UMR 8587 CNRS / Evry University / CEA (NUCLEAR ENERGY DIVISION), France

# Hydrolysis of hard cations, a molecular dynamics study

**Magali Duvail**
PhD Thesis started on October 2004

UMR 8587
Evry University (France)
Supervisor: Thierry Cartailler
co-supervising: Marc Souaille

UMR 8587
CEA Saclay DPC/SECR
co-supervising: Pierre Vitorge

## Context

**Aqueous Radio-Chemistry in nuclear fuel cycles, waste disposals and environment**

## Objectives

- **Modelling the hydration of $La^{3+}$, a cation analogue to lanthanides(III) fission products, $Am^{3+}$, $Cm^{3+}$ and $Pu^{3+}$**
- **Parametrization of a model potential for molecular dynamics simulations.**

## Methodology

**Potential:**

1. Definition

Model potential:

$$E = V^{Coul} + V^{pol} + V^{LJ} + V^{TF}$$

- The Coulomb electrostatic term is given by:

$$V_{ij}^{Coul}(r_{ij}) = \frac{e^2}{4\pi\varepsilon_0}\frac{q_i q_j}{r_{ij}}$$

- Polarisation…

$$V^{pol} = -\frac{1}{2}\sum_i \left(\vec{\mu}_i \vec{E}_i^0\right) \qquad \vec{\mu}_i = \alpha\vec{E}_i \qquad \vec{E}_i = \vec{E}_i^0 + \frac{1}{4\pi\varepsilon_0}\sum_{j\neq i}\left(T_{ij}\vec{\mu}_j\right)$$

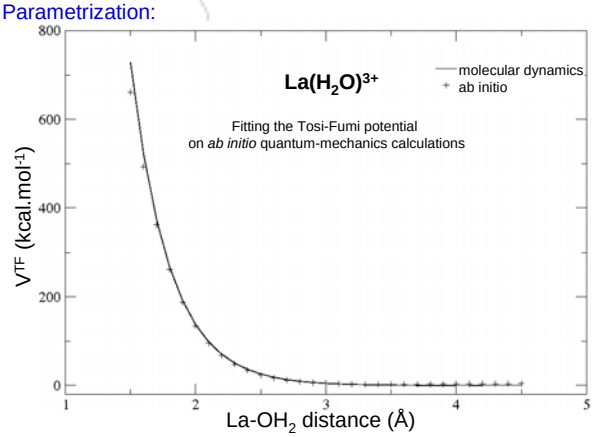
- Short-range interactions were accounted for by using12-6 Lennard-Jones Potential:

$$V_{ij}^{LJ}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

- and Tosi-Fumi Potential [1,2] with parameters fitted in the present work

$$V_{ij}^{TF}(r_{ij}) = a\exp(-br_{ij}) - \frac{c}{r_{ij}^6} - \frac{d}{r_{ij}^8} - \frac{e}{r_{ij}^{10}}$$

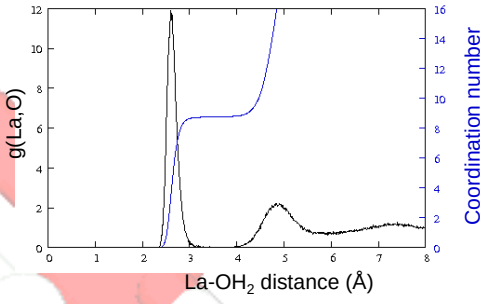
2. Parametrization:



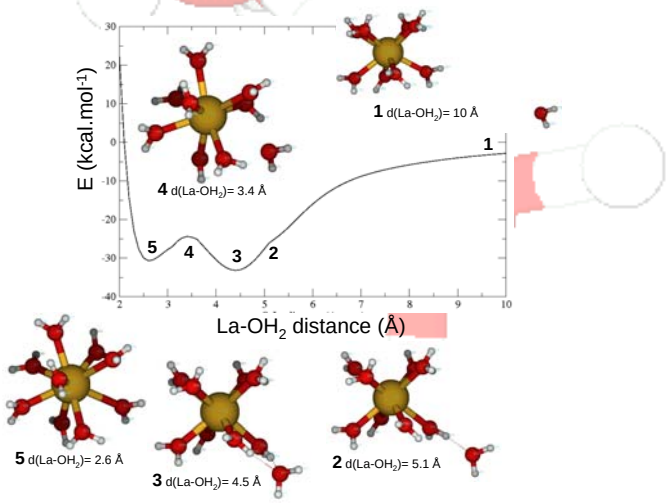

## First results

1. Molecular dynamics simulations

- **216 water molecules** - Temperature: 298 K - Length of the cubic box: 18.643 Å




2. *Ab initio* calculations




## Conclusion

- Parameterization of the Tosi-Fumi potential
- Comparison between molecular dynamics simulations, *ab initio* calculations and published data

| | 1st shell | | 2nd shell | |
|---|---|---|---|---|
| | O-La (Å) | CN | O-La (Å) | CN |
| Molecular dynamics | 2.60 ± 0.01 | 8.75 | 4.84 ± 0.01 | ~16 |
| *Ab initio* calculations | 2.6 ± 0.1 | 8 | 4.5 ± 0.1 | - |
| Published data | 2.54 ± 0.02 [3] | 9.2 ± 1.5 [3] | 4.63 [4] | 16.0 [4] |

## Prospect

- Influence of Temperature on the first shell coordination number of $La(H_2O)_{216}^{3+}$
- Study of $La(H_2O)_8(OH)^{2+}$ by *ab initio* calculations

References:
[1] F.Fumi, M.Tosi, *J.Phys.Chem.Solids* **25**, 31 (1964)
[2] M.Tosi, F.Fumi, *J.Phys.Chem.Solids* **25**, 45 (1964)
[3] P.Allen, J.Bucher, D.Shuh, N.Edelstein, I.Craig, *Inorg.Chem.* **39**,595 (2000)
[4] C.Clavaguera, R.Pollet, J.Soudan, V.Brenner, J.P.Dognon, *J.Phys.Chem.B.* **109**,7614 (2005)

**5ème Journée scientifique de la DEN – 23 juin 2005**