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Lanthanides and Actinides in Water: Insights from DFT-based Molecular Dynamics Simulations

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Solvation structure and chemical properties of lanthanides (Ln) and actinides (An) depend both on the environment and the solute electronic structure. By using DFT-based molecular dynamics it is possible to have information on solution properties taking into account specific solvent-solute interactions and to obtain a correct statistical sampling.
The problem of studying lanthanides and actinides by such a method reside in the difficulty of finding a DFT description that is enough accurate to keep the most important features. We have developed Ln and An pseudo-potentials for BLYP functional that are able to reproduce higher level ab initio calculations in the gas phase and known structural properties in solution.

We obtained the correct solvation properties of La^{3+} in water [1,2]. We thus inspected the La^{3+} f- and d-orbitals and how their are perturbed in the aqua-ion symmetry in solution. The level splitting dynamics obtained is discussed in terms of the group theory predicted one.

With the same approach we were able to explain differences in chemical reactivity between isoelectronic Pa(V) and U(VI) oxo- and hydroxo-cations in liquid water. In particular, the Pa(V) was found to interact much more with surrounding water molecules via an extended H-bond network, while U(VI) does not. This liquid phase results are also commented in terms of previous gas phase studies of Pa(V) [3].

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