

Answers (**in bold**) to anonymous referee #3

The authors present experiments of positively charged pyridine-water-clusters reacting with ammonia, and modelled concentrations of positive ion clusters formed from ammonia, pyridine, alkyl substituted pyridine compounds and water. This study is apparently the first to describe the laboratory experiments on these specific reactions. The measurements are well-planned and the results seem reliable. However, as stated by the other referees, the authors fail to express a substantial atmospheric relevance for their study. Furthermore, the results from the modelling part of this study do not, at least in the way presented currently, give significant new information: some of the modelling results are presumable and do not differ from the previous modelling studies, whereas the rest are based on assumptions that may not be relevant and the applicability of these results is thus questionable. I find that in order to make this manuscript worth to be published in ACP, the authors should continue measurements with related clusters and include the new results in the applied model. However, if the authors can substantially improve the manuscript by removing some of the below mentioned dubious assumptions and by clarifying and justifying the remaining assumptions as well as the motivation of the study, the manuscript may be published without conducting more experiments.

Specific comments

The motivation of the study should be more clearly expressed. If the main interest on the pyridine related ion clusters, shown in previous studies to be abundant or even dominant in tropospheric concentrations, is related to the ion-induced nucleation, it should be more accurately expressed and discussed.

Answer: We agree and the motivation of the study is now more clearly expressed in the end of the introduction. The introduction is also less focussed on aerosols formation. The end of the introduction now reads:

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 $H^+(pyridine)_m(H_2O)_n$ ($m = 1-2$, $n \leq 15$) and $H^+(NH_3)_1(pyridine)_1(H_2O)_n$ (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.

In addition to the motivation of the study, I was concerned with the relevance of the applied kinetic model. The results are based on assumptions that should be expressed more clearly because their reliability is, in my understanding, dubious.

Answer: See answers below.

In model A the applicability of Reaction (R1b) with all the possible values of m is not confirmed or discussed. Viggiano et al. have reported that the reaction rates are fast (I have not read the whole article but only the abstract) while $m + n$ is 5 or smaller. However, with NH_3 concentration of $2.5 \cdot 10^{10} \text{ cm}^{-3}$ the ion clusters may be attached to significantly more than 5 ammonias: if the evaporation is totally ignored the clusters gain tens of NH_3 molecules per second. The authors seem to point out indirectly (in pages 24547-24548), by discussing the basicity and proton affinity of the molecules, that the exchange of NH_3 to Py is not self-evident. If it does not happen, the abundance of the positive Py- NH_3 -clusters diminishes greatly. In my understanding these clusters have not been reported in the field studies.

Answer: Our model, in keeping with the model by Beig and Brasseur, does not explicitly deal with neither addition nor evaporation of NH_3 to the clusters. The formation of clusters containing NH_3 is achieved by a rate coefficient that adds p NH_3 molecules, and the model does not concern itself with whether this is one or several NH_3 . The cluster is implicitly assumed to contain a certain number of NH_3 , the exact number of which is governed by the rate of addition and evaporation. Furthermore, by using the rate coefficient by Viggiano et al (1988b)--determined for clusters with up to five water or ammonia molecules--it might be said that the model is assuming that this is the number of water or ammonia molecules that are present in these clusters. The reviewer raises an interesting point in that it is not self evident that the reaction in question,



should be valid for values of $p > 5$ as this has not been experimentally determined. Furthermore, the issue of charge transfer within the cluster is not trivial, as the stronger basicity of ammonia in solution means that charge transfer from ammonia to pyridine might not occur for this reaction, as suggested by Viggiano et al. (1988b), if the cluster is large enough, i.e. ammonia has sufficiently many hydrogen bonds to other H_2O or NH_3 molecules in the cluster. The exact size where this occurs is unknown. It should, however, be pointed out that the charge carrying ammonia molecule has a full solvation shell of water and ammonia molecules already for $n + p = 5$ (see *e.g.* Hvelplund et al., J. Phys. Chem. A, 114, 7301, 2010 and references therein).

For the reactions opposite the one above (that we have determined in these experiments): $\text{H}^+(\text{pyridine})_1(\text{H}_2\text{O})_n + \text{NH}_3$ and $\text{H}^+(\text{NH}_3)_1(\text{pyridine})_1(\text{H}_2\text{O})_n + \text{NH}_3$ we hardly see the exchange of NH_3 for pyridine at all, for any $n \leq 15$. This is a clear indication that either the cluster is not large enough to result in an intra cluster charge transfer from pyridine to ammonia, and the Reaction (R1B) is expected to occur as stated also for larger n ; or, intra cluster charge transfer do occur, but the cluster prefers to lose H_2O and keep both pyridine and at least one ammonia in the cluster, in which case Reaction (R1B) would also be valid for larger clusters. We can assume that water and ammonia molecules (with the exception of the first ammonia) can be used somewhat interchangeably in this context, i.e. with regards to cluster size and dissociation energies (Viggiano et al. 1988a and 1988b; Andersson et al. 2008; Hvelplund et al., J. Phys. Chem. A, 114, 7301, 2010; and branching ratios in this work).

I agree with the other referees that neglecting the evaporation rates of Py from all the clusters in model B is not justified.

Answer: Evaporation of pyridine is now included in the model. See also answers below.

It should be noted that as long as the evaporation is not taken into account, the clusters will end up in the largest cluster included in the model: Figures 8 a)-d) could as well have $H^+(NH_3)_mPy_{10}(H_2O)_n$ as the largest clusters, and they would look the same in steady state, the Py_5 -cluster would be replaced by Py_{10} and $Py_{1...9}$ would appear as $Py_{1..4}$ do now.

This is not universally true: since the formation of clusters with several pyridine molecules is in the model a competition between addition of pyridine to precursors and removal of precursors via recombination and aerosol scavenging. This is evident from the fact that clusters having only one pyridine dominate for some pyridine concentrations in Fig. 8a. However, the 5-pyridine clusters are formally missing a removal mechanism: the further reaction leading to clusters with 6 pyridines and so on. Clusters having 5 pyridine are really representing clusters having 5+ pyridine molecules; the manuscript is now changed to state this more clearly.

- In Fig. 8d) I also wonder, why concentration of $H^+(NH_3)_m(H_2O)_n$ is two orders of magnitude higher than the sum of $H^+(Py)_m(H_2O)_n$ at pyridine concentration equal to NH_3 concentration. The related reaction rates given are basically equal and I do not see what else could here affect the concentrations.

The main reason is that a large part of the $H^+(H_2O)_n$ clusters react with acetone: the rate coefficient is comparable to those for reaction with ammonia or pyridine; however, the acetone concentration is two orders of magnitude larger than the ammonia concentration for Fig. 8d, as seen in Table 2. Consequently, there are two orders of magnitude more clusters that can react to form $H^+(NH_3)_1(H_2O)_n$ compared to $H^+(pyridine)_1(H_2O)_n$.

- The authors state repeatedly that the evaporation of pyridine was not observed. However, in page 24545 (lines 14-23) they determine the maximum rate coefficient for loss of pyridine. I find that the authors should add in Fig. 3 a panel and depict the mass spectrum of $H^+Py_2(H_2O)_{11}$ in which the loss of pyridine should be seen, because the peaks in Fig. 3b) at m/z -116 and -98 are apparently taken as not statistically significant.

Panels depicting $H^+Py_2(H_2O)_{11}$ in the background measurement and reacting with NH_3 has been added to Fig. 3, as Fig. 3c and Fig. 3d, respectively. The rate coefficient determined in page 24525 is for loss of pyridine as a consequence of reaction with NH_3 , and not a rate coefficient for evaporation of pyridine. The peaks corresponding to loss of pyridine after reaction with NH_3 is not visible in Fig. 3c,d due to low intensity; however, the neat loss of pyridine or loss of pyridine accompanied by a water molecule can be seen. The referee is correct regarding the peaks at m/z -116 and -98 in Fig. 3b not being considered significant.

A short note on the relative intensity of these peaks has been added to the text regarding Fig. 3b. The new Fig. 3 is included as a supplement to this reply.

In consequence to the comments above I find that the authors should make some remarkable changes to the manuscript before reconsidering the publication in ACP. I suggest adding more measurements including

i) testing of whether Py really replaces the NH_3 in ion clusters with large number of NH_3 molecules (or if this is shown by Viggiano et al. or by somebody else, clearly stating it),

Answer: We have not been able to perform this experiment since these clusters (clusters containing large number of NH_3) can not be produced in our current equipment. Other instruments (not available to us) might be better suited to investigate the reaction in question.

ii) evaluation of the evaporation rate of cluster including 3(-4) Py-molecules. Expansion to other directions instead is also possible, of course. I find that with the current measured data set, there is no reason to present modelling results, because they are either very similar to previously published results, which can be expected because of only minor modifications to the previous studies, or too hypothetical. If the manuscript is published in ACP with only the current measurement data, the authors should present and discuss the evaporations of the bases both in measurement data and in the model much more thoroughly.

Answer: We have now studied the influence of evaporation of pyridine on the outcome from the models. These results are shown in a graph in a supplement to this reply. The main findings are that

1) evaporation of pyridine is negligible if the rate coefficient is less than $0.001 \times n_{\text{Py}} \text{ s}^{-1}$ where n_{Py} is the number of unprotonated pyridine in the cluster,

2) evaporation of pyridine is very important if the rate coefficient is larger than about $1 \times n_{\text{Py}} \text{ s}^{-1}$.

We have now also conducted measurements in order to estimate the evaporation of pyridine from clusters with 5 H_2O , 0 to 1 NH_3 and 1 to 4 pyridine molecules. A description of the experiments has been included in the paper. Unfortunately, the QTOF instrument is not suited to measure such a low level of evaporation, as a possible evaporation signal is lost in the background of collision induced dissociation leading to loss of pyridine in the ion optics of the instrument. Under the experimental conditions we obtain evaporation rate coefficient of less than around 0.1 s^{-1} . A figure showing the experimental results on evaporation of pyridine is attached in the end of this reply.

The importance of evaporation of pyridine is now discussed in the manuscript.

Minor comments

- notation needs unification, now m sometimes stands for number of NH₃, sometimes of Py. In some figures there are U, V, W etc., whereas in other and in text Py, Pic, and Lu.

This has been rectified.

- I would also replace the notation (pyridine)_{1,2} in page 24541, on line 18, e.g. with (pyridine)_{1...2}.

The text on page 24541 “That is, in the reaction between H⁺(pyridine)_{1,2}(H₂O)_n ...” has been changed to “That is, in the reaction between H⁺(pyridine)_m(H₂O)_n (m = 1-2) ...”.

- In the abstract the values for m (on line 5) should be given.

“(m=1-2)” is now included in the abstract.

- picoline and lutidine should be somehow described in abstract, if mentioned.

The mentioning of picoline and lutidine in the abstract is now accompanied by the parentheses “(methyl-pyridine)” and “(dimethyl-pyridine)”, respectively.

- p. 24536, line 23: should be N₂⁺, not NO⁺

Answer: This has been changed on the line indicated.

- the similarity of the reaction rates with the molecule collision rate in atmosphere should be mentioned in the end of p. 24539

Answer: We have now included this. The sentences in the end of p. 24539 now reads "The rate coefficients for the first three reactions have been determined by Viggiano et al. for the case X=pyridine (Viggiano et al., 1988a, b). The rate coefficients were found to be approximately equal to the collision rate constant. The rate of Reaction (R2b) is unknown; Beig and Brasseur assumed 10⁻¹¹ cm⁻³ s⁻¹ as an upper limit for the rate coefficient for all pyridine derivatives in their study, this is two orders of magnitude lower than the rate coefficient for Reaction (R1b) at 298 K."

- p. 24540, line 9: abbreviation QTOF should be opened

Answer: This is now corrected.

- p. 24540, line 25: “number of collisions below 10

Answer: This has been changed.

- p. 24541, line 12: production of protonated water clusters from O₂⁺ and N₂⁺ should be explained in few words

Answer: The text has been modified according to the reviewer's suggestion, and now reads: "In their model, protonated water clusters, $H^+(H_2O)_n$ are continuously produced in a series of reactions starting from O_2^+ and N_2^+ . Initially, ions O_2^+ and N_2^+ are formed by galactic cosmic rays and by radioactive decay (close to ground). Charge transfer reactions with molecular oxygen convert N_2^+ to O_2^+ . The latter ion then forms O_4^+ , which in turn reacts with H_2O to form $O_2^+(H_2O)$. Additional H_2O molecules add to the cluster, which forms $H^+(H_2O)_n$ via loss of O_2 and OH (Beig et al. J. Geophys. Res. 98, 12767 (1993))."

- p. 24542, line 25 and thereafter: "m/z -18 relative the parent ion" should be expressed perhaps as "m/z 18 u smaller than parent ion"

Answer: This has been changed according to the reviewer's suggestion.

- p. 24548, lines 14-17: this should be mentioned in Methods and/or Results

Answer: A note regarding this issue has been added to the Methods section.

- p. 24550, lines 5-18: these are results and should be moved at least partly to Results section

While these are results, they are used in this paper solely to illustrate the effect of the used reduced collision energy versus the collision energy at atmospheric conditions in terms of branching ratios. As such, they are an extension of the immediately preceding discussion on the interplay of the dissociation energies of H_2O and NH_3 and their effects on product branching ratios. As the purpose of the experiments in question is merely to illustrate a point in the discussion, we feel that separating them into pure Results/Discussion would lead to unnecessary fragmentation, impair the text flow, and deteriorate the text as a whole.

- p. 24550. lines 27-28: how significant was the difference in rate coefficient to that assumed by Beig and Brasseur?

Answer: Two orders of magnitude ($\approx 1 \cdot 10^{-9}$ vs 10^{-11} cm^3/s). A note has been added to the text in question.

- Table 1: notations, there are some m:s appearing (e.g. in the third and 18th reaction), some m:s are changing to x (e.g. 7th reaction).

Answer: This has been corrected.

- Table 1: rate coefficients for "cluster + aerosol" and "recombination" seem to be in wrong order, recombination coefficient should be higher.

The rate coefficients in question have been cited in the correct order from Beig and Brasseur (2000), who assumed $5 \cdot 10^{-6}$ cm^3s^{-1} for the cluster + aerosol reaction as a

representative value; in addition, they reported that sensitivity tests indicated that the results were not strongly dependent upon this value. We have opted to use the same rate coefficient in order not to deviate from the original model in this respect. The cluster-cluster recombination rate coefficient: $k_{17} = 6 \times 10^{-8} (300/T)^{0.5} + 1.25 \times 10^{-25} [M] (300/T)^4$ gives a numerical value of $3.31 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ at 298 K and 1 atm, which is not so different from the aerosol rate coefficient.

- Table 2: are there any negative ions to recombine with?

Answer: Yes, the concentration of negative ions available for recombination was in the model put equal to the concentration of positive ions. Table 2 has now been modified to include this information. In addition, the information has also been added to Section 2.2, the Positive ion model description.

- Fig. 4: Why is there no curve for $-\text{H}_2\text{O}$ in 4a)?

Answer: The curve is not shown because the intensity is very low $< 5 \times 10^{-3}$, and the reaction channel is considered insignificant compared to the main products. Especially since the data is afflicted by large statistical (low count rates) and experimental (noisy signal) uncertainties. For some clusters, we were not able to measure the signal as it was lost in the background.

- Fig 6.: Some value is needed for the rate coefficient with which the rates are normalized.

Answer: The value of the rate coefficient with which the rates are normalised is now given in the figure caption ($1.91 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at 298 K).

Attachment

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 $\text{H}^+(\text{pyridine})_m(\text{H}_2\text{O})_5$ 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.

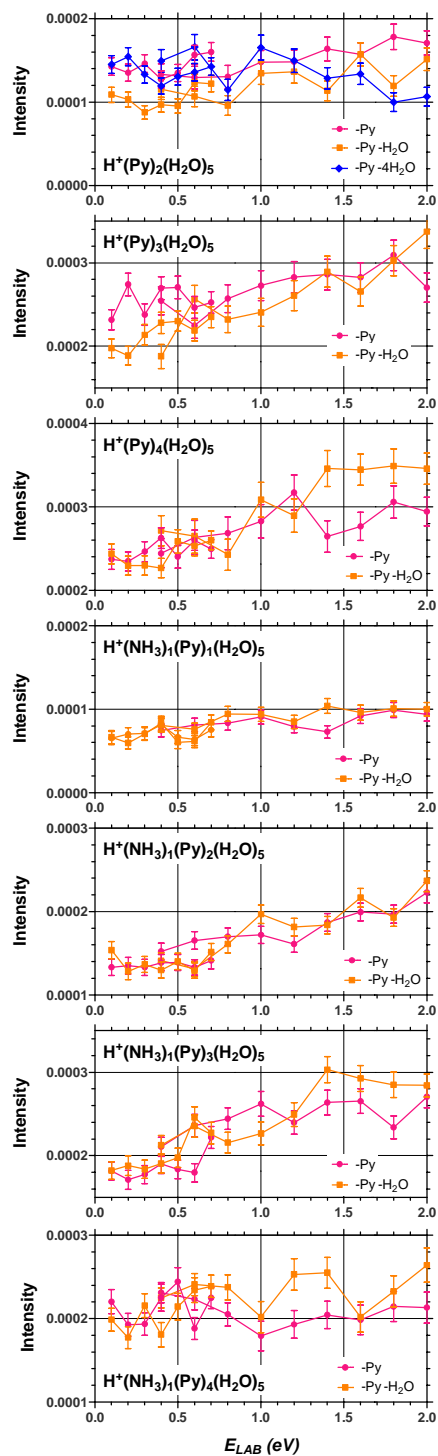


Figure S1. The main reaction channels for loss of pyridine (Py) as the clusters $H^+(\text{pyridine})_m(\text{H}_2\text{O})_n$ ($m = 2 \dots 4$) and $H^+(\text{NH}_3)_1(\text{pyridine})_m(\text{H}_2\text{O})_n$ ($m = 1 \dots 4$) pass through an empty collision cell at various collision energies in the lab frame (E_{LAB}). $H^+(\text{pyridine})_1(\text{H}_2\text{O})_5$ is not included as no loss of pyridine was detected.