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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

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This manuscript reports substitution of ammonia by dimethyl amine (DMA) in positively-charged and neutral clusters using quantum chemical calculations and cluster dynamic model. The results show some differences between positively-charged and neutral clusters for the substitution. For positively-charged clusters, the study shows that substitution would occur quickly and the results are in excellent agreement with the experimental results from Bzdek et al., (2010a, b). For neutral clusters, this substitution would happen but not as quickly and easily as that for positively-charged clusters. The topic itself sounds very interesting, but the following issues need to be fully addressed before the manuscript can be published in ACP.

1. There are several assumptions used in the kinetic model when calculating the dynamic cluster distribution. The clusters are assumed to be spherical and their radii

were calculated from bulk properties. At the microscopic levels, the clusters might not be spherical any more as can be seen from the geometries of the clusters. How good are these assumptions for the bulk-based properties? How these assumptions affect the calculations of the evaporation rates especially for the neutral cluster?

2. For the Gibbs free energy calculation, how do the basic set and level of theory affect the accuracy of the geometry and energy calculation? Even for clusters containing a known number of molecules, the potential energy surface is complex and how the authors assure that the pathway found is global? The errors associate with picking a wrong global minimum path may be huge; even several kcal/mol seems to significantly affect the results. Can the authors give an estimation of errors for the calculated free energies and the evaporation rates in Tables 2 and 3?

3. The mechanism shown in Figure 1 seems ambiguous: the added or exited molecules are not shown in the scheme. Instead of showing a too-general scheme like Figure 1, the authors should show a potential energy surface to illustrates that the cluster becomes unstable upon addition of an amine to the ammonia cluster and become more stable after the ammonia is kicked out of the cluster;

Bzdek, B. R., Ridge, D. P., and Johnston, M. V.: Amine exchange into ammonium bisulfate and ammonium nitrate nuclei, Atmos. Chem. Phys., 10, 3495–3503, doi:10.5194/acp-10-3495-2010, 2010a. 30855, 30859, 30860, 30873

Bzdek, B. R., Ridge, D. P., and Johnston, M. V.: Size-Dependent Reactions of Ammonium Bisulfate Clusters with Dimethylamine, J. Phys. Chem. A, 114, 11638–11644, doi:10.1021/jp106363m, 2010b. 30859, 30862

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 30853, 2011.