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

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The formation of ammonium water clusters is an interesting natural phenomenon that is believed to play a role in atmospheric cloud and aerosol formation. This study focused on the clustering of $NH4^+(H_2O)_n$ where n=5-7. Molecular dynamics simulations were performed at various temperatures to produce 200 input structures for MP2 level quantum mechanics calculations. By using a wide variety of input structures, we were able to adequately sample the conformational space around the ammonium. We chose three basis sets, 6-31G*, aug-cc-pVDZ, and aug-cc-pVTZ, for these calculations. In the course of developing our methodology we gained insight into the accuracy of these basis sets, complete basis set extrapolation methods, and the applicability of counterpoise corrections to strong hydrogen bonded systems. The resulting structures were varied, and the low energy structures are presented below. We determined $\Delta E°$, $\Delta E°_{0K}$, and $\Delta G°_{298}$ values for the sequential addition of 1-7 waters and the theoretical concentration of these clusters under atmospheric conditions. These results suggest that ammonium with a cluster of up to 5 waters is energetically favorable and that most of the ammonium in the atmosphere will be clustered. Further research involves expanding the number of water and ammonium molecules to completely understand how aerosols form on a molecular level.

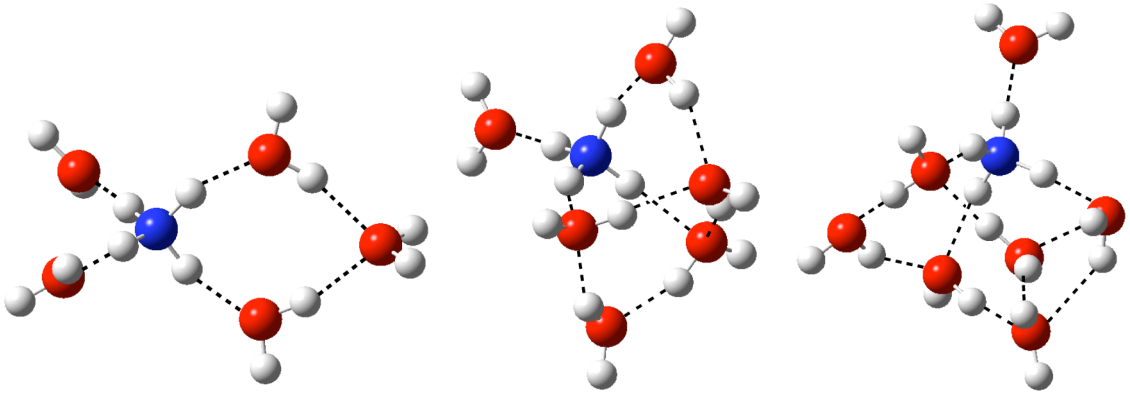

Figure 1. The low energy structures for $NH4^+(H_2O)_n$ where n=5-7 at the MP2/aug-cc-pVDZ//MP2/6-31G* level of theory