

Context:

Aqueous chemistry of actinide ions is investigated for the management of radioactive wastes produced during nuclear fuel cycles. In this framework the PhD thesis aims at **completing macroscopic approaches with molecular simulations**. In anoxic deep ground-waters Actinides are stable at the +3 and +4 oxidation states. We started by studying the hydration of ion La³⁺, since hydration is the first step for handling aqueous chemistry, and La³⁺ is a natural chemical analogue for actinide ions of interest (Pu³⁺, Am³⁺ and Cm³⁺).

Method:

The total energy of our system is modelled as a sum of potential energy terms:

$$V_{tot} = V_{elec} + V_{O-O}^{LJ} + V_{La-O}^{Buck6}$$

where is composed of a Coulomb and a polarization terms [1],

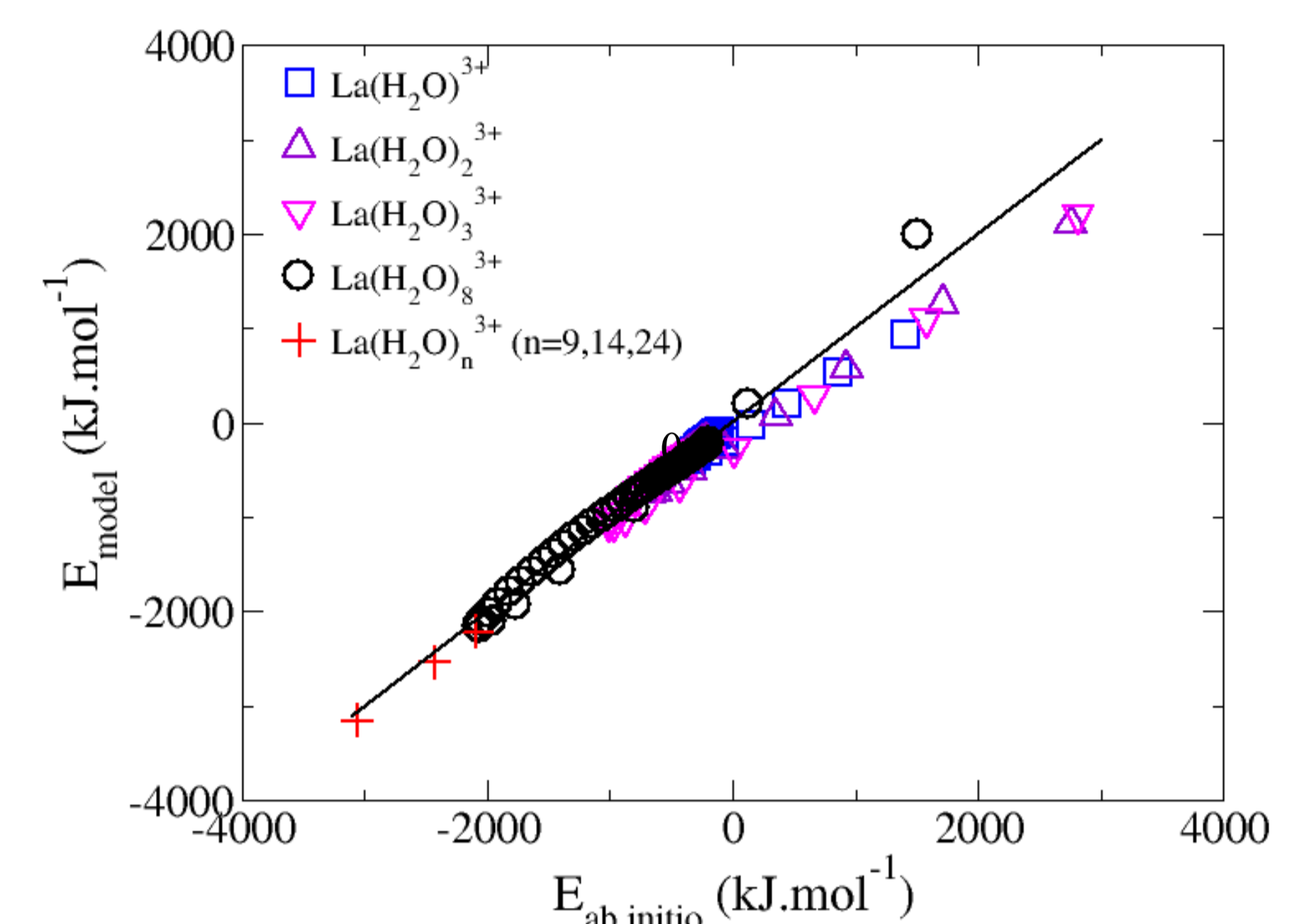
$$V_{elec} = \frac{1}{2} \sum_{i,j,i \neq j} (q_i + \mathbf{p}_i \cdot \nabla_i) (q_j - \mathbf{p}_j \cdot \nabla_j) \phi^s(r_{ij}) + \frac{1}{2} \sum_i \mathbf{p}_i \cdot (\overline{\alpha_i})^{-1} \cdot \mathbf{p}_i$$

The polarization equations have been solved by using a Car-Parrinello type of dynamics where additional degrees of freedom are associated with induced dipoles [2]. This approach allows to **divide the CPU time by 13** as compared to the usual self-consistent resolving method. Furthermore, **the CPU time is virtually the same for simulations with and without polarization**.

The O-O interaction is described by a 12-6 Lennard-Jones potential, and the non-electrostatic La-O interaction by a 6-exponential Buckingham potential:

$$V_{ij}^{Buck6} = A_{ij}^{Buck6} \exp(-B_{ij}^{Buck6} r_{ij}) - \frac{C_{6,ij}^{Buck6}}{r_{ij}^6}$$

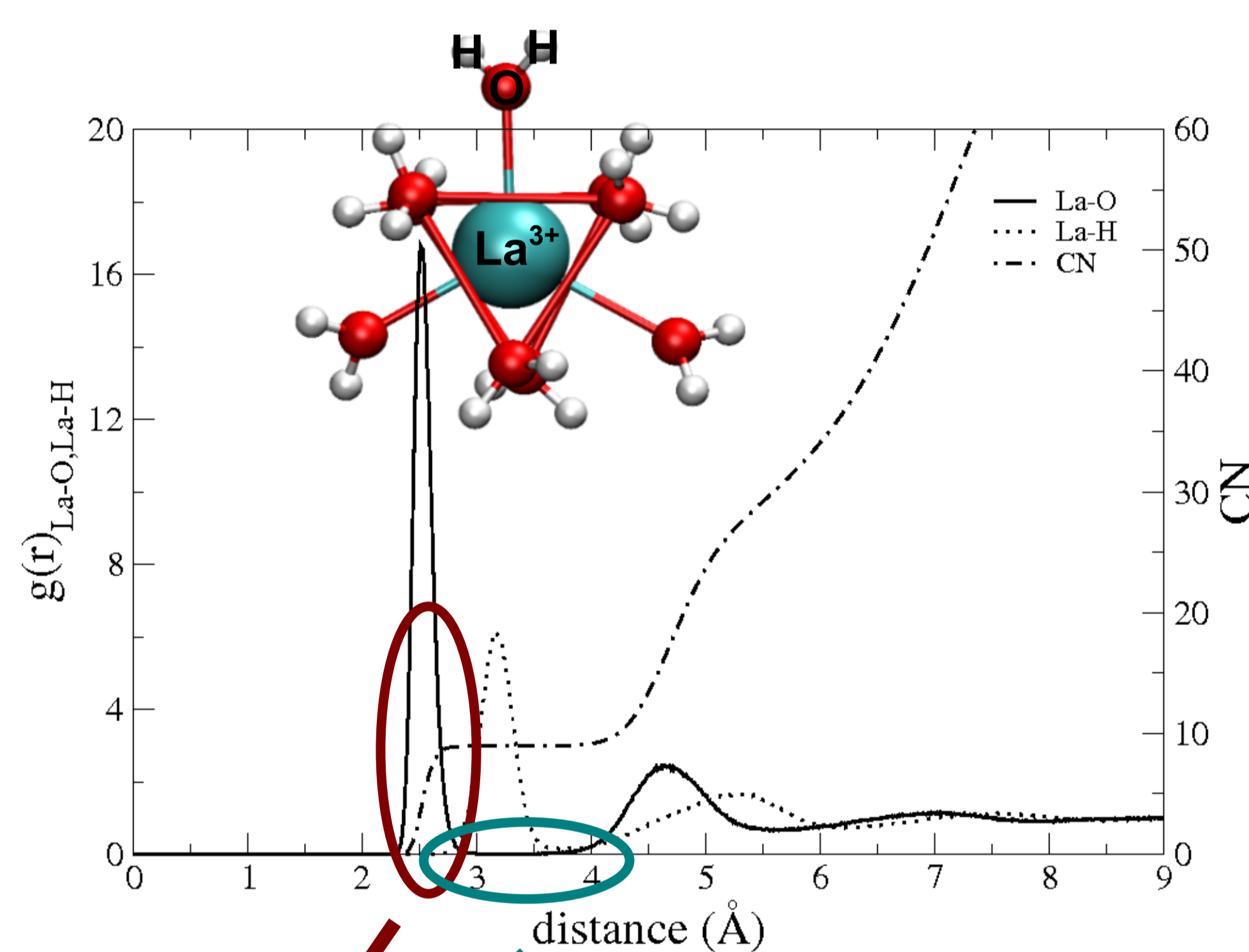
The La-O interaction was parametrized from *ab initio* calculations, on La³⁺ clusters at the MP2 level of theory.



Results:

MD simulations:

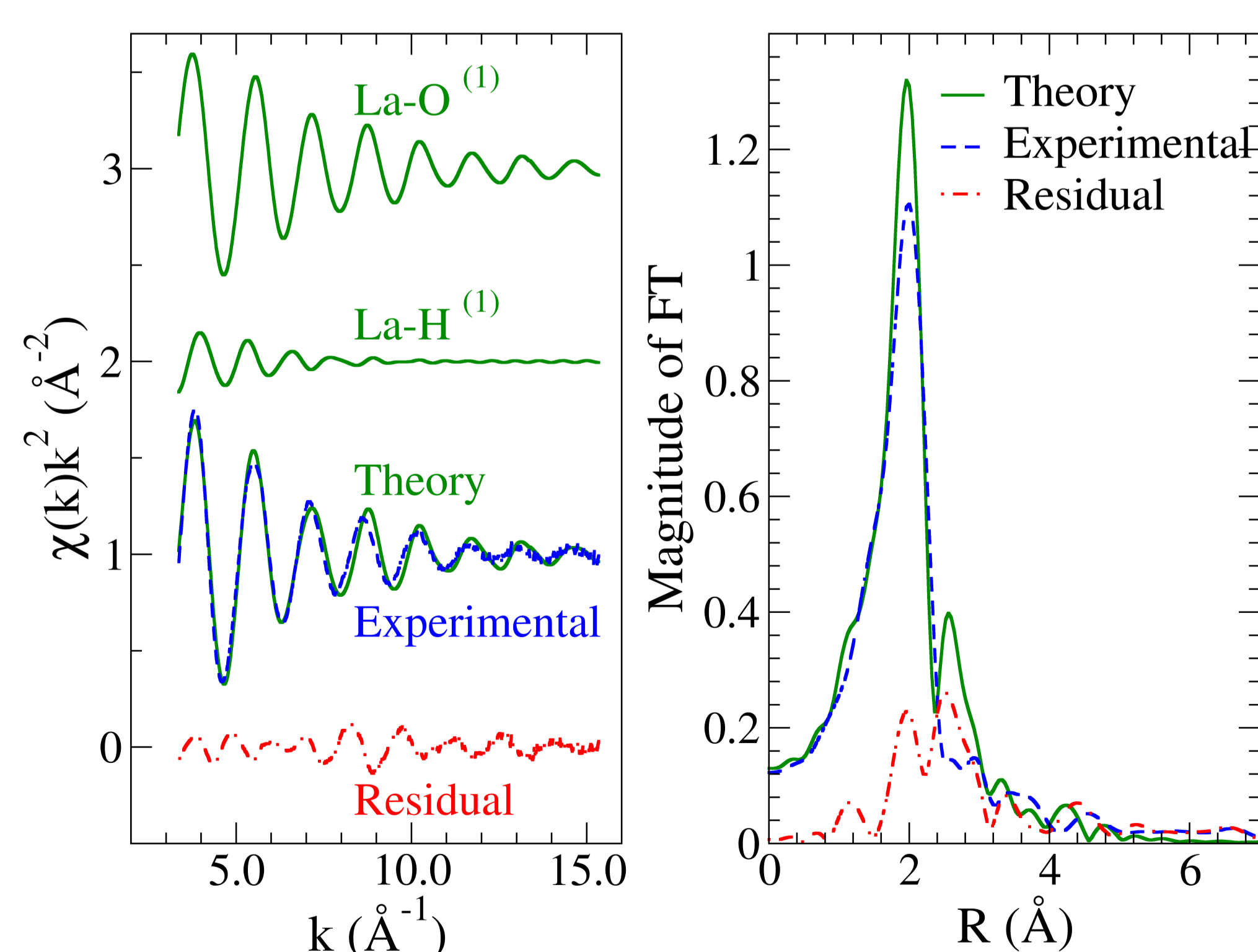
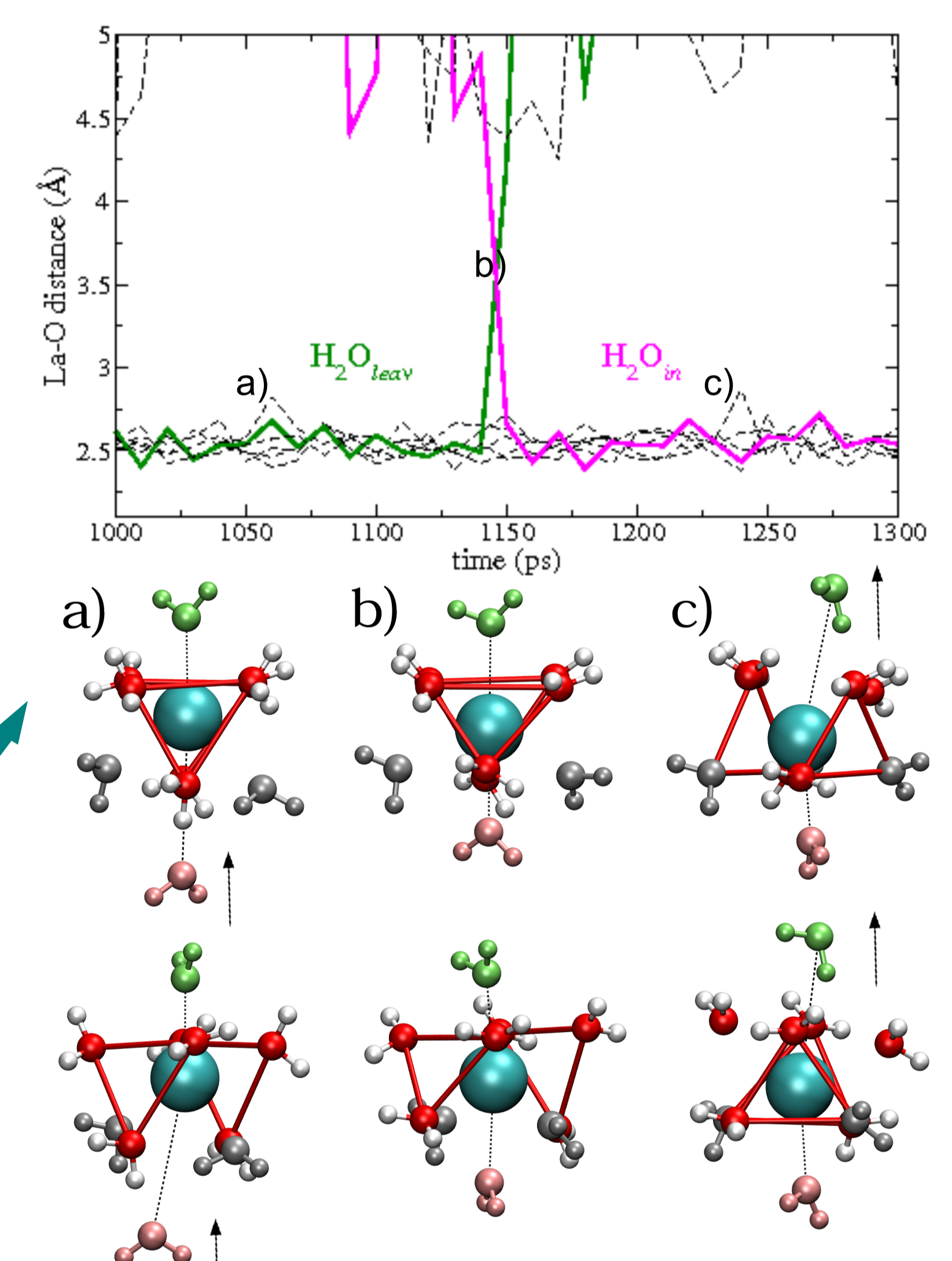
- * La³⁺ + 216 H₂O
- * NVE ensemble
- * Periodic boundary conditions
- * <T> = 299 K
- * Equilibration during 2 ps
- * Simulation time: 3 ns
- * CPU time (2.4 GHz AMD Opteron):
 - explicit polarization: 30 hours
 - without polarization: 24 hours
 - self-consistent polarization: 390 hours (> 16 days!)



Reconstruction of the first hydration shell EXAFS signal

Water Exchanges

$$\chi(k) = \int_0^\infty dr 4\pi r^2 g(r) A(k, r) \sin[2kr + \phi(k, r)]$$



Conclusion and outlooks:

	$r_{La-O}^{(1)*}$	CN ⁽¹⁾	MRT ^{(1)*}	$r_{La-O}^{(2)*}$	CN ⁽²⁾	MRT ^{(2)*}
Buck6 [3]	2.52	9.02	1082	4.65	18.8	7.6
MD [4]	2.56	8.90	980	4.68	15.9	-
EXAFS [5]	2.56	9(6+3)	-	4.63	18	-

* The distances are in Å, and the mean residence times in ps.

A simple potential form describes correctly the La³⁺-OH₂ interaction: the Buck6 potential only composed of a repulsion and a dispersion term. This simplicity will facilitate, in the future, **extrapolation of parameters** we have determined for the La-O interaction **to the other Ln-O interactions** (Ln = Ce - Lu), since the Ln³⁺ hydration properties in aqueous solution depends essentially on the Ln³⁺ ionic radius, and **our Buck6 potential** indeed **essentially reflects ionic radius**.

The present study encourages us to proceed further with other lanthanide ions hydration studies and with La³⁺ solvation in aqueous solutions containing anions and other cations.

References:

- [1] M. Souaille *et al.*, *MdVry*: Molecular dynamics program developed at the University of Evry (2006)
- [2] M. Sprik, *J. Phys. Chem.* **95**, 2283 (1991)
- [3] M. Duvail *et al.*, *J. Chem. Phys.* **127**, 034503 (2007)
- [4] C. Clavaguéra *et al.*, *J. Phys. Chem. B.* **109**, 7614 (2005).
- [5] J. Näslund *et al.*, *Inorg. Chem.* **24**, 3047 (2000).

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