New Thermochemical Predictions for the Formation of Ammonium Water Clusters

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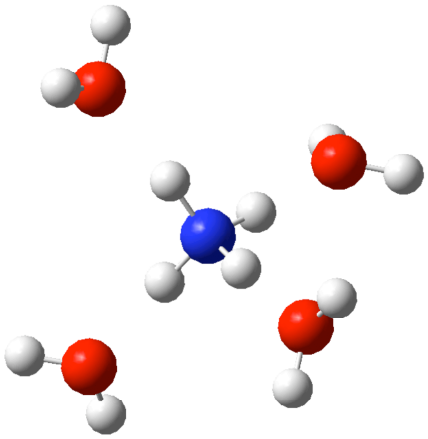
Using both *ab initio* methods and a density functional theory the thermochemical data for the reaction $NH_4^+(H_2O)_{n-1} + H_2O \rightarrow NH_4^+(H_2O)_n$ where n=1-4 has been computed. Starting with structures published from this laboratory last year the G3B3, MP2, and PBE1W methods were applied using Gaussian03. The MP2 and PBE1W methods used the aug-cc-pVDZ basis set, and the PBE1W method also used the aug-cc-pVTZ basis set. Structures resulting from these calculations exhibit near C_3, C_2, C_3, and T_d symmetry moving from 1 to 4 waters. The resulting $\Delta E°_{0K}$, $\Delta H°_{298}$, and $\Delta G°_{298}$ values fit both experimental and previous computational results. The range of $\Delta G°_{298}$ values between these methods is from -11.36 to -13.11 for one water, from -8.99 to -9.30 for two waters, from -4.95 to -6.00 for three waters, and from -4.90 to -5.01 in kcal•mol^{-1} for four waters. Experimental data from two sources has a range of $\Delta G°_{298}$ values is from -11.4 to -13.3 for one water, from -8.9 to -8.20 for two waters, from -5.9 to -6.3 for three waters, and -4.10 in kcal•mol^{-1} for four waters. Since our ranges are close to the experimental ranges, these methods are valid to study ammonium water clusters. This is especially important for the new GGA functional PBE1W method, as it has never been applied to ionic clusters before. A result of this work will be the selection of a method and basis set used to calculate future optimizations of ammonium, ammonia, and sulfuric acid water clusters in a study of the nucleation of aerosols. Currently we are using MD simulations to explore configurational space in hopes of finding the lowest energy structures for these clusters.



Structure for $NH_4^+(H_2O)_4$ using the G3B3 method