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# *Interactive comment on* "Amine substitution into sulfuric acid – ammonia clusters" *by* O. Kupiainen et al.

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Physical chemistry of the atmospheric pre-nucleation clusters containing organic species is currently one of the hottest topics in the atmospheric sciences. The paper by O. Kupiainen et al. is nicely written and easy to follow. However, several issues, some of them are serious, should be addressed prior to the further consideration of the manuscript for publication in the ACP. 1. Experimental value of the dipole moment of the sulfuric acid (Table 1, Kuczkowski et al. (1981)) is outdated and should be replaced with the one from more accurate recent measurements of Leopold et al. 2008 [1]. 2. Amines are not the only organic species that may enhance nucleation rates in the Earth's atmosphere. A brief review of the frontier research on organics-enhanced nucleation should be included in the Introduction to the revised manuscript. The literature review should be written in a balanced way and should cover not only work done by the Helsinki group but also research published by others. 3. The main problem of the paper is that the application of "a multi-step quantum chemistry method" (Ortega et al. 2012)[2]. The authors use non-standard composite B3LYP /CBSB7 /RI-CC2/aug-cc-pV(T+d)Z method , citing their previous work [2] as the only study supporting the validity of their newly invented multi-step method. This sort of the justification is at best questionable. Composite methods, such as G2, G3, G4 and their modifications are widely used in the computational quantum chemistry. However, they have been tested on a hundreds of species and validated against experimental data, while Ortega et al. (2012) [2] used theoretical calculations of only 4 reaction free energies and no experimental data to evaluate the predictivity of their new method. For some reason, their new composite method include B3LYP density functional , which is incapable, according to their recent study (Kurten et al. 2006) [3], to describe the hydrogen bonding in large weakly-bonded complexes such as e.g. neutral anime-sulfuric clusters studied in their work. The B3LYP density functional was used in the pioneering studies of Bandy and Ianni (1999-2001) and was shown to fail in predicting the hydration free energies of small and simple atmospheric sulfuric acid hydrates [3]. Moreover, the comparison of their B3LYP /CBSB7 /RI-CC2/aug-cc-pV(T+d)Z method [2] with other composite methods generally makes little to no sense (Herb et al. 2011) [6]. The main problem is that while both high level ab initio methods with large basis sets and composite methods such as e.g. G3, G2 reproduce enthalpy changes within chemical accuracy, their predictions of stepwise changes in the Gibbs free energies have never been studied systematically and validated against large sets of experimental data. On the other hand, the agreement of enthalpies predicted by ab -initio and composite methods with experimental values may not necessarily be a sign of perfection. Although reaction enthalpies reported in the literature are denoted as 'experimental thermochemical values', they are usually obtained indirectly, from the experimental reaction rates using the linearized form of the van't Hoff equation. The van't Hoff plot typically appears quite linear, with a correlation coefficient close enough to unity to be taken as indicating linearity within experimental uncertainty. However, if one subjects the same data to a non-linear least-squares analysis, employing the more general form of the van't Hoff equation the curvature of the van't Hoff plot may become evident. The difference between reaction enthalpies obtained from the same experimental data set using the oversimplified linear and 1more accurate non-linear form of the van't Hoff equation can be very large (>5 kcal/mol) [6]. The uncertainties in the van't Hoff analysis and discrepancies between direct calorimetric and indirect van't Hoff estimates of enthalpies are well-known; however, as for now, these issues remain unresolved. The authors should perform simple calculations of free energies small neutral clusters containing water and sulfuric 'acid for which experimental data are available, for example sulfuric acid monohydrates and di-hydrates. It would also be useful to include data for water dimer and a few complexes of H3O+ with (H2SO4) and (H2O), for which experimental data of Froyd and Lovejoy (2003) [7] are available, in the comparison. The deviation of B3LYP /CBSB7 /RI-CC2/aug-cc-pV(T+d)Z [2] from the experimental data should be estimated . 4. The impact of the propagation of the uncertainties in the computed Gibbs free energies should be investigated thoroughly and conclusions about the role of amines made in the paper should be modifief with accounting for the aforementioned uncertanties. 5. A brief discussion on the recently discovered controversy (Nadykto et al. 2011 [4]; Kurten, 2011 [5]) over the role of amines in the atmospheric nucleation should be included in the revised manuscript. References 1. Sedo, G.; Schultz, J; Leopold, K.R. (2008) J. Mol. Spectrosc., 251, 4-8. 2. Ortega, I. et al. (2012) Atmos. Chem. Phys., 12, 225–235 3. Kurten, T. et al. (2006) J Phys Chem A. 110(22):7178-88. 4. Nadykto, A.B. et al. 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