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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 #3

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The manuscript, "Proton affinities of ambient cations in the boreal forest," describes molecular modeling of cationic nitrogen compounds that were observed in a study of ambient positive ions in Hyytiälä, Finland. The ultimate goal of this study was to gain insight into the concentration of neutral gas phase bases using observations from Ehn et al. (2010). The ability to identify and quantify gas phase bases in the atmosphere is a key need in the atmospheric chemistry community, since such compounds are expected to play important roles in nucleation and early particle growth. The calculations reported here appear to be of high quality, utilizing the variations of the "Complete Basis Set" (CBS) method that provide higher accuracy proton affinities (or the Gibbs free energy change of the protonation reaction) at a reasonable computational cost. Using this information, the authors are able to make some statements as to the relative

abundance of pyridine vs. compounds such as alkyl di- or triamines. In the case of the latter, pyridine was observed at higher abundance compared to the C2-3 amines, however was calculated to have a lower proton affinity, so the authors could conclude that pyridine must have a higher ambient concentration compared to those compounds.

The proton affinity information from this study would be useful for any observational scientists who measure ambient cationic nitrogen compounds either as ambient ions or using proton transfer reactions. The subject matter of this manuscript is appropriate for publication in this journal. To conclude, this is a focused paper, and its single, simple message is refreshing in an era of ever-increasing manuscript sizes. I recommend publication of this manuscript as-is.

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