Quantum chemical insight into proton transfer and structural rearrangements in reactions between $HSO_4^-(H_2O)_n$ and D_2O

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Sulfuric acid (both neutral and ionic forms) play a central role in gas-phase nucleation mechanisms, and is widely considered to be a key precursor of cluster formation and eventual droplet growth, under favorable conditions, including also the upper troposphere. Small aqueous clusters grow faster around molecule ions than neutral molecules due to the strong ion dipole interaction, and bisulphate anion is no exception. Moreover, hydration of sulfuric acid itself possesses many interesting aspects of fundamental nature, both in terms of specific solvation and acid/base behavior. For example, sulfuric acid has several binding sites for hydrogen bonding, acting both as a proton donor and a proton acceptor.

The present investigation aims at understanding the initial stages of water cluster formation from the bisulphate ion, emphasizing the size dependent properties, in particular structural rearrangements of bisulphate ion water clusters related to proton transfer processes. This insight will be obtained by studying hydrogen/deuterium exchange reactions of $HSO_4^-(H_2O)_n$ clusters with D_2O in the gas phase under near thermal conditions.

We report the results of an experimental study of H/D-exchange in reactions between $HSO_4^-(H_2O)_n$ (n = 1 – 25) with D_2O, done in modified quadrupole/time-of-flight mass spectrometer equipped with electrospray source (QTOF2, Micromass). According to our mass-spectrometric experiments, for small bisulphate water clusters (up to n=8), reacting with D_2O, the dominating reaction is D_2O/H_2O ligand swap. For larger clusters (n>8) the situation is very different, and H/D exchange is observed to be swift. This reaction has been found to be proton catalyzed. This, generally speaking, is a good example of size-dependent properties.

A series of quantum-chemical calculations (B3LYP/6–311++G(2d,2p), using GAUSSIAN09) has been conducted to obtain better insight into the experimental results. The quantum chemical calculations have been concentrated around the energetics and structures of relatively small bisulphate water clusters $HSO_4^-(H_2O)_n$ (n = 1 – 10). They show that ability of proton to migrate between the water part of the cluster and HSO_4^- core determines the amount of H/D exchange, and this property is essentially size-dependent when it comes to bisulphate clusters. Based on our calculations we suggest an original see-saw mechanism to explain how proton mobility, and thereby H/D exchange takes place.