A consistent molecular model to predict the behavior of tetravalent actinides from thorium to berkelium.

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The aim of the present study is to investigate and revisit the behavior of tetravalent actinides from thorium to berkelium in aqueous solution by the use of classical mechanics simulations. While spectroscopy provides a good insight into the interatomic distances, the hydration structure, exchange dynamics and coordination numbers remain quite inaccurate [1]. Our objective is to probe the local structure and explore the trends along the early actinide series in the bulk conditions with classical molecular dynamics (MD) simulations: the only modelling approach that allows us to monitor the dynamics of a hydrated actinide by a large number of water molecules in a long time-scale (> 10 ns). However, the reliability of the MD results entirely depends on the quality of the force-field (FF), i.e., the description of the interaction between the solute and the solvent (An/water molecule interaction), and also on the description of the solvent properties. The FF model that we developed accounts, not only for the standard electrostatic and repulsion interactions, but also for polarization and charge-transfer terms, many-body effects, and explicit hydrogen bonds in the water/water interactions.
Pursuing the efforts initiated by Réal et al. to simulate the Th(IV) and Cm(III) in aqueous solution [2, 3, 4], we present here a consistent force-field model adjusted to state-of-the-art *ab initio* calculations, i.e., without using any experimental input, for the early tetravalent actinides series from thorium to berkelium, and the associated results coming from bulk simulations. The average actinide/water distances almost perfectly agree with the reported EXAFS values and our MD simulations predict that all early actinides hold around 9 water molecules in their first hydration sphere. These results represent a first step towards a better description of these elements in solution or at interface.

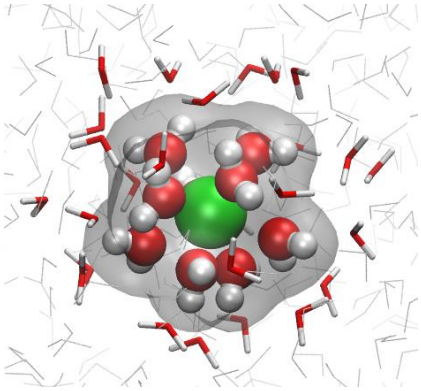

Figure 1: An^{IV} coordination structure by water: an MD snapshot.

References

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