

Understanding Lanthanoids(III) Hydration by Molecular Dynamics Simulations: Bridging the Gap between XAS Experiments and Microscopic Structure

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ABSTRACT (HEADING 1)

Understanding molecular organization around heavy metal cations – like lanthanoids or actinoids – is of fundamental importance to address their chemical reactivity. For aqueous solutions, the first step is to understand solvation properties. Molecular dynamics simulations can provide a real help in understanding the molecular structure of hydrated ions as a tool to better interpret X-ray absorption experiments. Being able to address correctly dynamical and structural properties needs the use of a reliable metal-water and water-water interaction potential and a good statistical sampling of the system phase space. Classical molecular dynamics generally allows to correctly sampling the phase space but needs a particular work on the interaction potentials. When structural experimental data are mainly due to a unique conformation, and the ligand exchange events are negligible in determining the XAS signals, ab initio based calculations, both statically and dynamically, can help in the interpretation of those signals [1-3]. However, lanthanoids can exchange between different structures with two different coordination numbers (9 and 8), especially in the middle of the series. This can now be accounted for by classical molecular dynamics.

In the present work we focused our attention on hydration of the whole lanthanoid(III) series. To understand at an atomic level structure and dynamics of hydration, we have developed a classical interaction potential with explicit polarizability that was parameterized and tested on the first atom of the series, La³⁺ [4,5] that can be used in classical molecular dynamics simulations in explicit water. This potential was able to correctly reproduce experimental results and also to reproduce the EXAFS signal using the full information statistically averaged provided by the radial distribution functions as naturally obtained from simulations, being in good agreement with experiments [6].

The classical potential developed for La³⁺ was thus extended to the whole series, just taking into account modifications in ionic radii and atomic polarizabilities of the cations in the series [7,8]. This physical based extrapolation of atomic potential parameters was compared with high level ab initio calculations done on Lu³⁺, that is the last atom in the series, providing a good agreement between energies obtained with the model potential and the ab initio ones. Then a set of classical molecular dynamics simulations was performed on the nanosecond time scale for all the atoms in the series to obtain both structural and dynamical properties. To the best of our knowledge, such a systematic theoretical study in liquid water has not been done before.

Our microscopic data, in agreement with recent experimental results, suggest that the changing in coordination number from 9 to 8 across the series does not occur via the so-called gadolinium break model but in with a continuous shape. Our simulations are able to

explain not always structural properties but also self-exchange dynamics mechanisms changing across the series.

Concluding, we have proposed a model that is able to catch crucial properties for a complete chemical series. This approach is based on taking into account physical properties such as ionic radii and polarizabilities and relating parameters of a classical interaction potential to those physical quantities. As demonstrated for the Lanthanoid(III) series, this approach could be used to understand structural and dynamical behaviour of other chemical series, such as Actinoids.

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