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# Ammonia in positively charged pre-nucleation clusters: a quantum-chemical study and atmospheric implications

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Abstract. The quantum-chemical treatment of pre-nucleation clusters consisting of atmospheric nucleation precursors is critically important for the understanding of the molecular nature of atmospheric nucleation. In the present study, the influence of ammonia on the thermochemical stability of positively charged pre-nucleation clusters has been studied using the Density Functional Theory (DFT). The formation of binary $(NH_4^+)(H_2O)_n$ and ternary $(NH_4^+)(H_2SO_4)(H_2O)_n$ ionic clusters and the conversion of $(H_3O^+)(H_2O)_{n-1}$ into $(NH_4^+)(H_2O)_n$ and $(H_3O^+)(H_2SO_4)(H_2O)_{n-1}$ into $(NH_4^+)(H_2SO_4)(H_2O)_n$ have been investigated. The thermochemical analysis carried out in the present study shows both $(H_3O^+)(H_2O)_{n-1} \rightarrow (NH_4^+)(H_2O)_n$ and $(H_2SO_4)(H_3O^+)(H_2O)_{n-1} \rightarrow (NH_4^+)(H_2SO_4)(H_2O)_n$ transformations to be favorable thermodynamically and gives us a clear indication of the important role of ammonia in the conversion of positively charged clusters containing hydronium $(H_3O^+)$ into those containing protonated ammonia. Under typical continental boundary layer condition, a large fraction of small positive ions may contain ammonia, but most of neutral and negative hydrated sulfuric acid monomers do not contain ammonia. In term of absolute concentrations, around 1000 $cm^{-3}$ out of $10^7$ $cm^{-3}$ of sulfuric acid momoners contain ammonia. $(NH_4)^+(H_2O)_n$ clusters appear to dominate the concentrations of small positive ions. Because of the weak affinity of sulfuric acid molecules to $(H_3O^+)(H_2O)_n$ and $(NH_4^+)(H_2O)_n$ ions ($n \leqslant 6$), the concentrations of both ammoniated and un-ammoniated sulfuric acid water proton clusters are quite low. The atmospheric implications of the obtained results are discussed.

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