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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Proton affinities of candidates for positively charged ambient ions in the boreal forest" *by* K. Ruusuvuori et al.

Anonymous Referee #1

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This is an interesting manuscript presenting fundamental numerical thermodynamic data on very important and current topic. Which ambient gaseous chemicals in practice could have a potential to have a major effect on positive charged ambient molecular ions, and thereby also partly on the new particle formation in the atmosphere?

The authors have surveyed a large group of nitrogen containing bases, experimentally known to significantly prevail in the atmosphere in connection with positive ions, and estimated their proton affinities. Proton affinity is known to govern the role of a compound in gaseous ion-molecule reactions in case of positive ions. In the estimation both literature data and computational tools have been used. The numerical results computed by different quantum chemical methods are first compared with each other for a bunch of common compounds such as ammonia, pyridine and some simple

amines, as a benchmark. Later on, the obtained data is compared with existing NIST data, when possible. In fact, the paper somewhat updates the data given by NIST. Also some interesting differences found in the data are discussed. The paper is very clear and straightforward, and gives some additional new thermodynamic data for the community. Finally, a graphical illustration is given for the compounds having highest calculated PAs, presented with measured ambient concentrations.

I believe the paper will help the community in atmospheric science to interpret ambient field data on molecular ions, having further contribution to understanding ambient processes in molecular and nanoscale. Here, positive ions were discussed. A similar updated study should be performed in forthcoming research on negative ion compounds as well.

I'm willing to support publishing of the manuscript practically almost in this form. Minor: The text at P3 L11 & P8 L23 and in caption of Fig 2 in connection with the reference Ehn et al., 2010, should be opened a bit more. It is not obvious for a random reader whether the concentrations given (in 1/cm3) are for neutral gas molecules or molecules detected in cluster ions. I believe the latter, but the calculations were performed for neutral base compounds, after all, so this should be clarified.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 10603, 2013.