Thermodynamic Analysis of Small $NH_3 \bullet H_2SO_4 \bullet (H_2O)_n$, n=1-4, Cluster Configurations

Andrew P. Beyler '10, Charles J. Borton, Kristen S. Alongi '08, Karl N. Kirschner, George C. Shields

Department of Chemistry, Hamilton College, Clinton NY 13323

Both sulfuric acid and ammonia are suspected to be key molecules in the formation and growth of water clusters in the atmosphere. However, there has been little computational or experimental research into the thermodynamics of water clusters containing both molecules. In this research, different cluster configurations containing one ammonia, one sulfuric acid, and from one to four water molecules were compared in terms of their potential energies to determine which configurations are most likely to exist in the atmosphere. The clusters were built and optimized using the PM3 method in Spartan. It was expected that many of these unoptimized configurations would optimize to the same configuration. So, before the potential energies of the clusters were measured, the clusters were first optimized by Gaussian03 at B3LYP/6-31G*. The duplicate configurations were removed and their potential energies were measured with G3B3 calculations. It was found during B3LYP/6-31G* optimizations that the ammonia molecule gained a proton from the sulfuric acid molecule in clusters where the ammonia was hydrogen bonded to a sulfuric acid and at least one water molecule, thus forming a $NH_4^+ \bullet HSO_4^- \bullet (H_2O)_n$ cluster.

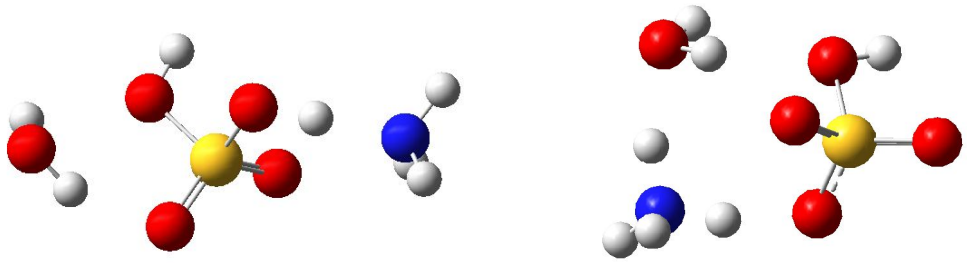

Figure 1. $NH_3 \bullet H_2SO_4 \bullet (H_2O)_1$ and $NH_4^+ \bullet HSO_4^- \bullet (H_2O)_1$ clusters.

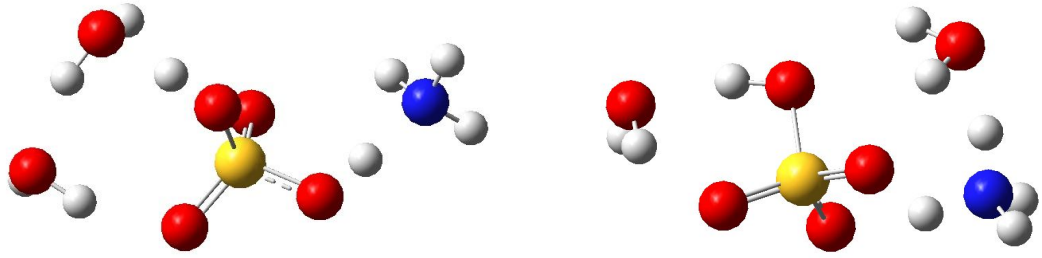

Figure 2. $NH_3 \bullet H_2SO_4 \bullet (H_2O)_2$ and $NH_4^+ \bullet HSO_4^- \bullet (H_2O)_2$ clusters.