Understanding the Formation of Ammonium Water Clusters Using A High Level Computational Model

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The formation of aerosols and clouds is known to begin with the interaction of a small number of water and other molecules. Such small clusters cannot be studied experimentally, since the detection limit is around 3 nm, and classical nucleation theory fails for clusters with fewer than 10 molecules, because of its reliance on bulk properties. Therefore computational chemistry can provide useful data about these systems. This study focused on $NH_4^+(H_2O)_n$ clusters where n=1-10, since ammonium plays an important role in various atmospheric processes. Molecular dynamics simulations were performed to sample the configuration space and produce input structures for an MP2//6-31G* geometry optimization and single point calculations with the aug-cc-pVDZ and TZ basis sets. The resulting structures were varied, and some of the low energy structures are presented below. We determined ΔE_{el}, ΔE_{0K}, and ΔG_{298} values for the sequential and absolute addition of 1-10 waters along with the theoretical equilibrium concentration of these clusters under atmospheric conditions. These results suggest that ammonium will primarily form 4mer and 5mer water clusters and that all of the ammonium in the atmosphere will be clustered. The sequential energies of formation tend to zero as the size of the cluster increases, which means that the critical cluster size for ammonium water clusters is greater than 10. Further research involves expanding the number of water and other molecules in our model and increasing our understanding of how our results impact cloud formation.

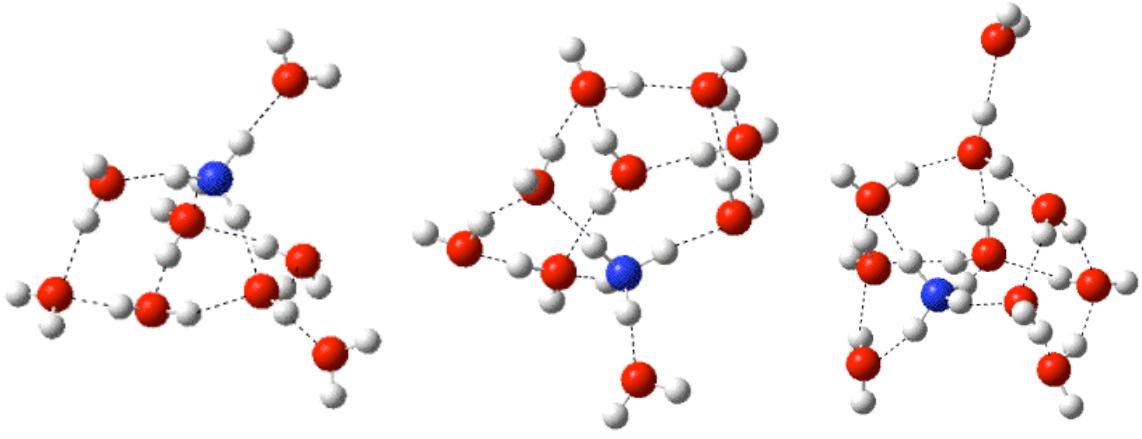

Figure 1. The low energy structures for $NH4^+(H_2O)_n$ where n=8-10 at the MP2/aug-cc-pVDZ//MP2/6-31G* level of theory