clusters. Analogously, the rate coefficient for the cluster having a pyridine and four water molecules was used to represent clusters with pyridine. We feel this to be justified (in both cases) given the weak size dependence of the rate coefficients in Fig. 6.

- Fig 2. Is there no loss of U1-U4 clusters, or is this only missing in the figure? If this truly is lacking in the model, then this could cause major errors in the resulting cluster distributions.

Answer: The loss of U1 to U4 clusters is included in the model, i.e. they are only missing in the figure. The figure is now corrected (see attachment in this reply).

Minor comments

- Introduction: - The authors state that ion clusters are more stable than neutral clusters, but this is not correct for all clusters. Adding a charge to some clusters will cause them to become much less stable, e.g. small clusters of one strong base and one strong acid. This statement should be reformulated.

Answer: We agree. However, the statement is not reformulated but removed in the rewriting of the introduction.

- The ion formation process description only talks about cluster formation, but charge transfer should also be discussed.

Answer: In our measurements and in published literature on water containing clusters we do not see any evidence of charge transfer. We would therefore prefer not to include a discussion about charge transfer.

- 24537, row 18. Should be Eisele 1983?

Answer: The Eisele 1983 paper is mainly a description of the measurement instrument, although some specific ion peaks are mentioned. The Perkins and Eisele 1984 paper is the first real paper on atmospheric ion measurements (although the actual experiments were performed in 1983). However, the text has been changed slightly to avoid confusion and now reads: "The first ground based measurement of atmospheric ion composition was performed by Perkins and Eisele in 1983 (Eisele 1983; Perkins and Eisele 1984). In the measurements, several unidentified positive ions were observed (Perkins and Eisele 1984)."

- Please also define the range of n in H+(Py)_m(H2O)_n

Answer: The range of n has now been added at relevant places in the manuscript.

- Results: - 24543, rows 8-24 are hard to follow, and the authors might consider adding a diagram to make the reactions more clear.

Answer: A more thorough description of the model employed to a specific example has been added to the supplementary material. This material is attached in the end of this reply.

- 24546, row 14. Including this reaction in a model that also includes reaction R1b does not make sense to me. In practice these are opposite reactions, exchanging between Py and NH3 in the clusters. What is the net effect of these reactions, and how are the rate coefficients determined in the situation where both are used compared to when only one is used?

Answer: It is true that these are opposite reactions; however, the reaction rates are quite different. In the original model by Beig and Brasseur (2000), the two proposed mechanisms for formation of pyridine + ammonia containing clusters were:

$$\mathbf{H^+(H_2O)_n + mNH_3 \rightarrow H^+(NH_3)_m(H_2O)_n} \qquad \mathbf{(R1a)}$$
$$\mathbf{H^+(NH_3)_m(H_2O)_n + X \rightarrow H^+(X)_1(NH_3)_{m-x}(H_2O)_{n-y} + xNH_3 + yH_2O} \qquad \mathbf{(R1b)}$$

and

$$\mathbf{H^+(H_2O)_n + X \rightarrow H^+(X)_1(H_2O)_{n-x} + xH_2O} \qquad \mathbf{(R2a)}$$
$$\mathbf{H^+(X)_1(H_2O)_n + NH_3 \rightarrow H^+(NH_3)_1(H_2O)_n + X} \qquad \mathbf{(R2b)}$$

$H^+(NH_3)_m(H_2O)_n + X \rightarrow H^+(X)_1(NH_3)_{m-x}(H_2O)_{n-y} + xNH_3 + yH_2O$ (R1b).

That is, it was assumed that if pyridine was added to the cluster prior to ammonia, it would first be ejected by addition of ammonia, and then it would add to the cluster a second time.

The rate coefficients are (cm^3s^{-1}):

R1a	**$1.91*10^{-9}*(300/T)^{0.39}$**
R1b	**$2.1*10^{-9}*(300/T)^{0.7}$**
R2a	**$2.08*10^{-9}*(300/T)^{0.89}$**
R2b	**10^{-11}**

where the first three are from Viggiano et al. (1988a-b) and the fourth (R2b) was assumed by Beig and Brasseur. The reaction R2b, which is also the one on page 24546 row 14, was removed from the models in our work on the basis of our experimental results, and replaced with the reaction $H^+(pyridine)_1(H_2O)_n + NH_3 \rightarrow H^+(NH_3)_1(pyridine)_1(H_2O)_{n-x} + xH_2O$. The text in question (p 24546) states that in order to investigate the effect on the modelling results, we tried Model A both with and without replacing the reaction R2b. In essence reverting our model to the Beig and Brasseur model. As evident from the rate coefficients, the net effect of the R2b reaction on the total formation of "pyridinated cluster ions" will be minor.

- 24550, row 27: "give loss of" should be reformulated.

Answer: The sentence has been modified. It now reads "Our experiments show that the reaction between $H^+(pyridine)_1(H_2O)_n$ and NH_3 does not result in loss of pyridine and that the reaction have a higher rate coefficient than assumed by Beig and Brasseur".

Attachment

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.

$H^+(H_2O)_{15} + NH_3 \rightarrow H^+(NH_3)_1(H_2O)_{14} + 1H_2O$ −1 u relative PI (RA)
$\rightarrow H^+(NH_3)_1(H_2O)_{13} + 2H_2O$ −19 u relative PI (RB)
$\rightarrow H^+(NH_3)_1(H_2O)_{12} + 3H_2O$ −37 u relative PI (RC)

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

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

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

$H^+(H_2O)_{15} \rightarrow H^+(H_2O)_{14} + 1H_2O$
$H^+(H_2O)_{14} + NH_3 \rightarrow H^+(NH_3)_1(H_2O)_{13} + 1H_2O$ (RBF).

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 → $H^+(NH_3)_1(H_2O)_{13}$ + $1H_2O$ relative to the reactant abundance is calculated as described above. We now assume that the frequency of the $H^+(H_2O)_{14}$ + NH_3 → $H^+(NH_3)_1(H_2O)_{13}$ + $1H_2O$ 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).