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Atmospheric Chemistry and Physics Discussions

Interactive comment on "From quantum chemical formation free energies to evaporation rates" *by* I. K. Ortega et al.

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We would like to thank the referee for the useful comments which certainly helped us to improve the quality of the manuscript.

Answer to the referee comments:

"In page 5, Conformational sampling section, the authors state that "the energies of all conformations are computed, and those with the lower energies are saved". The authors should clarify at which level these energies are computed."

The energies are computed at the same level as the geometries, using DFTB. We have re-written the paragraph to make this clearer:

“The choice of interaction potential for the energy calculations and geometry optimization step is also not a simple one. Because acids and bases are involved, the likelihood of a proton transfer is high. This precludes the use of simple (and fast) empirical potentials. Through the use of the CP2K simulation package (http://cp2k.berlios.de/), we used various semi-empirical wavefunction-based methods (AM1 (Dewar et al. 1985), PM3, (Stewart 1989) and PM6 (Stewart 2007)), as well as tight-binding self-consistent density functional theory (Cohen et al. 1994). In early tests, it was noticed that tight-binding DFT geometry optimization seemed to give the best structures, so this was used for the bulk of the configurations.”

“I guess that one of the headers of Table 3 (B3LYP/CBSB7+RICC2 should read B3RICC2. “

The referee is right. We have fixed the typo in the final version of the manuscript.

“The Gibbs free energy of formation of sulfuric acid dimer written in the text (-7.91 kcal/mol, second line below Table 2), does not match with the number written in the Table (-7.89 kcal/mol). This should be ïňĄxed.”

The Gibbs free energy of formation given in the text corresponds to the high level calculations explained in more detail in the supplementary material section. We have changed the text to make this clearer:

“The Gibbs free energy of formation of the sulfuric acid dimer calculated with the high level method combination (described in the supplementary material) is -7.91 kcal/mol (Table S.1.6)”.

“It is very interesting the fact that the key factor for the stability of the cluster is the proton transfer. However, this fact in not clearly reïňĆected, neither in the cluster names in Figure 1 nor in the reaction in Tables 3 and 4. I would suggest the authors, indicating in Tables 3 and 4, which reactions involve proton transfer. In connection to this point, it is also not clear whether the evaporation and ïňĄssion processes are associated to acid

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base reactions, and I think this is an important point. Has this any effect in the cluster fragmentation in over-critical clusters?."

The proton transfer is an important factor for the stability of the clusters (since having more ion pairs increases the stability of the cluster), but it is important to note that it is not the only factor determining the stability. The number of hydrogen bonds and the interaction energy between the acid and the base (stronger base leads to a stronger interaction) also contribute to the stability. We have re-written the paragraph related to proton transfer to reflect this.

"When the numbers of sulfuric acid and base molecules grows, the structures for DMA and ammonia clusters start to differ, since ammonia can form four hydrogen bonds while DMA can only form two. The number of hydrogen bonds is not the only factor that determines the stability of these clusters. The identity of the base is also important. As DMA is a stronger base than ammonia, DMA molecules will interact more strongly with the sulfuric acid molecules. Proton transfers from the acid to the base molecule will also play an important role in stabilizing the cluster, since it leads to the formation of ion pairs, which stabilizes the cluster. In the case of ammonia-containing clusters, at least two sulfuric acid molecules are needed to promote the proton transfer if only one ammonia molecule is present. In clusters where the number of ammonia molecules is larger than the number of sulfuric acid molecules, the extra ammonia molecule is not able to receive a proton from a HSO4- ion (thus forming SO42-) until the cluster contains three sulfuric acid molecules. On the other hand, in DMA-containing clusters, proton transfer occurs already when just one sulfuric acid and one DMA molecule are present in the cluster. In contrast to ammonia clusters, if the cluster contains more DMA molecules than acids, the proton from an HSO4- is transferred to the extra DMA molecule, forming SO42- even when only one sulfuric acid molecule is present in the cluster. However, it should be noted that only one SO42- is formed, so for example in the (H2SO4)2 ((CH3)2NH)4 cluster three DMA molecules are protonated instead of four. The number of protonated bases molecules for each cluster can be found on

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supplementary material table S-5.1”

In addition, we have included the proton transfer in the cluster names in Figure 1 as suggested by the referee. On the other hand, is quite difficult to do the same in Tables 3 and 4, so we have decided to add an additional table in the supplementary material showing the number of protonated bases in each cluster. (TableS-5.1)

“There are two Tables “3”. The table in page 9 should read Table 5.”

We have fixed the typo.

“In the last paragraph of page 11, the authors compare the DMA evaporation rate of the (H2SO4)4(CH3)2NH cluster 2.83x10-4 s-1 with the ïňĄssion rate 35.29 s-1. The value 2.83x10 -4 s-1 does not match with the value in table of page 9 (2.72x 10-4 ′ s-1). The authors should indicate the Tables these numbers come from”

This is a typo, the correct value is 2.72 x 10-4. We have corrected the value in the text.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 27327, 2011.