HYDRATION STRUCTURE AND DYNAMICS OF LANTHANIDES BY MOLECULAR DYNAMICS SIMULATIONS WITH A POLARIZABLE FORCE FIELD

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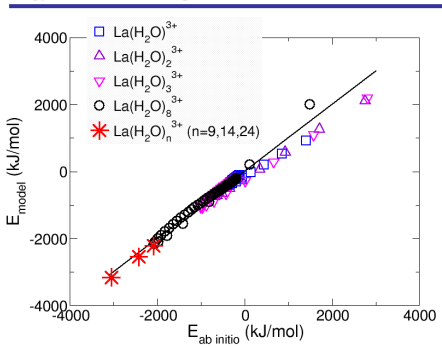
FORCE FIELD DEVELOPEMENT

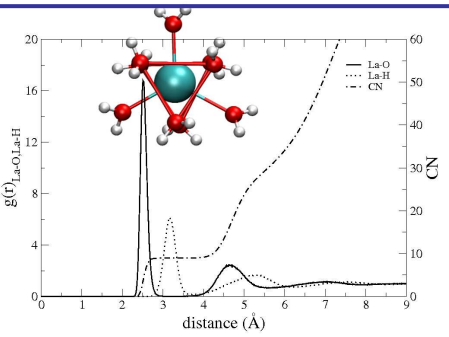
$$V_{tot} = V_{elec} + V_{O-O}^{LJ} + V_{La-O}^{Buck6} \longrightarrow V_{ij}^{Buck6} = A_{ij}^{Buck6}\exp(-B_{ij}^{Buck6} r_{ij}) - \frac{C_{6,ij}^{Buck6}}{r_{ij}^{6}}$$

$$V_{elec} = \frac{1}{2}\sum_{i,j}\left[\frac{q_i q_j}{r_{ij}} + \frac{1}{r_{ij}^{3}}(-q_i\mathbf{p}_i + q_j\mathbf{p}_j)\cdot\mathbf{r}_{ij} + \mathbf{p}_i\cdot\overline{\overline{\mathbf{T}}}_{ij}\cdot\mathbf{p}_j\right] + \frac{1}{2}\sum_i \mathbf{p}_i\cdot(\overline{\overline{\alpha}}_i)^{-1}\cdot\mathbf{p}_i$$

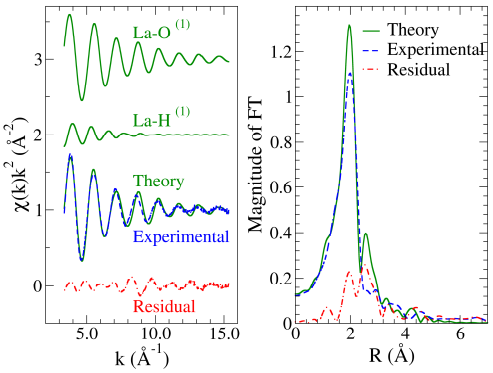
We have used an alternative way of resolving the self-consistent equation by using a Car-Parrinello type of dynamics of additional degrees of freedom associated with induced dipoles. This approach allows us **to reduce the CPU time by a factor of 13** as compared to the SCF resolution. Thus the CPU time comes back to about the same as for unpolarizable systems. We were able to perform **3 ns MD** simulations of all the cations in bulk water.
Buckingham parameters were obtained by fitting MP2 calculations on a symmetric $La(H_2O)_8^{3+}$

La^{3+} HYDRATION





Duvail et al., J.Chem.Phys. 127, 034503 (2007); Chem.Phys.Lett. 448, 41 (2007).

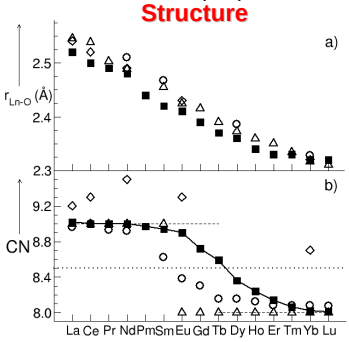


EXAFS data provided by P.D'Angelo (Rome)

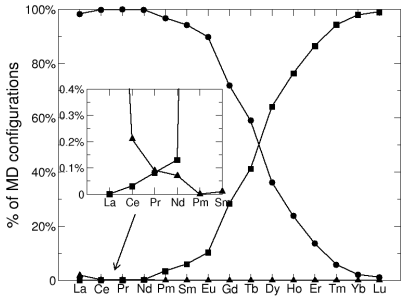
EXTENDING POTENTIAL TO THE WHOLE SERIES

Parameters were changed along the series following the modification in atomic polarizability and ionic radius of Lanthanides, keeping A_{ij} constant and calculating new B_{ij} and C_{ij} terms. This did not require ab initio calculations for each atom but only the access to atomic properties.

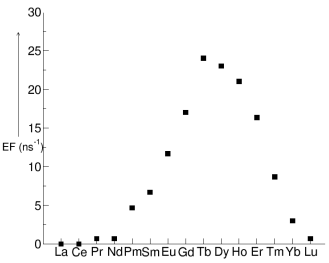
Structure



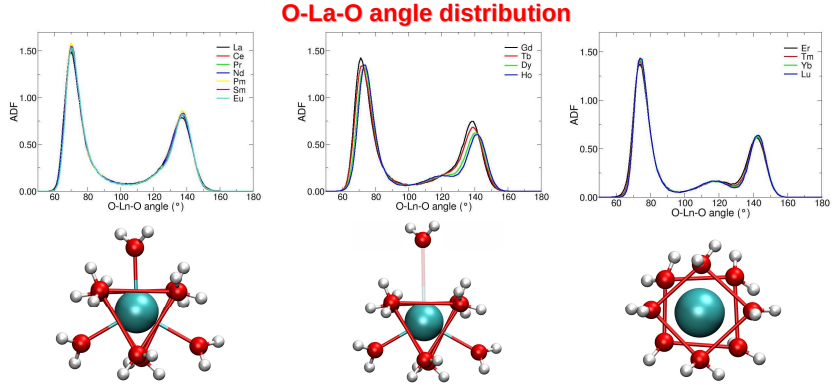
9 vs 8 population



Exchange frequency

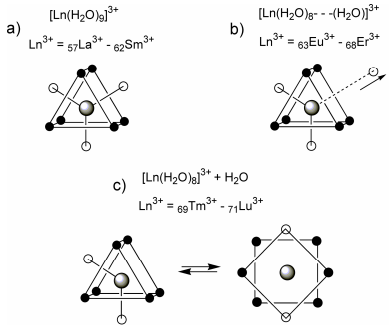


O-La-O angle distribution



Duvail et al., J.Chem.Phys. 130, 104501 (2009).

Dynamical model



Duvail et al., ChemPhysChem 9, 693 (2008)