

# A Density Functional Theory Study of the Hydration of Cs<sup>+</sup> and Sr<sup>2+</sup>

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## INTRODUCTION

The legacy of many years of civil nuclear power generation in the UK includes storage ponds containing magnox nuclear fuel casings. When magnox alloy corrodes in storage pond conditions, the initial product is brucite, Mg(OH)<sub>2</sub>, a microcrystalline material with a reactive surface which accumulates actinides and their fission products. An understanding of this accumulation and the processes by which it occurs is critical in the context of the future management and cleanup of these storage ponds. Of particular interest to this project is the aqueous chemistry of uranium and two of its fission products, caesium and strontium. Uranium readily forms the uranyl dication, UO<sub>2</sub><sup>2+</sup>, in aqueous solution, while Cs and Sr exist as mono- and dications, respectively. Here we report preliminary results of an ongoing computational study into the aquo complexation of these ions. We focus primarily on the stabilities of Sr<sup>2+</sup> aquo-complexes, and look to apply our understanding to the study of the Cs<sup>+</sup> analogues. The stable complexes identified here will serve as candidate species in our studies of brucite surface complexation.

## COMPUTATIONAL DETAILS

Two codes were used in the present study: Gaussian 03 (G03) and TURBOMOLE 6. In both cases calculations were performed using density functional theory (DFT) employing the TPSS exchange correlation functional with a basis set of TZVP quality. G03 was used to generate gas phase structures, with TURBOMOLE being used to study the effects of a bulk solvent.

## RESULTS

### Solvation of the Bare Sr<sup>2+</sup> Ion

Figure 1 shows a selection of G03 calculated [Sr(H<sub>2</sub>O)<sub>n</sub>(H<sub>2</sub>O)<sub>m</sub>]<sup>2+</sup> structures. The maximum Sr<sup>2+</sup> coordination number for which stable structures could be

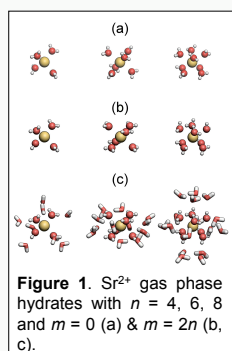


Figure 1. Sr<sup>2+</sup> gas phase hydrates with  $n = 4, 6, 8$  and  $m = 0$  (a) &  $m = 2n$  (b, c).

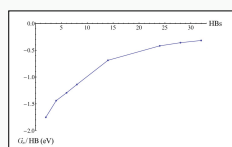


Figure 2. Relative free energies per hydrogen bond for Sr<sup>2+</sup> hydrates

obtained was  $n=8$ . The influence of waters in the secondary shell on the primary shell structure can be seen by comparing frames 1(a) and 1(b). For  $n = 6$  & 8, an ordered hydrogen bonded water network forms in the secondary shell, and this network strongly distorts the primary shell structure. Such high order is probably an artefact of the calculation, and due to the absence of the polarising effect of a surrounding medium. The relative free energy of stability of each complex per hydrogen bond,  $G_n/\text{HB}$ , is shown in Figure 2. This shows the onset of the H-bonded network for  $n > 4$ .  $G_n/\text{HB}$  appears to be asymptoting towards a constant value for large HB. For bulk water, this measure should become constant as waters are added to the system.

## CONCLUSIONS AND FUTURE WORK

Stable gas phase complexes can be obtained for both Sr<sup>2+</sup> and Cs<sup>+</sup> hydrates, but accurate modelling of the secondary and tertiary solvation shells appears to be required in order to represent the bulk solvent. Future work will aim to include the tertiary shell via Born-Oppenheimer molecular dynamics before complexation with the brucite surface is considered.

### Solvation of the Bare Cs<sup>+</sup> Ion

Calculations on the more weakly binding Cs<sup>+</sup> hydrates are more prone to the formation of 'over-ordered' water networks (see Figure 3). Here, coordinating waters form hydrogen-bonded ring networks which sandwich the central ion, and are stable up to  $n=10$ .  $G_n/n$  becomes approximately constant for  $n>5$ , indicating that the major contribution to the stability of these complexes comes from the hydrogen bonding. A more sophisticated model incorporating the effects of the bulk solvent is almost certainly required in order to realistically describe these systems.

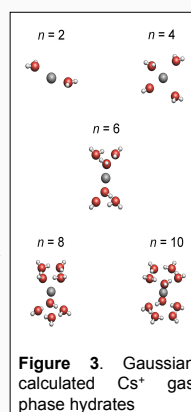


Figure 3. Gaussian calculated Cs<sup>+</sup> gas phase hydrates

### The Effect of the Bulk Solvent

TURBOMOLE 6 was used to recalculate the Sr<sup>2+</sup> hydrate structures in both the gas and aqueous phases. The effect of the bulk solvent was approximated using the COSMO polarisable continuum model.

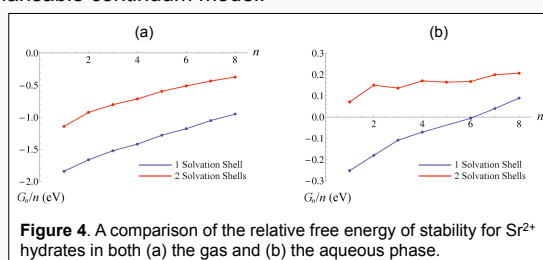


Figure 4. A comparison of the relative free energy of stability for Sr<sup>2+</sup> hydrates in both (a) the gas and (b) the aqueous phase.

Figure 4 shows that calculations using a model solvent lead to complexes that are strongly destabilised. This may indicate that the COSMO model is insufficient for the accurate representation of the bulk solvent.

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