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Atmospheric
Chemistry
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Discussions

Interactive comment on “The role of ammonia in sulfuric acid ion induced nucleation” *by* I. K. Ortega et al.

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General comments

Over the last years molecular dynamical simulations employing principles of quantum physics enjoyed increasing popularity in atmospheric aerosol science. Last but not least this trend was supported by the availability of powerful state-of-the-art simulation software. Compared to classical approaches, such as classical nucleation theory and Gibbs' classical thermodynamic theory of heterogeneous substances, these methods allow new insights in hitherto inaccessible by direct measurements physical interrelations. Unfortunately, this enormous progress is accompanied by a certain loss of "vividness" in comparison with classical approaches. This refers, e.g., to the use of the simulation software, which itself represents a high (but hidden) amount of hypostatised a priori knowledge of physical chemistry chemical physics. The use of these software packages deserves a salutary portion of chemical intuition and large experience and specific knowledge across classical and non-classical physics and chemistry. To broaden the circle of potential users of the results obtained by quantum chemical simulations and to further enhance the acceptance of such modern approaches contributions like the present one are absolutely essential and highly welcome to the ACP community.

Ortega et al. presented a multi-step computer simulation approach to elucidate the role of ammonia in sulphuric acid ion induced nucleation. Their approach includes the following four steps: 1) Initial guess of cluster geometry employing a priori knowledge and "chemical intuition" (sic!); 2) Pre-optimisation of these structures (software SPARTAN); 3) Optimisation of the more stable isomers employing density functional theory (software SIESTA); 4) Single point energy calculations for the optimised structures (software TURBOMOLE). The authors critically evaluated their results by emphasising the following problems reflecting the "state-of-the-art": a) improper treatment of the high unharmonicity of the, b) impossibility/impracticality of hydration modelling for sulphuric acid-ammonia clusters due to increasing CPU time, increasing number of possible conformers and questionable validity of the harmonic oscillator rigid rotor approximation for relatively large clusters. While subject a) might be considered as a temporary malaise (e.g., such as comparable to limited sensor resolution in direct measurements), which can be safely corrected with time, subject b) represents a more principle shortcoming (cf. also last paragraph of referee 1). As a matter of course the authors know about - the affinity of sulphuric acid to form hydrates, - the impact of hydrate formation on the critical cluster formation work, and - the impact of hydrates on the cluster kinetics, which altogether affect the nucleation rate by many orders of magnitude (one of co-authors, Markku Kulmala, published a number of papers on the role of hydration in new particle formation). With reference to a previous paper Ortega et al. argued, that the binding of ammonia to the clusters is only weakly dependent on the water content with a tendency to somewhat decrease the binding of ammonia

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to the cluster. Thus, the binding of a few water molecules to the cluster is unlikely to significantly disrupt the bonding pattern of the sulphuric acid-ammonia cluster. The authors came up with further - let me say more tentative - arguments to motivate their restriction to dehydrated clusters, which - I apologise for my words - would certainly have not been given without the technological restrictions mentioned by Ortega oneself. This neither limits the scientific value of the presented results nor the potential for atmospheric application. It reflects what can be done right now. I expect, that the question of hydration in sulphuric acid-ammonia cluster formation will be addressed in future studies, regardless of the supposed here redundance.

Specific comments and technical corrections

- The approach is described in a straightforward and traceable manner. - The results presented in Tables and Figures are well interpreted in the textual description. - The interpretation and conclusions concerning the role of ion-induced nucleation are physically sound. - It would be helpful to insert some sentences (or footnotes) to relate the parameter input/output more clearly to the software modules. It has been done throughout the manuscript, but sometimes not unambiguously (cf. p. 5418, lines 8-9: Which of the listed parameters belong to TURBOMOLE?). - p. 5424, line 4-6: "This probably indicates that the presence of a second molecule of ammonia would lower this addition energy, allowing the cluster grow to larger sizes. In other words, clusters with four sulfuric acid molecules will probably contain 2 rather than 1 ammonia molecules in atmospheric conditions". I agree with the first sentence, but is the second one conclusive? I cannot see, that this conclusion is compelling here. In cases it is trivial, let me know without changing the sentence. - p. 5434, Fig. 1 Most stable clusters: Compared the first version of the manuscript, Figs. 1b 1e have been replaced with new stable cluster configurations (n=3) (cf. location of the hydrogen bonds). I suspect, the new ones are a "bit" more stable than the previous ones. Please eventually comment principal problems of the identification of stable cluster configurations (in a footnote or so).

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Technical: - p. 5421, line 8, ref. to Table 2: "the presence of ammonia in the neutral clusters is favored thermodynamically" I think in comparison with $(H_2SO_4)_n$. Please add. - p. 5422, line 13: "For neutral clusters we can observe that when only two sulfuric acids are present". Please add. - p. 5422, line 25, ref. to Fig. 2: I see the local minimum for n=3, corresponding to $(H_2SO_4)_2 \cdot HSO_4^-$ and $(H_2SO_4)_2 \cdot HSO_4^- \cdot NH_3$ (according to the chosen annotation). "The formation energy is higher for charged two-acid clusters containing ammonia than for ones without it". To avoid misinterpretation , please add number of n in brackets. - p. 5433, Table 5: remove misplaced "dots" in the reaction nb. 16 (dots related to ammonia) - p. 5435, Fig 2: without (typo)

I agree in form and content with the interactive comment given by referee 1.

I recommend the editor to publish the paper after minor (technical) corrections. The authors presented a very nice and instructive paper.

Olaf Hellmuth

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 5413, 2008.

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