

Molecular Dynamics study of $\text{La}(\text{H}_2\text{O})_{216}^{3+}$

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Context and objectives:

★ 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 La^{3+} , since hydration is the first step for handling aqueous chemistry, and **La^{3+} is a natural chemical analogue for actinide ions of interest (Pu^{3+} , Am^{3+} and Cm^{3+})**.

★ Objectives:

- Modelling the hydration of ion La^{3+} , first element of the Lanthanide series,
- Parameterisation of the La-O interactions,
- **Influence of the temperature on the hydration of ion La^{3+} .**

Methodology:

1. Model potentials

The total energy was modelled as a sum of potential terms:

- ★ Coulomb electrostatic potential
- ★ Polarization potential
- ★ 12-6 Lennard-Jones potential (O-O interactions)
- ★ **Buckingham exponential-6 potential (La-O interactions):**

$$V_{\text{La-O}}^{\text{Buck}} = A_{ij}^{\text{Buck}} \exp\left(-\frac{r_{ij}}{\sigma_{ij}^{\text{Buck}}}\right) - \frac{C_{6,ij}^{\text{Buck}}}{r_{ij}^6}$$

2. Parameterisation

The Buckingham 6-exponential potential was parametrized from *ab initio* calculations (Gaussian98-package [1]) on $\text{La}^{3+}(\text{OH}_2)_n$ and $\text{La}^{3+}(\text{OH}_2)_8$ clusters. The quality of the resulting fitted potential was evaluated by comparing the *ab initio* and the model energies of several $\text{La}^{3+}(\text{OH}_2)_n$ ($n=2,3,9,14,24$) clusters. By increasing the number of water molecules, the difference between *ab initio* and model energies decrease up to 0.6% for the $\text{La}^{3+}(\text{OH}_2)_{24}$ cluster including the first and second hydration shells.

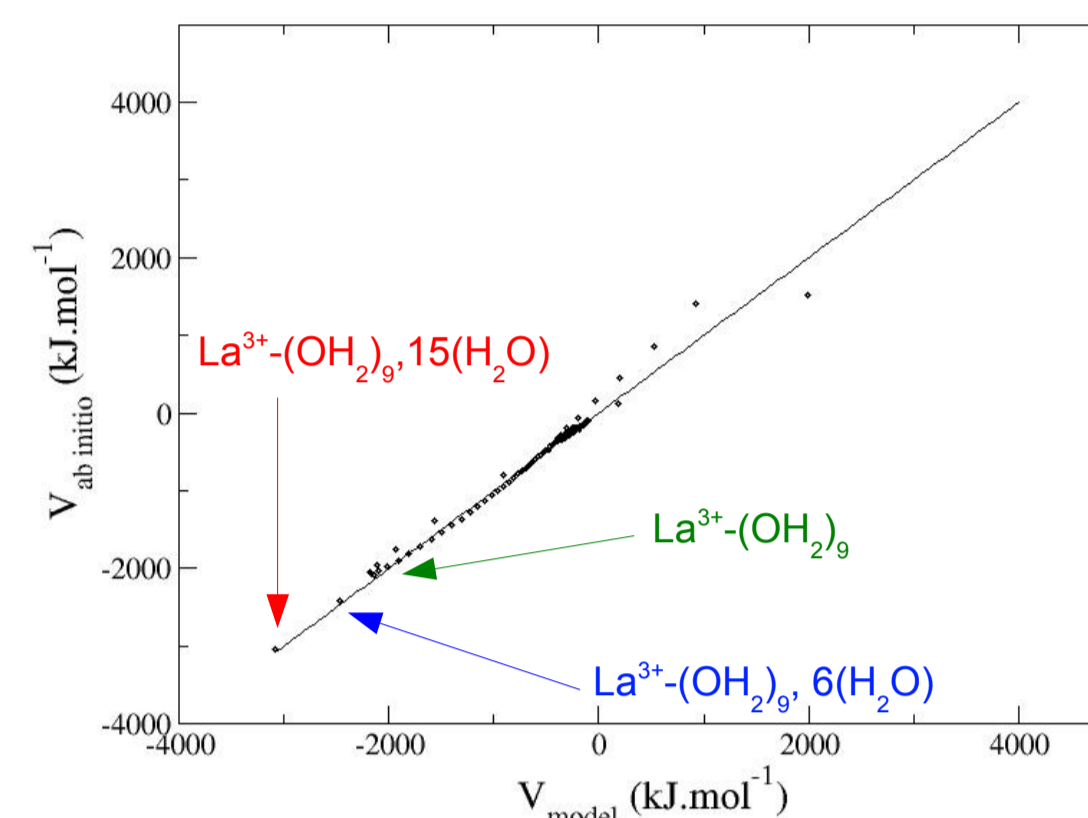


Fig. 1: Comparison of *ab initio* and model energies.

3. Molecular Dynamics

Conditions:

- ★ Temperature: 277 K to 623 K
- ★ 216 water molecules
- ★ Cubic box⁽¹⁾

⁽¹⁾ The sizes of cubic boxes were adjusted to reproduce the densities at the total pressure of 1 atm. for the simulations at temperatures less than 373 K, and at saturating vapour pressure for the higher temperatures.

Results:

1. Water exchanges

1.1. Trajectories

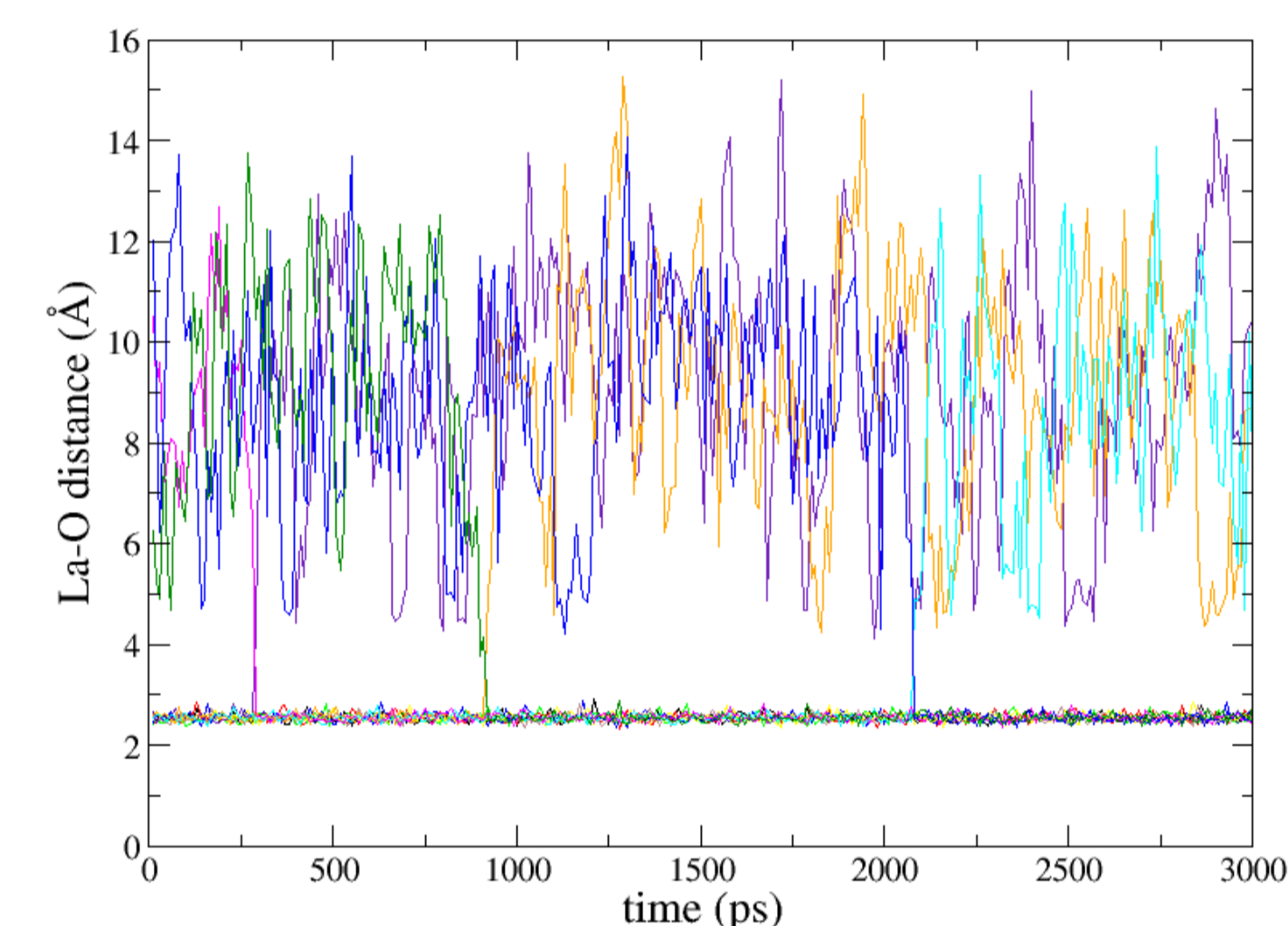
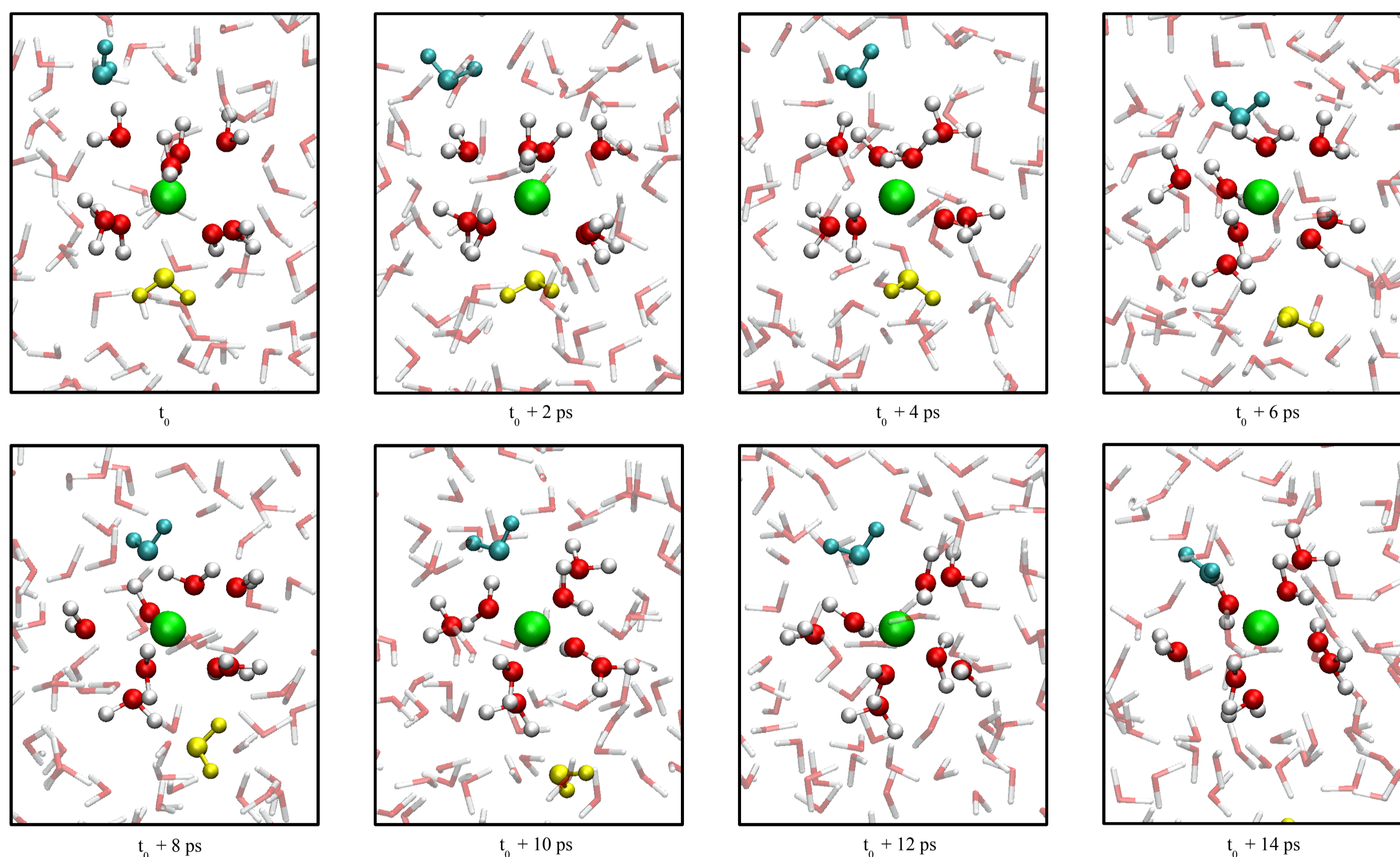
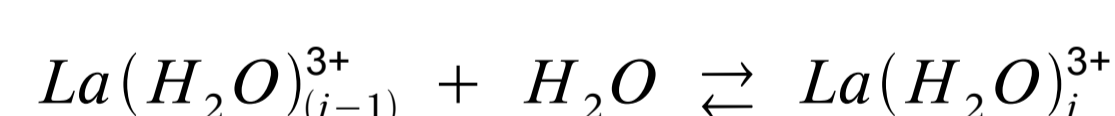


Fig. 2: Observation of water exchanges, for 12 water molecules among 216 at 277 K.

The trajectories of the water molecules suggest **associative** and **dissociative interchange activation modes**.

The associative interchange activation mode corresponds to the incoming of a water molecule in the first hydration shell allowing the formation of an activated complex. While the water molecule is incoming, a water molecule in the first hydration shell is leaving. Similarly in dissociative interchange activation mode, a water molecule is leaving the first hydration shell while another is incoming.

1.2. Enthalpies of reactions



★ **Mass Action Law:**

$$K_i = \frac{a(\text{La}(\text{H}_2\text{O})_i^{3+})}{a(\text{La}(\text{H}_2\text{O})_{(i-1)}^{3+}) \cdot a(\text{H}_2\text{O})}$$

★ **Van't Hoff Law:**

$$R \ln(K_i) \approx -\frac{\Delta_r H_i^0}{T} + \Delta_r S_i^0$$

Tab.1: Thermodynamic values as a function of the number of water molecules in the first hydration shell.

$i-1$	$\Delta_r H_{298}^0$ (kJ.mol ⁻¹)	$\Delta_r S_{298}^0$ (J.mol ⁻¹ .K ⁻¹)	$\Delta_r G_{298}^0$ (kJ.mol ⁻¹)	$\log(K_i)$
8	-71	-164	-22	+3.5
9	-33	-146	+11	-1.7
10	-12	-145	+32	-5.5

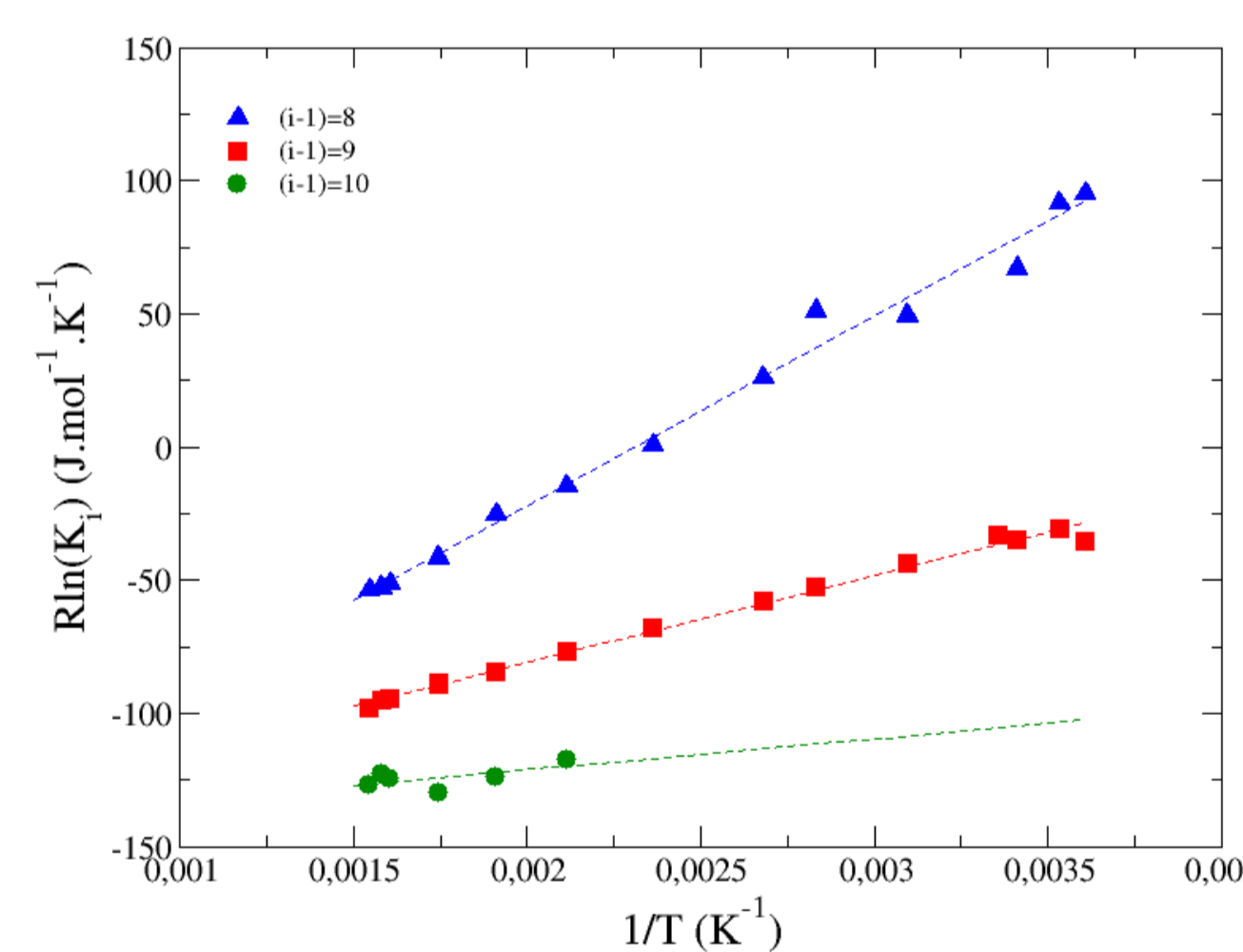


Fig. 3: Van't Hoff plots for equilibrium $\text{La}(\text{H}_2\text{O})_{i-1}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{La}(\text{H}_2\text{O})_i^{3+}$. Linear plots are indeed obtained for $R \ln(K_i)$ vs. $1/T$.

$R \ln(K_i)$ variations appear to be linear as a function of $1/T$ (Fig. 3). This indicates that the Van't Hoff Law is a reasonable approximation in our range of temperature: **the enthalpy of reaction $\Delta_r H^0$** was obtained as the slope of $R \ln(K_i)$ vs. $1/T$. $R \ln(K_i)$ are the intercepts of these lines for $\frac{1}{T} = \frac{1}{T^0}$, from which

$$\Delta_r G_i^0 = -RT^0 \ln(K_i^0) \quad \text{and} \quad \Delta_r S_i^0 = \frac{(\Delta_r H_i^0 - \Delta_r G_i^0)}{T^0}$$

were obtained (Tab. 1).

The Van't Hoff Law means that **temperature has negligible influence on $\Delta_r H^0$ and $\Delta_r S^0$** in our range of temperature, *i.e.* **the influence of the Heat Capacity can be neglected.**

2. Structural results

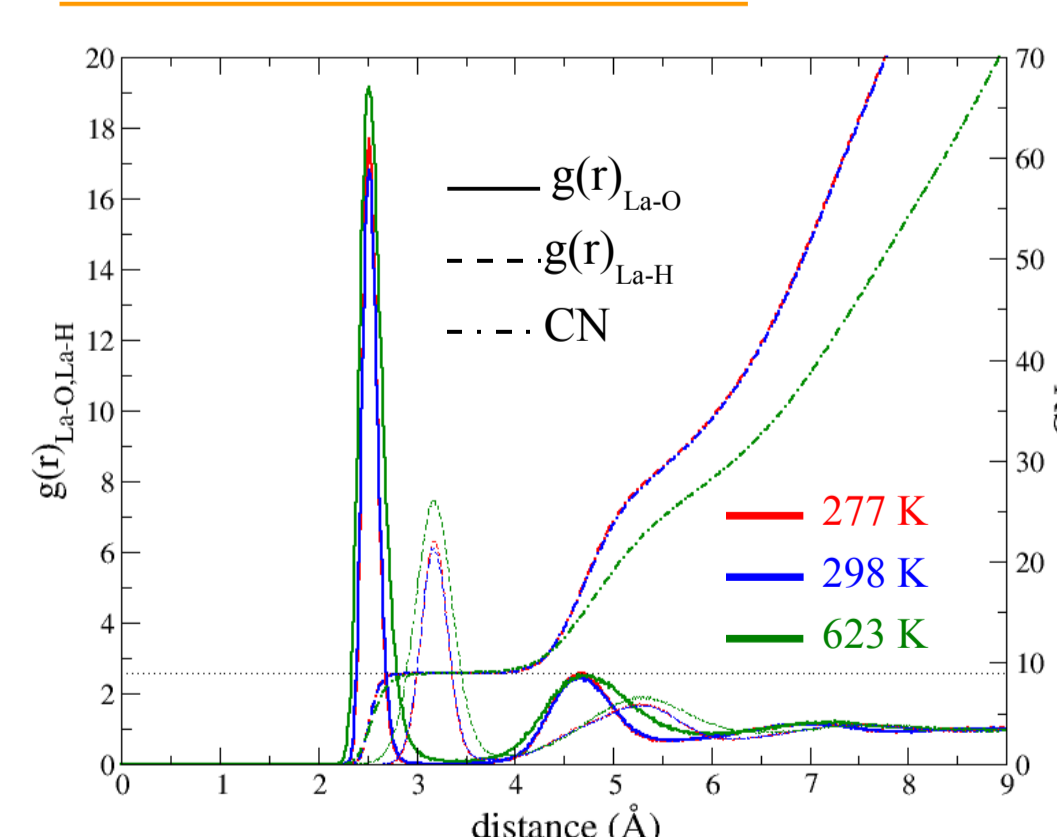


Fig. 4: Radial Distribution Functions of La-O (solid line), La-H (dash line), and coordination number (dash-dot line) as a function of the La-O distance.

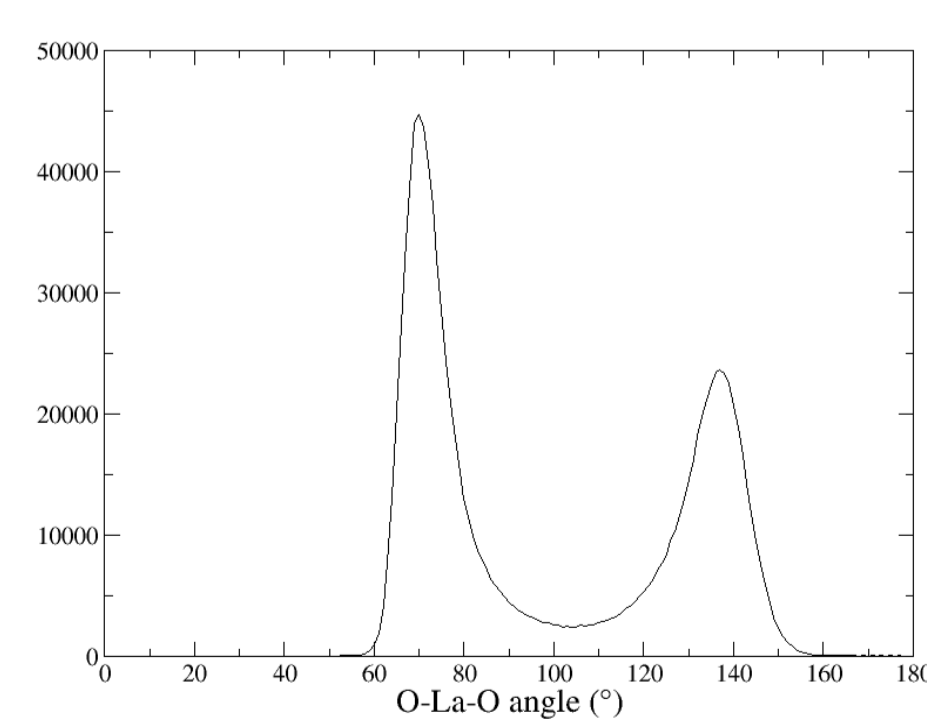


Fig. 5: Angular Distribution Function of the O-La-O angle in the first hydration shell.

Temperature has **no effect on the first hydration shell**. The influence of the temperature is more important at larger La-O distances. At larger distance a dilatation is observed, dilatation mainly due to the increase of the temperature.

Conclusion and prospects:

1. Conclusion

Tab.2: Summary of results obtained from MD simulations at 298K.

	$r^{(1)}$ (Å)	CN ⁽¹⁾	$r^{(2)}$ (Å)	CN ⁽²⁾	$\tau^{(1)}$ (ps)	$\tau^{(2)}$ (ps)
Present study	2.53	9.02	4.65	18.8	1082	7.7
Clavaguera <i>et al.</i> [2]	2.56	8.90	4.68	15.9	980	-
Näslund <i>et al.</i> [3]	2.55	6+3	4.63	18.0	-	-

2. Prospects

- ★ Study of the Co^{2+} hydration (in progress)
- ★ Study of the La^{3+} hydrolysis: MD on $\text{La}(\text{OH})_i(\text{H}_2\text{O})_{(216-i)}^{2+}$ with $1 < i < 5$
- ★ Influence of ionic radii
- ★ Study of the Ln³⁺ series hydration: decrease of the coordination number in the first hydration shell from 9 for La^{3+} to 8 for Lu^{3+} .

Acknowledgements

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[1] M. Frisch *et al.*, Gaussian 98, Revision A.9. Gaussian, Inc., Pittsburgh PA (1998).
[2] Clavaguera *et al.*, *J. Phys. Chem. B*, **109**, 7614 (2005).
[3] Näslund *et al.*, *Inorg. Chem.*, **24**, 3047 (2000).