Review of: Enhancing effect of dimethylamine in sulfuric acid nucleation in the presence of water—a computational study by Loukonen et al., 2010

General Comment:
This paper uses computational methods to explore the effect of ammonia and dimethylamine on addition of sulfuric acid to an existing one-acid cluster and the effect of these bases on the hydration of one- and two-acid clusters. Based on their calculations, the authors suggest that dimethylamine will enhance the addition of sulfuric acid to clusters when either zero or more than two waters are contained in the cluster. The authors also conclude that all dimethylamine-containing two-acid clusters will remain unhydrated in tropospherically-relevant conditions. The paper is within the scope of ACP and should be published subject to the recommendations given below.

Specific Comments:
Overall:

1. The authors mention on several occasions the uncertainties associated with the calculations performed in this work (for instance, the discussion of scaling factors on pg. 2327). Do the authors have any quantitative values for their uncertainties? How different would two calculated values have to be for the authors to consider them to be statistically different? As an example, in Figure 7, what minimum difference in ΔG of addition values is required for two different clusters at the same level of hydration to be considered having differing thermodynamic stabilities by the authors?

Introduction:

1. References to key field measurements where amines have been detected in nucleation mode particles are lacking. Suggested references to include are: (Smith et al., 2010;Smith et al., 2008).
2. Additionally, recent laboratory work has suggested that amines may play a significant role in new particle formation and growth. The reviewer refers the authors to: (Bzdek et al., 2010;Wang et al., 2010).
3. Finally, can the reader consider dimethylamine as a model compound? Is it reasonable to extrapolate the results of dimethylamine to the class of alkylamines? A discussion of this somewhere in the paper may be useful.

Computational details: This reviewer does not have much expertise in computational models; however, what was presented appears reasonable.

Results and discussion:

1. Some brief comments on the content of each of Figures 1-6 would be helpful before discussing the results. Six figures are a lot for the reader to take in without guidance from the authors.
2. Acid addition:
    a. Pg. 2328, lines 1-5: When the authors present Figure 7, it would be beneficial to add a statement describing how the ΔG values were obtained (it appears they come from subtracting relevant values in Table 1).

b. This reviewer spent a significant amount of time trying to find the relevant clusters in Figures 1-6 while reading this section. This resulted in making it difficult to follow the discussion. The authors should consider referencing the relevant figure(s) for each section of discussion. For instance, when discussing the 2-water clusters, direct the reader to structure (c) in the relevant figures.
c. Pg. 2329, line 6: For the sentence beginning with "As for the one-water case", it was not clear if the authors were discussing the one-water case (which seems out-of-place) or alluding to a similarity to the one-water case. This should be clarified.

3. Hydration:
   a. Pg. 2332, line 20: This sentence is confusing. The authors should consider breaking it into two sentences where one deals with the general idea and the second explains the specific example being given.
   b. The authors mention in this section that they are looking at hydration as a function of relative humidity (RH) and temperature (pg. 2333, lines 12-15); however, it seems only data for different RH is presented in the manuscript, while the temperature remains constant at 298.15 K. The authors should clarify whether indeed they were looking at hydration as a function of temperature or are maintaining constant temperature for their calculations. If temperature is constant, it may be worthwhile to note this when going through the equations (i.e. "at constant *T*" when defining the variables).
   c. The authors make reference to differences that appear at RH higher/lower than 45% several times (pg. 2334, line 7; pg. 2334, line 18). Where did this RH value come from? The relevant figures only show data at RH 20%, RH 50%, and RH 80%. Did the authors also perform experiments at RH 45% but are not including them in the figures?
   d. Pg. 2334, line 6: Change "…hydrates quite effectively." To "…hydrates quite effectively at higher RH."

Atmospheric relevance:

1. The clarity of Table 2 may be improved by changing the first column from 1:1, 1:10, 1:100, etc. to 1, 0.1, 0.01. This is more in line with the format of the second column and will emphasize the fact that even low levels of dimethylamine will result in significantly more amine than ammonia in clusters.

Technical Corrections:

Introduction:

1. Pg. 2322, line 20: Change "in troposphere" to "in the troposphere"
2. Pg. 2323, line 19: Change "This compound" to "These compounds"; change "stabilize sulfuric acid solution" to "stabilize the sulfuric acid solution"
3. Pg. 2324, line 12: "This" – what does this refer to? Perhaps change to "This study"

Computational details:

1. Pg. 2325, line 4: Change “as a guess structures” to “as a guess structure”
2. Pg. 2326, line 1: Change “error have even” to “error have an even”

Results and discussion: Hydration

1. Pg. 2332, line 14: Change “as there is” to “as there are”
2. Pg. 2332, line 15: Change “than any of the other” to “than any other”
3. Pg 2333, line 8: Change “is under study, e.g. while calculating…” to “is under study. For instance, while calculating…”
4. Pg. 2334, lines 10-11: Change “as opposite to” to “as opposed to”
5. Pg. 2334, line 18: Change “how much more water” to “how much water”
6. Pg. 2335, line 18: Change “of the order 250%” to “on the order of 250%”

Atmospheric relevance:

1. Pg. 2336, line 4: Change “The effect of the concentrations to the cluster distributions” to “The effect of concentration on the cluster distributions”
2. Pg. 2337, lines 7-8: Change “again indicating towards their possible importance” to “again indicating their possible importance”
3. Pg. 2337, line 27: Change “successfull” to “successful”

Conclusions:

1. Pg 2338, line 13: Change “molecules with either ammonia or dimethylamine molecule” to “molecules with either an ammonia or a dimethylamine molecule”

References:

Bzdek, B. R., Ridge, D. P., and Johnston, M. V.: Amine exchange into ammonium bisulfate and ammonium nitrate nuclei, Atmospheric Chemistry and Physics Discussions, 10, 45-68, 2010.

Smith, J. N., Dunn, M. J., VanReken, T. M., Iida, K., Stolzenburg, M. R., McMurry, P. H., and Huey, L. G.: Chemical composition of atmospheric nanoparticles formed from nucleation in Tecamac, Mexico: Evidence for an important role for organic species in nanoparticle growth, Geophysical Research Letters, 35, L04808, doi: 10.1029/2007gl032523, 2008.

Smith, J. N., Barsanti, K. C., Friedli, H. R., Ehn, M., Kulmala, M., Collins, D. R., Scheckman, J. H., Williams, B. J., and McMurry, P. H.: Observations of aminium salts in atmospheric nanoparticles and possible climatic implications, Proceedings of the National Academy of Sciences of the United States of America, 107, doi: 10.1073/pnas.0912127107, 2010.

Wang, L., Khalizov, A. F., Zheng, J., Xu, W., Ma, Y., Lal, V., and Zhang, R.: Atmospheric nanoparticles formed from heterogeneous reactions of organics, Nature Geoscience, 3, doi: 10.1038/ngeo778, 2010.