Isomers and energy landscapes of micro-hydrated sulfite and chlorate clusters

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1 Challenges

To explore the potential energy landscapes of two hydrated Hofmeister ions, generate large numbers of low energy minima for these systems and perform structural analysis to investigate trends in physical properties with hydration number.

2 Background

Ions play important roles in nature, they can influence protein folding inside cells, change the surface tension of electrolytic solutions and can act as nucleation sites for the formation of water droplets in the atmosphere. One system for classifying some of these effects is the Hofmeister series, which orders ions according to their ability to desolvate proteins. Ions which promote disorder within the hydrogen-bonding network of water and disrupt protein stability are labelled as chaotropes, while ions which promote long-range order and protein stability are classified as kosmotropes. Studying the hydration of ions is important as it has a large bearing on the atmospheric nucleation of water clusters and other areas of atmospheric science.

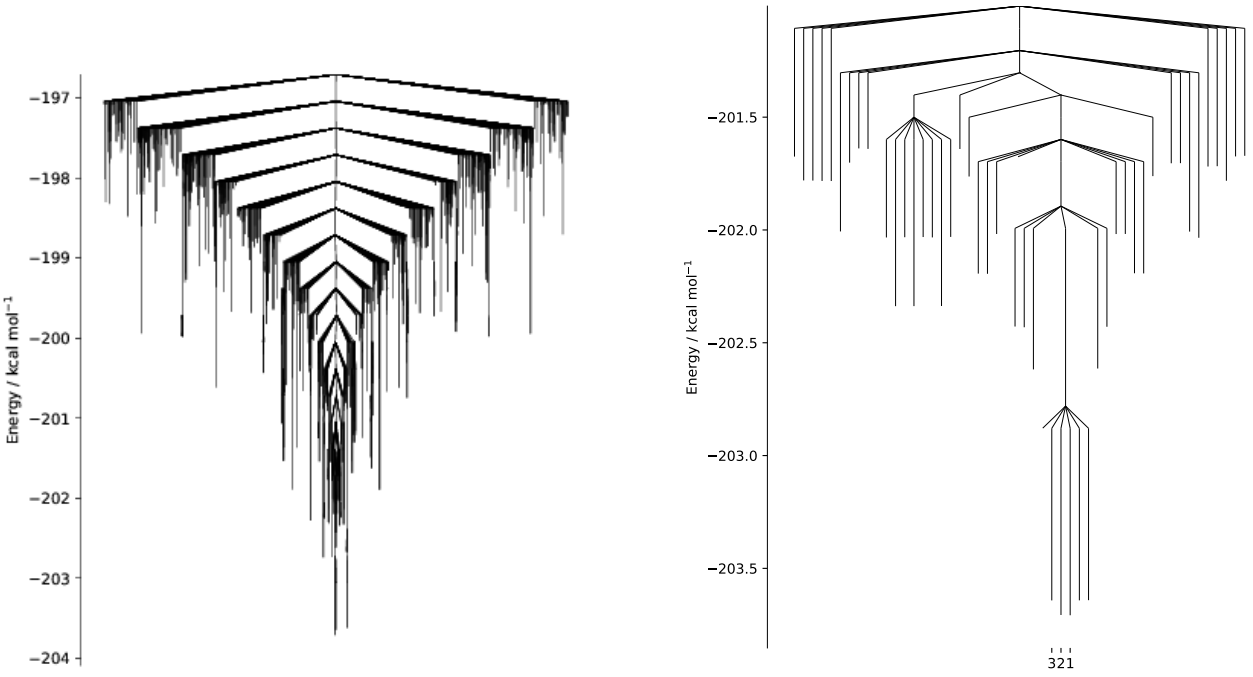
The SO_2 released from natural and synthetic sources is quickly oxidised in the atmosphere to form sulfur(IV) and sulfur(VI) species. Sulfite (SO_3^{2-}) and other sulfur(IV) ions are commonly found in inorganic aerosols and are important in atmospheric science as they contribute to the formation of acid rain. In this work we examined the hydration of the strongly kosmotropic sulfite ion and the chaotropic chlorate ion (ClO_3^-) which is isoelectronic and shares a similar geometry, but with a lower charge and thus provides a useful comparison with sulfite.

3 Results

Low-energy minima on the potential energy surface for the ion-water clusters with 3-50 water molecules were explored using basin-hopping.A simple OPLS style force field is used to model the ions and the TIP4P potential is used for water. This method allows us to efficiently search the energy landscapes of different sizes of these molecular clusters in parallel on BlueBEAR.

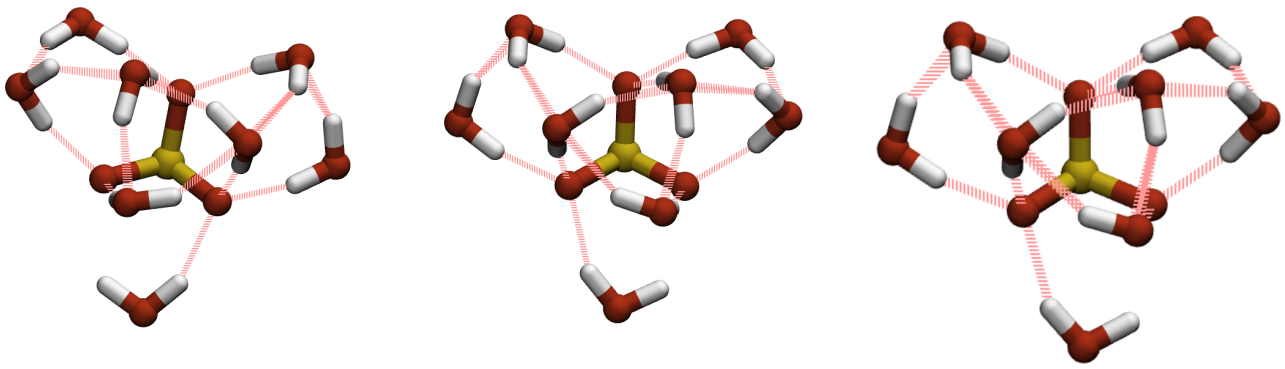
We perform structural analysis on the databases of minima found, and show that the sulfite ion exhibits a greater patterning effect on the hydrogen-bonding networks of clusters than the strongly kosmotropic sulfate ion. Conversely, the chlorate ion is shown to favour surface sites on the water cluster, and confers a lesser degree of patterning to the hydrogen-bonding network within the water clusters, the effect is stronger than that previously shown for the perchlorate ion using the same model, but less pronounced than the effect of sulfite.

We then take the databases of minima and connect pairs of minima and refine the resulting transition states to explore the wider energy landscape of the system. We can then visualise these large energy landscapes as disconnectivity trees and extract information about the kinetics of these systems and compare the differences in the landscapes between hydrated sulfite and chlorate systems.



(a) (b)

Figure 1: Disconnectivity trees showing the putative global minimum and connected minima for the $SO_3^{2-}(H_2O)_8$ system. The explored landscape comprises 18860 minima and 425478 connecting transition states. The graphs show connected minima within (a) 7 and (b) 2.8 kcal mol^{-1} of the global minimum, with the three lowest energy minima labelled in (b).



(a) Min1 (0.00) (b) Min2 (1.66x10^{-4}) (c) Min3 (1.19x10^{-3})

Figure 2: Three lowest energy minima for $SO_3^{2-}(H_2O)_8$. Energies (in kcal mol^{-1}) relative to the GM energy are given in parentheses.

4 Client Profile

John C. Hey
Computational Nano-Solvation
School of Chemistry
College of Engineering and Physical Sciences
University of Birmingham
Edgbaston
B15 2TT

5 Contact Details

JCH936@bham.ac.uk

6 Products Used

NWChem
Python Energy Landscape Explorer
BlueBEAR HPC
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8 Contributors

Roy L. Johnston
Yuting Chen
Emily J. Doyle