# Response to the Referee #1

We thank the reviewer for his/her constructive criticism and comments. The manuscript has been significantly improved by many of the suggestions made in the review. In this response we clarify the issues pointed out by the reviewer and answer the specific comments and questions.

Overall:

> The uncertainty of the absolute ΔG values are likely several kcal/mol, as reaching even a 1 kcal/mol accuracy typically requires coupled-cluster – level energy corrections, which can not be done for this size of system. However, the relative ΔG values (for example, the differences between acid addition free energies to “bare”, ammonia-containing and amine-containing clusters) are likely reliable to within 1-2 kcal/mol or so. This assessment is based on the observation that while absolute values for the formation free energies of small sulfuric acid – containing clusters predicted by different computational methods differ significantly, the relative values usually fall within a much narrower range, typically around 2 kcal/mol or even less. See e.g. Kurtén and Vehkamäki (2008) for a longer discussion on the subject. Thus, we would consider a difference between for example two acid addition free energies significant if it is larger than about 2 kcal/mol.

Introduction:

1. We have added the suggested references to the field (Smith et al., 2008 and Smith et al., 2010) and laboratory studies (Bzdek et al., 2010 and Wang et al., 2010), thus making the experimental background and motivation more solid.
2. (cf. above)
3. In some sense, the reader can consider dimethylamine as a model compound. It can form an “average” amount of hydrogen bonds in the context of substituted amines and it is neither the least nor the most most basic of the small alkylamines. On the other hand, of course the specific bonding patterns cannot be extrapolated from dimethylamine to all amines. A short discussion of this was added to the manuscript: *”Focusing particularly on dimethylamine is a choice guided partly by previous*

*results. For instance, in one study dimethlyammonium ((*$(CH_3)_2NH_2^+$*) concentrations in accumulation mode aerosol particles during nucleation event days in boreal forest conditions was measured to be 50 times higher than during non-event days, thus strongly indicating that dimethylamine was involved in particle formation (Mäkelä et al., 2001). Furthermore, as a disubstituted amine dimethylamine may be regarded as a sort of "average amine" with respect to the basicity and the number of hydrogen bonds it can form. The choice was also partly guided by practical limitations: inclusion of e.g. all the other alkylamines in this study would be computationally unfeasible."*

Results and discussion:

1. It is true that six figures which each have six structures contains a lot of information. We have added the following description regarding the contents of the figures in the manuscript: *"In all the Figs. 1–6, the a)-structures are the non-hydrated ones, the b)-structures the monohydrates, the c)-structures the dihydrates, and so on. The sulfur atoms are depicted in yellow, oxygen atoms in red, nitrogen atoms in blue, carbon atoms in green and the hydrogen atoms in white. The hydrogen bonds are indicated with dotted lines."*
2. Acid addition:
    a. The acid addition values are indeed obtained from the free energy values summarised in Table 1 of the discussion paper, and we added the explicit formula for this to the manuscript: *"The results, obtained from the values given in Table 2 as (*$\Delta G$ *of acid addition) =* $\Delta G(n_{acids}) - \Delta G(n_{acids} - 1)$*, where* $\Delta G(n_{acids})$ *is the formation free energy for a complex with* $n_{acids}$ *sulfuric acid molecules, are shown in Fig. 7."* (Here the Table 2. refers to the revised manuscript.)
    b. We found the reviewer's suggestion to enhance the legibility of the section; now the reader is directed to the relevant structure of the relevant figure while discussing the clusters.
    c. The particular sentence is now rephrased as follows: *"Similarly to the case of sulfuric acid, dimethylamine and one water, acid addition to*

*the dimethylamine-containing two-water cluster is made relatively less favourable by the need to break one of the existing amine-water hydrogen bonds."*

3. Hydration:
    a. We have broken the long sentence into two parts, now hopefully conveying the idea more clearly: *"As we are interested in the relative fractions of the different hydrates of the cluster cores, the absolute concentrations of the nonhydrated core clusters are not needed. For example, in the particular case of hydration of one sulfuric acid molecule, the concentration of free sulfuric acid is eventually cancelled out from the final expressions."*
    b. We did study hydration as a function of relative humidity **and** temperature. However, it turned out that the hydrate distributions are quite insensitive with respect to changes in temperature, while keeping the relative humidity fixed. The reason for this is most probably the oppositely directed temperature dependences of the free energy changes and the absolute water content at constant RH. We elaborated on these issues as follows: *"To assess the extent of hydration in different circumstances, we calculated the hydrate distributions for the plain sulfuric acid clusters (one and two acids) and for the clusters containing either one or two acids together with one ammonia or dimethylamine molecule, at different relative humidities and temperatures. Assuming that the enthalpy and entropy of cluster formation are fairly constant with respect to the temperature, one can approximate the Gibbs formation free energies at different temperatures based on the values calculated at 298.15 K (and given in Table 2) as* $\Delta G(T)=\Delta H(298.15K)-T\Delta S(298.15K)$*. The temperature sensitivity of the hydrate distributions with constant relative humidity was observed to be weak. This is most likely due to the opposed temperature-behaviour of the formation free energy and the absolute water concentration. For instance, lowering the temperature shifts the Gibbs free energies into more negative direction, and as such implies more hydration. However, decreasing temperature also diminishes the absolute water concentration, and to a large extent these two competing effects cancel out, thus leaving the hydrate distributions reasonably temperature-independent."*

For this reason we decided to show the distributions only at one temperature (298.15 K). However, qualitatively the behaviour of the distributions can be extrapolated to lower (or higher) temperatures as well.

c. W studied hydration for a wide range of different relative humidities, from almost zero to over 250%. The chosen values (20, 50 and 80%) cover typical tropospherical conditions and contain a wide enough range of RH values to show the essential behaviour of the hydrate distributions. The first of the unfortunately confusing references to the RH value of 45% appears because it is the threshold-value for the core clusters of one sulfuric acid and ammonia to have more than half of the clusters hydrated. To emphasize this more clearly, the sentence is now rephrased as: *“More than 50% of the clusters are hydrated already with the relative humidities greater than 45%.“* The second reference to the value of 45% is due to the same threshold; here it is approached from a different viewpoint and it marks the value under which more than half of the one acid and ammonia clusters are unhydrated. The sentence is now rephrased: “*This also implies that at lower values of relative humidity (RH<45%), a single sulfuric acid molecule bound to dimethylamine binds water slightly better than a single sulfuric acid molecule bound to ammonia.”* This particular threshold-value applies only when the temperature is taken to be 298.15 K. With different temperature, the specific threshold-RH would not be the same. However, the overall behaviour of the hydrate distributions would remain qualitatively the same.

d. We clarified the sentence as suggest.

Atmospheric relevance:

1. We switched the format of the first column in Table 2 of the discussion paper from 1:1, 1:10,… to 1, 0.1,…, as suggested by the reviewer.

Technical Corrections: we have implemented all the suggested corrections.

## References

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Kurtén, T. and Vehkamäki, H.: Investigating Atmospheric Sulfuric Acid–Water–Ammonia Particle Formation Using Quantum Chemistry, Advances in Quantum Chemistry, 55, 407-427, 2008.

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