Review of: "Proton affinities of candidates for positively charged ambient ions in the boreal forest" by Ruusuvouri et al., *Atmospheric Chemistry and Physics Discussions*, **2013**, *13*, 10603-10620

This article presents benchmarking information for the proton affinity of base cations that correspond to measured mass spectral peaks using the atmospheric pressure interface time of flight mass spectrometer. The proton affinity is a key player in the formation of atmospherically relevant clusters, as it will determine the strength of the electrostatic interactions which drive their formation. The topic is of interest in the atmospheric community as experimental values are difficult to determine and can have varying relative values. This article is within the scope of *Atmospheric Chemistry and Physics* and may be suitable for publication once the comments below are addressed.

Specific Comments:

1. A Supporting Information document of raw values for all thermodynamic quantities as well as optimized structures (as Cartesian coordinates) should be included.

2. Page 10604, line 24: The authors should be more precise here. Proton affinity relates to enthalpy, whereas gas phase basicity relates to the free energy.

3. Page 10606, lines 3-8: Why not use a lower level of quantum theory, such as semi-empirical method (for example, AM1, PM3, PM6) which would do substantially better at generating initial configurations? Unless parametrized properly for distances and weak electrostatic interaction, force fields like UFF are not suitable, even for configuration searching. Skipping the configuration sampling step may lead to local minima which could potentially augment the generated values for proton affinity. It would be nice to know which molecules were skipped in the configuration search process.

4. Page 10608, lines 7-9: This sentence appears not to correspond exactly with Fig. 1. In Fig. 1, it appears that the CBS-QB3 method more nearly approaches the horizontal lines (presumed by the reader to indicate the accurate value) than the CBS-4M method only in the case of ammonia and methylamine. The reader would then infer that CBS-4M may be more accurate. What exactly is the definition of "accurate" that is used here?

5. Page 10609, lines 7-8: What do the authors mean when they say they were unable to resolve the issue of the tropylium proton affinity? Was addressing this too computationally demanding? Additionally, when the authors say in line 9 that "the reliability of this value needs to be questioned", are the authors referring to their computationally-determined value or the value reported by NIST? Finally, this paragraph seems a bit out of place since it focuses on what appears to be a special instance where computation and experiment disagree for (presumably) known reasons. Why, then, bother including it in the tables at all?

6. Page 10610, lines 3-5: In the discussion of Eq. 1, the authors should again be clear that the form of Eq. 1 used assumes that the difference in gas phase basicities is similar to the difference in proton affinities. Was this the case for all the data the authors compiled?

7. Table 1: The authors list several calculations in the table that are not listed in the Computational Methods section of the paper. Were these performed by the authors? The RI methods and those basis sets are not available in Gaussian09, unless another modeling package was used. If so, please amend the Computational Methods section to include these methods. If they were not performed by the authors, please cite the papers from which they were taken.

8. Figure 2: This figure would benefit from a legend in the plot that indicates that the green squares are the proton affinities and the black circles are average ambient concentrations.

Typographical Errors:

1. Page 10605, line 26: Please insert an "of" in between "PA" and "all".

2. Page 10606, line 1: Change "molecule" to "molecular".

3. Page 10607, lines 13-14: The first instance of the word "change" should be removed, as it is doubled in this sentence.

4. Page 10609, line 22 and 24: Change "molecule" to "molecular".

5. Page 10611, line 5: Change "has" to "have".

6. Figure 1 caption: The lines in the figure are horizontal, not vertical as described in the caption.