# Response to the Referee #2

We thank the reviewer for his/her constructive criticism and comments. In this response we clarify the issues pointed out by the reviewer and answer the specific comments and questions.

Comments for Introduction:

1. In the discussion paper we refer to the fourth assessment report of the IPCC (which was published in 2007) because it is the latest thoroughly reviewed and official report by the panel. However, there are more recent updates, as noted by the reviewer. For instance, *The Copenhagen Diagnosis* summarizes the research related to the IPCC Working Group I ("The Physical Science Basis") done after the 2007 report. This reference is added to the manuscript.

Comments for Computational Details:

1. We generated the initial guess structures using *all* the methods mentioned for *all* the clusters, whenever it was possible. That is, if we could find optimized structures from the literature, we used them as initial guesses. However, for most of the clusters there were no structures available from earlier studies (or there were only a few), so we created the needed initial guess structures using chemical/physical intuition (based on experience of the preferred structures and bonding patterns of similar clusters). On the other hand, creating initial guesses for larger structures using chemist's or physicist's intuition is very challenging. For this reason, we used molecular dynamics (MD) simulations to obtain additional initial guess structures for all the clusters. Some of the structures obtained with MD were used as such, some were discarded as being clearly far from the global minimum energy geometry, and some were further edited "by hand" before using them as initial guesses for the optimization.
2. We obtained a large number of initial guess structures as described above (and in more detail in the discussion paper and in the supplementary material), but these methods, unfortunately, do not inform the user when the global minimum energy structure is found. Ultimately, one has to rely on intuition and experience to judge when there are

enough different initial guesses for any particular cluster, that is, to know when the configuration-space is satisfactorily covered. So by a “fair set” we mean a set of structures that most probably contain the global minimum energy geometry, or a structure reasonably close (i.e. within a kcal/mol or so) to it in energy. Our experience was that after ten distinct and reasonable structures had been obtained by the MD sampling method, continuing the sampling very seldom resulted in a better minimum-energy structure. Thus, for these particular systems, ten distinct structures seems to be a “fair set”, though as with any approach (apart from the complete sampling of the 3N-dimensional space, where N is the number of atoms) there is no guarantee that the global minimum is found. Also, the obtained minimum energy geometry is always tied to the specific methods used and different geometry optimization methods do not necessarily agree on the minimum geometry. Indeed, in the sub-nanoscale theoretical nucleation studies, finding the correct cluster structures (those appearing in nature) is one of the main challenges. (A separate issue that can unfortunately not be assessed with the methods used here is that the global minima, especially if they are very difficult to reach from the immediate monomer-cluster collision products by normal thermal motion, may not necessarily be the most relevant structures for nucleation.)

3. We have tried to use the hindered rotor approximation (as implemented in the Gaussian 03 and 09 program suites) to explore the anharmonicity of sulfuric acid hydrates, but so far without a success (see e.g. the appendix of Kurtén et al., 2007). Even though the implemented package works well for textbook examples such as hydrocarbons (and also works for e.g. dicarboxylic acids), it fails (crashes) even for the hydrogensulfate ion, at least for those method/basis set combinations that predict a low-barrier hindered rotation. (For simple cases, hindered rotors can naturally be identified and treated “manually”, but for the larger clusters treated here an automated algorithm such as that of the Gaussian package would be essential.) In general, the hindered rotor approximation would be physically more appealing and most probably more accurate than any scaling approach, and would still be computationally feasible for much larger systems than anharmonic frequency calculations. However, in the absence of a functioning, automated package for carrying out the calculations, these methods are beyond the scope of this study, where the main emphasis is on the usage of applied quantum mechanics, rather than the methods themselves. These methods,

and in general the effect of anharmonicity to the energetics, should be kept in mind especially when absolute, chemical accuracy is desired.

4. The sentence was rephrased as suggested by the reviewer.
5. All the used individual scaling factors are now given in the manuscript. We also added a small comparison between the scaling factors used in this study and more standard scaling factors, available in the literature (e.g. Scott and Radom, 1996; Merrick et al., 2007).
6. We agree with the reviewer that most probably the scaling factors will never stabilize as the size of the system grows. For any system, the dimer will be more anharmonic than the monomer, and the trimer will be more anharmonic than the dimer and so on. However, we observed that the difference in anharmonicity between the free sulfuric acid and a monohydrate was larger than the difference in anharmonicity between the dihydrate and monohydrate. A similar observation was made also in an earlier study, at a higher level of theory (Kurtén et al., 2007). So it would seem that the relative differences in the scaling factors do get smaller as the system grows. However, as the size of the system grows, also other complications arise. For example, the possible existence of several (local) minima within a small energy range begins to be perhaps a larger problem than the vibrational anharmonicity. Nevertheless, at the chosen level of theory, the qualitative inaccuracy caused by applying the scaling factor of dihydrate of sulfuric acid to all of the larger clusters, is small.

Comments for Results and Discussion

1. We studied the hydration as a function of temperature **and** relative humidity. However, we noticed that while keeping the relative humidity fixed, changes in temperature had only a weak effect on the hydrate distributions. This is probably explained by the fact that the formation free energy change and the absolute water content have opposite temperature dependencies. We added an explanation of this to the manuscript: *"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."*

2. Typically the relative humidity in the troposphere would roughly range between 20% and 80% (see e.g. Girolamo et al., 2009; Mattis et al., 2002), so the chosen values (20%, 50% and 80%) should cover reasonable well the tropospherical RH-conditions. On the other hand, it is true that the temperature of 298.15 K is probably not the best possible choice for representing tropospherical temperatures in general. However, as the temperature-dependence of the hydration distributions was observed to be weak, qualitatively the results obtained at 298.15 K can be extrapolated to more realistic, lower tropospheric temperatures as well. This is now described with a few words in the manuscript as well: *"The sensitivity of the hydrate distributions to the relative humidity is more noticeable and thus worth a more detailed analysis. The general trend in all cases is more extensive hydration with the growing RH, as expected, although all the clusters do pose a different characteristics of hydration. The hydrate distributions for all the studied core clusters are presented in Figs. 8–10 for three values of the relative humidity (20%, 50% and 80%) with a constant temperature of 298.15 K. This temperature does not represent the conditions of the whole troposphere, but as mentioned, the hydrate distribution at constant RH does not significantly change upon temperature changes of a few tens of degrees."*

3. In the discussion paper, we refer to the value RH=45% because it is the threshold-value at which the half of the clusters of one sulfuric acid and ammonia are nonhydrated. Thus, for any RH-value below 45%, more than 50% of these clusters are nonhydrated. On the other hand, the hydration distributions of one sulfuric acid with

dimethylamine are quite static with respect to relative humidity, indicating that the vast majority of these clusters are monohydrates in all conditions. So what is meant by "low RH" in this context is "lower than 45%". Physically it translates into: "at lower relative humidities than 45%, dimethylamine-containing one-acid clusters bind more water than the corresponding ammonia-containing clusters." This is clarified in the manuscript as follows: *"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."*

4. We agree with the reviewer, and as explained above, we do believe that the results obtained using the "standard conditions" of 298.15 K and RH=50%, can be qualitatively extrapolated to a different conditions as well. We added to the manuscript discussion explaining this (the excerpts in 1. and 2.) and the reader is now reminded about this also in the section of atmospheric relevance.

## References

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