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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Reactions of H$^+$(pyridine)$_m$(H$_2$O)$_n$ and H$^+$(NH$_3$)$_1$(pyridine)$_1$(H$_2$O)$_n$ with NH$_3$: experiments and kinetic modelling under tropospheric conditions" *by* M. J. Ryding et al.

Anonymous Referee #2

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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$_4^+$ - H$_2$O clusters corresponds to (NH$_4^+$)(H$_2$O)$_n$, then given equilibrium constants for all (NH$_4^+$)(H$_2$O)$_x$ + H$_2$O 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.)

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 cluster ion + aerosol coagulation rate constant k$_{16}$ 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 k$_{16}$) and polluted (higher k$_{16}$) air.

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?

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.

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.

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 N_2-O_2-H_2O-NH_3-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.

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).

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 24535, 2011.