Development and application of a polarizable force-field for actinides in aqueous solution including cooperative charge-transfer terms

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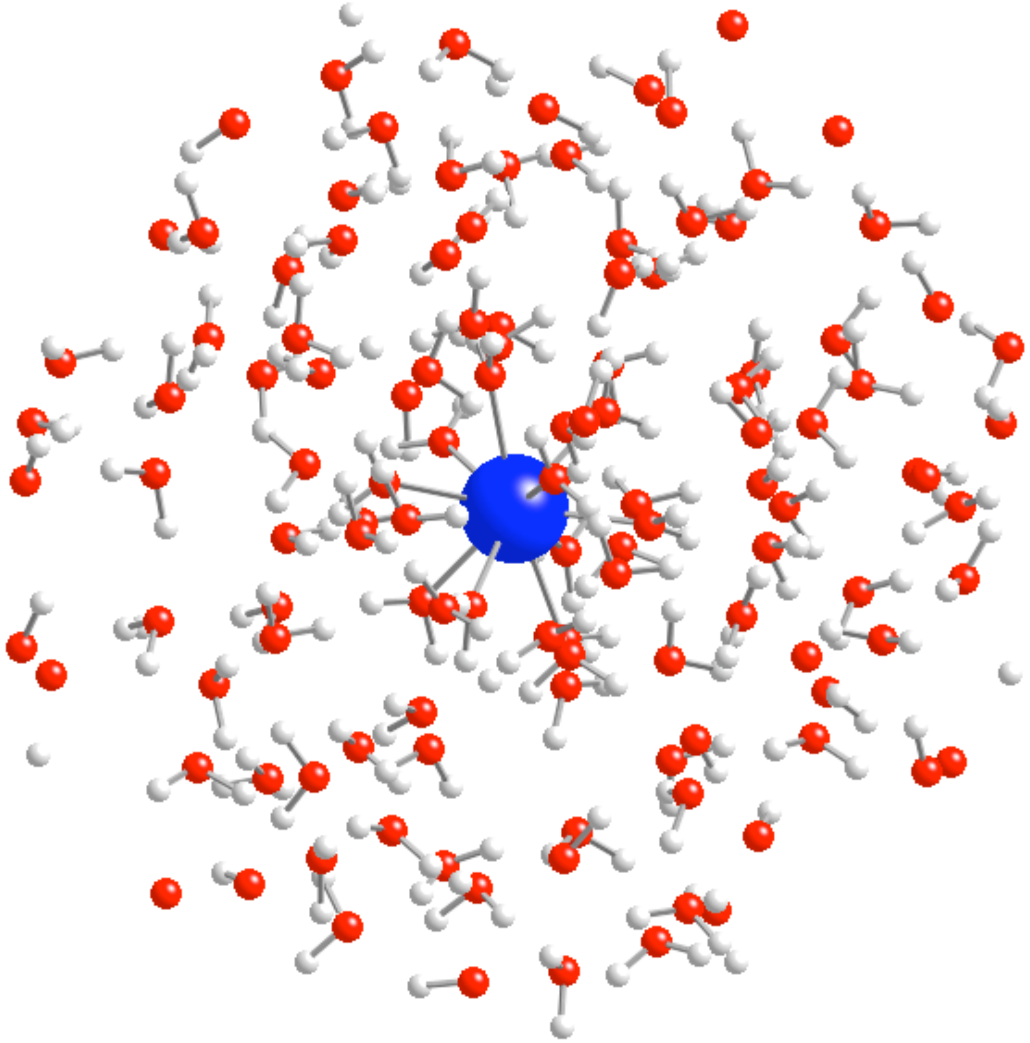


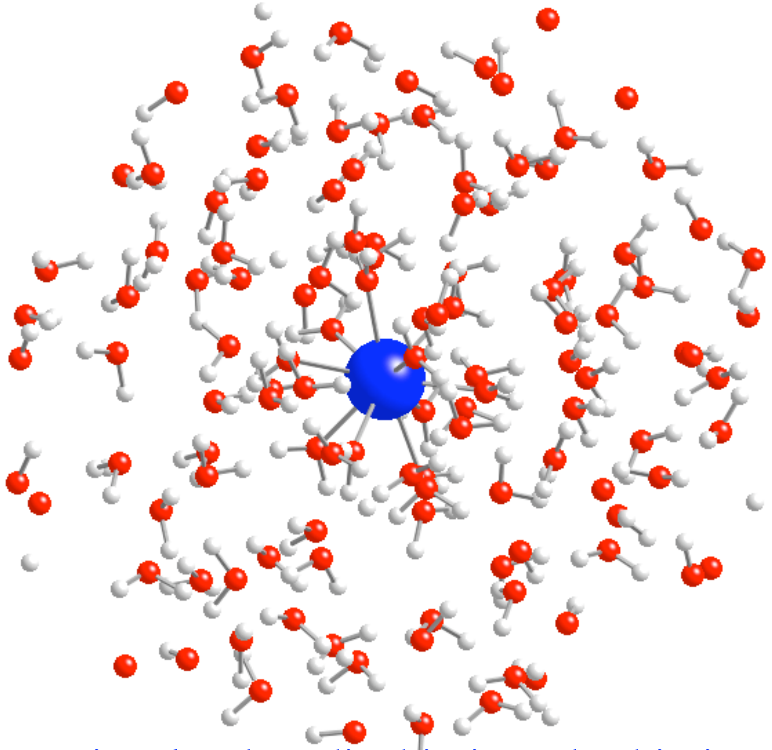
XIIIe journées nationales de radiochimie et de chimie nucléaire

Challenges for theoretical modeling in actinide science

- Obtain information on radionuclide mobility in the environment
- Experimental data on radionuclides have some limitations
  - Radioactivity
  - Scarce gas-phase data
  - Most data are in the condensed phase
- Main goals of theoretical modeling is
  - Improve our understanding of existing compounds
  - Help the interpretation of current experimental data
  - **Predict** properties for unknown species or species difficult to manipulate experimentally (Plutonium, ….)

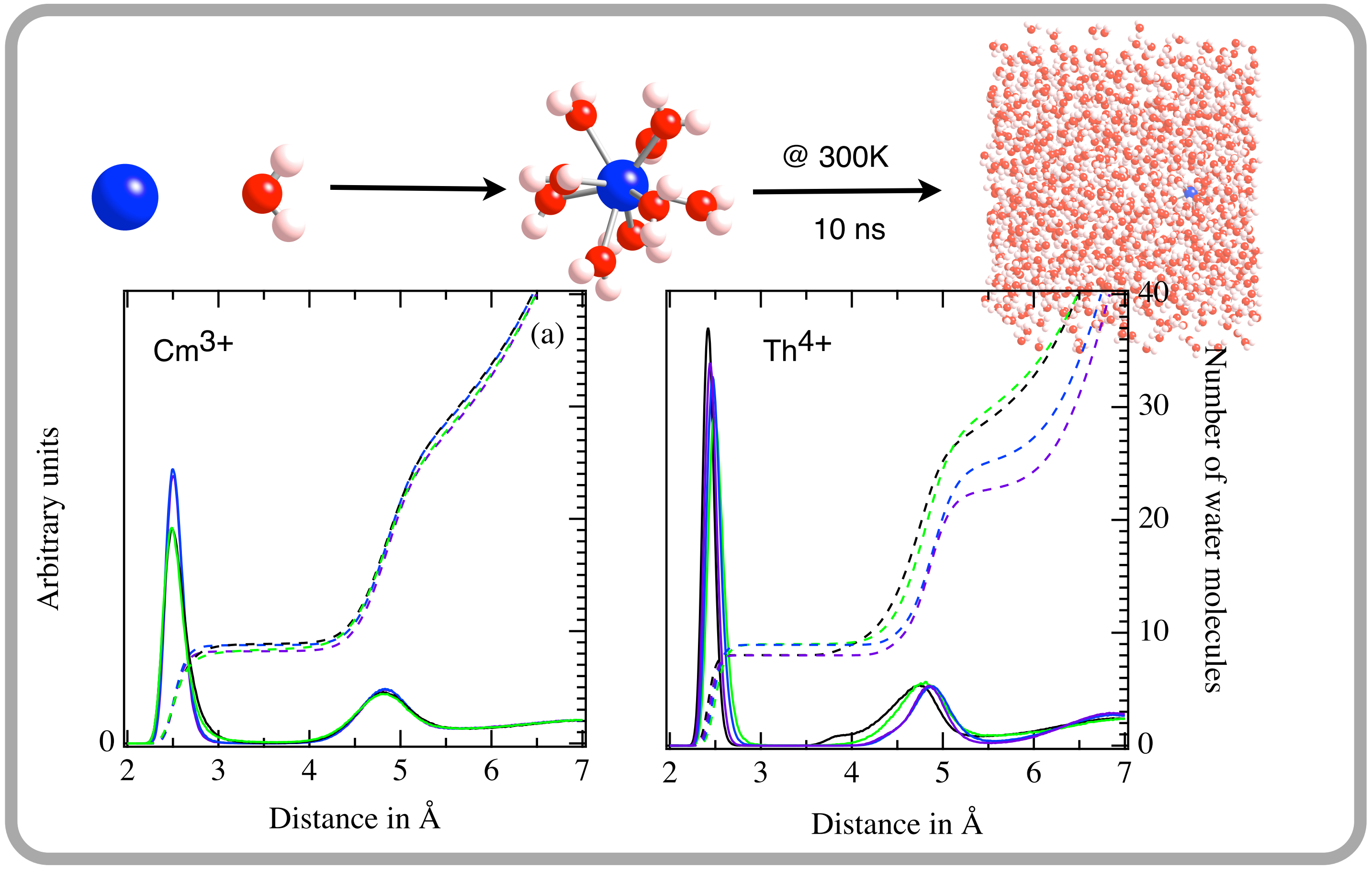
cf poster J. Champion et al.

"Combined experimental and theoretical investigations of the heavy highlight electromobility. (I^- and At^-)."



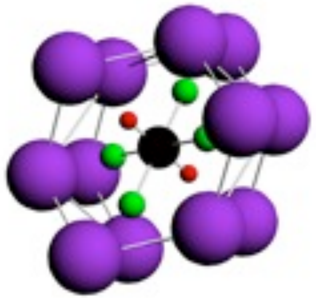
Goals:

- System studied: Thorium(IV) and Curium(III)
- Establish a predictive model
- investigate the counter-ion effect
- Comparison to available experimental data:
  - X-Ray spectroscopy: EXAFS, HEXS
  - NMR for structural properties and ligand exchange dynamics

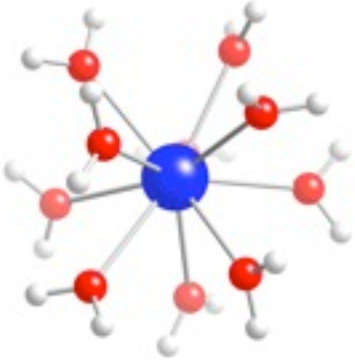


Approach to the theoretical modeling in actinide science

Microscopic



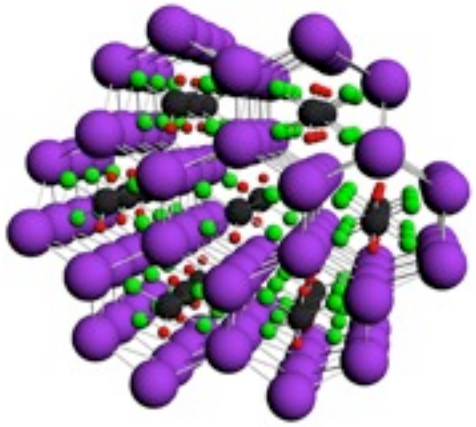
“Simpler”, “Model” systems

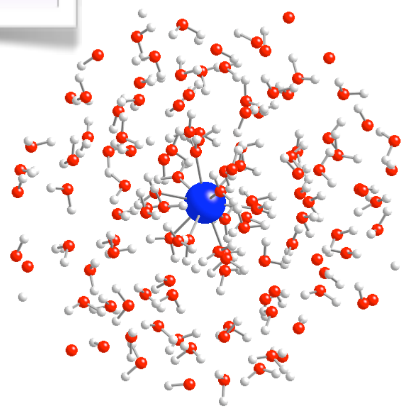


Electronic structure calculations
Quantum chemical methods

Hybrid quantum/classical methods
Ab initio molecular dynamics

“Real” large-scale systems





Hybrid quantum/classical methods
Classical methods
Macroscopic & Embedding effects

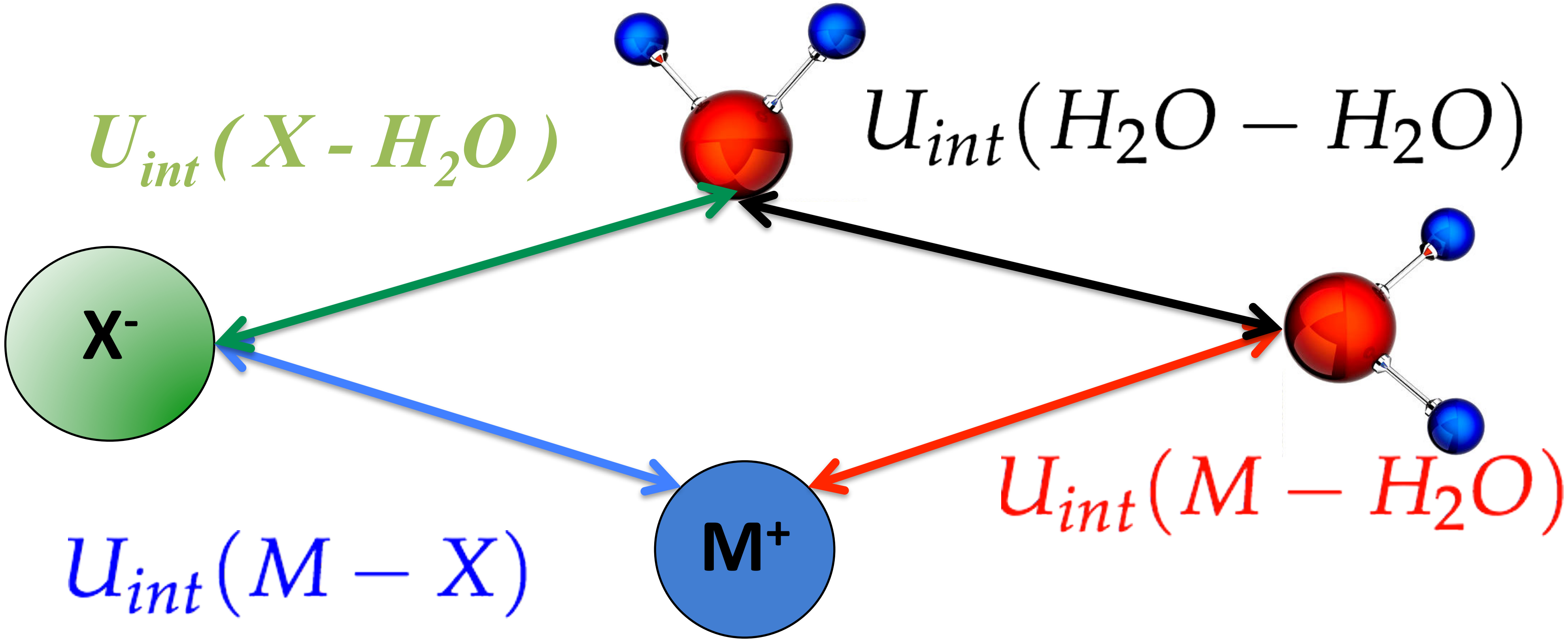
Macroscopic scale

Theoretical models for solvation

- Why not using ab initio MD (Car-Parinello MD)?
- too short time scales (~100 ps)
- problems with the accuracy of density functional theory (DFT) for
  - water-water interactions
  - ion-water interactions (most functionals overestimate M-ligand interactions)

Why developing classical polarizable force-fields?

- Solve the Newton's equations. $\sum \vec{F} = -\sum \vec{grad} U_{int}$
- Parametrized M^{n+}-L interaction potentials:
  - repulsion
  - electrostatic
  - polarization
  - **metal-oxygen bond (covalency)**



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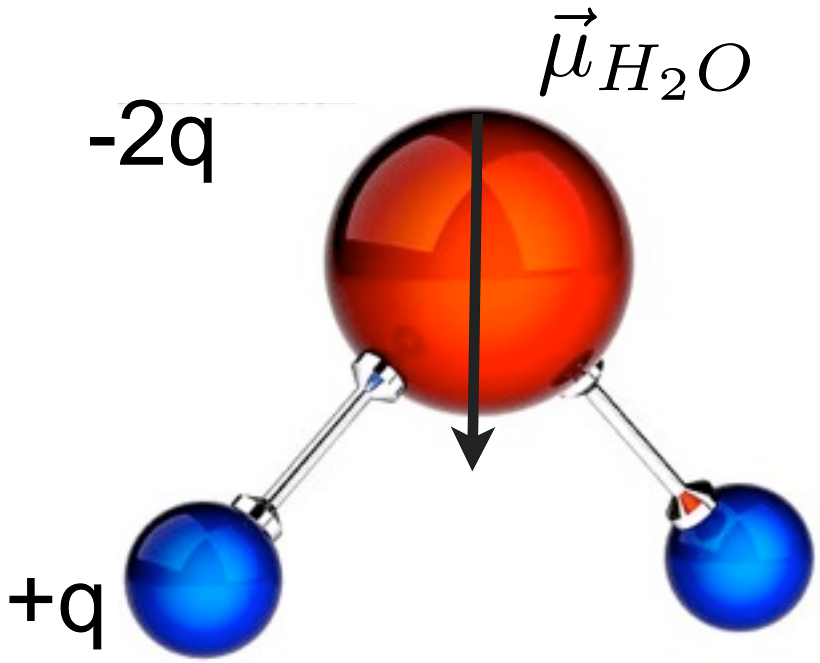
- Solve the Newton’s equations.
- Parametrized M^{n+}-L interaction potentials:
  - repulsion
  - electrostatic
  - polarization
  - **metal-oxygen bond (covalency)**
- No experimental data used to parametrize the force field
- Build a predictive force field using ab initio quantum-chemical reference data

Polarizable water model

tcpep water model: 1 polarized center



$$U = U_{rep} + U_{qq'} + U_{pol} + \underline{U_{HB}}$$

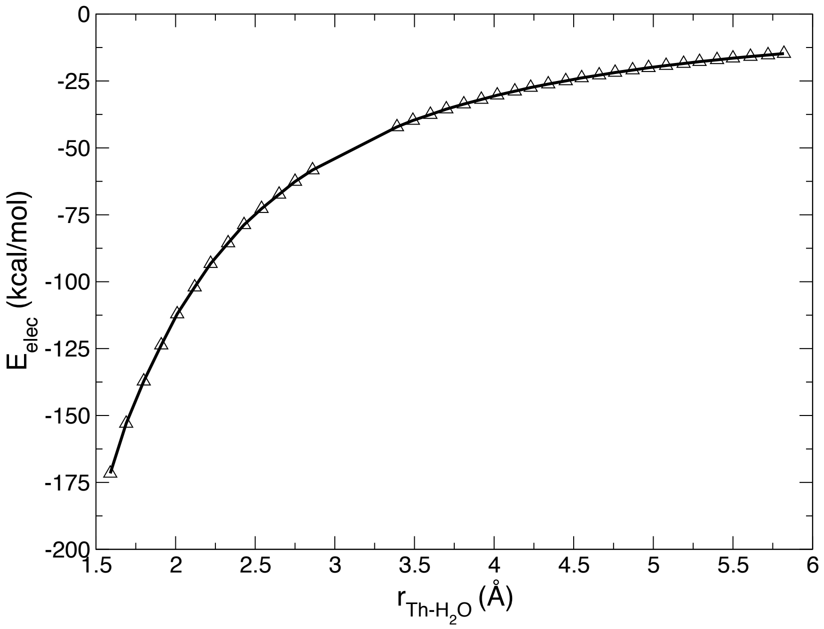
M. Masella and P. Cuniasse, *J. Chem. Phys.* **119**, 1866 (2003)

Polarizable force fields for ion-ligand interaction

$$U = U_{rep} + U_{qq'} + U_{pol} + U_{CT}$$

Electrostatic

$$U_{qq'} = \frac{1}{4\pi\varepsilon_0} \sum_{i<j} \frac{q_i q_j}{r_{ij}}$$



Repulsion

M. Masella and P. Cuniasse, *J. Chem. Phys.* **119**, 1866 (2003)

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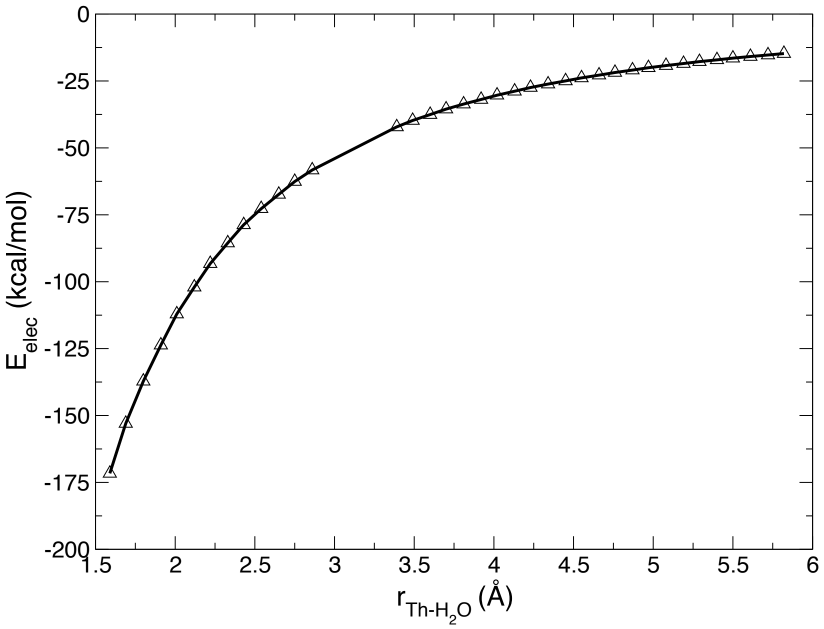
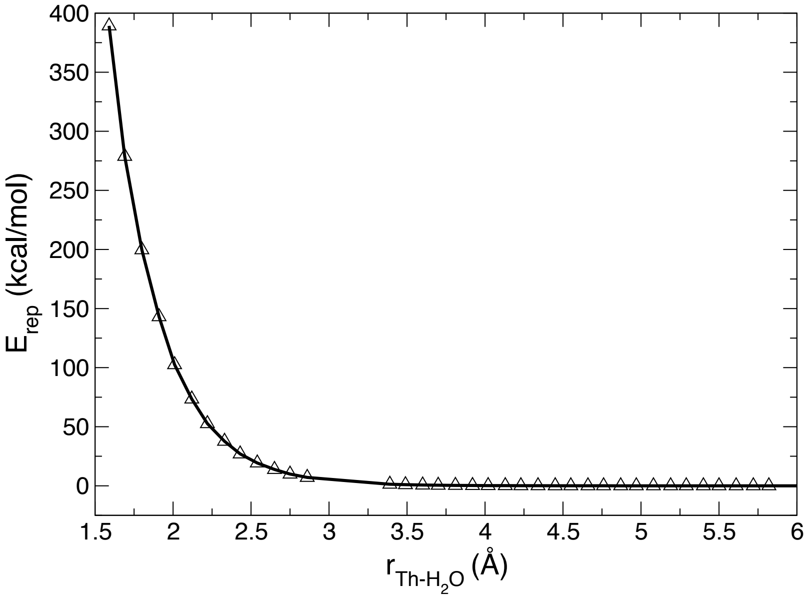


Repulsion

$$U_{rep} = \sum_{i \neq j} A_{ij} \exp(-B_{ij} r_{ij})$$



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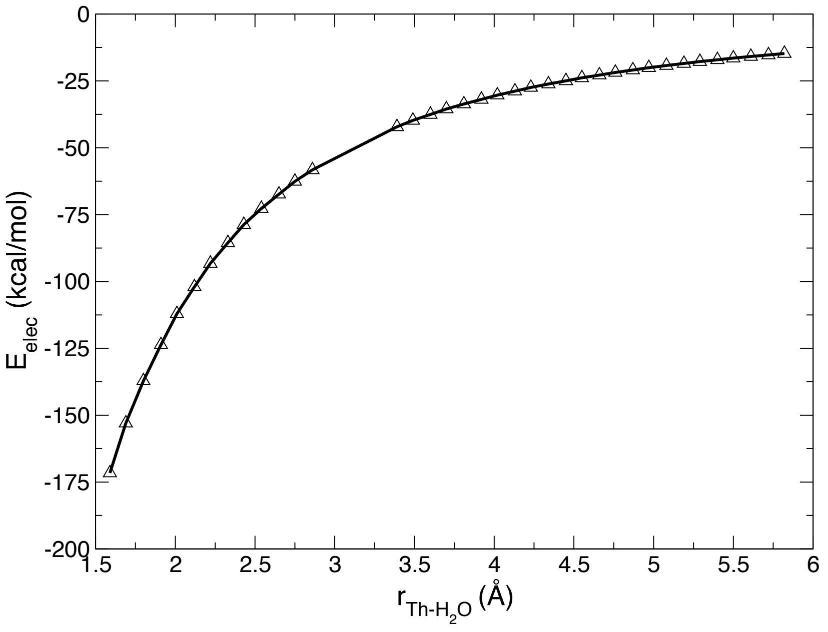

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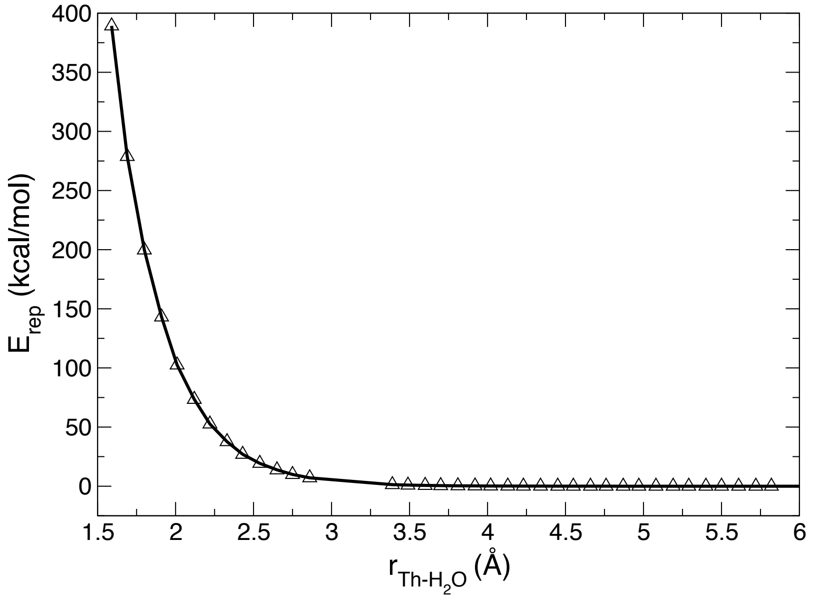


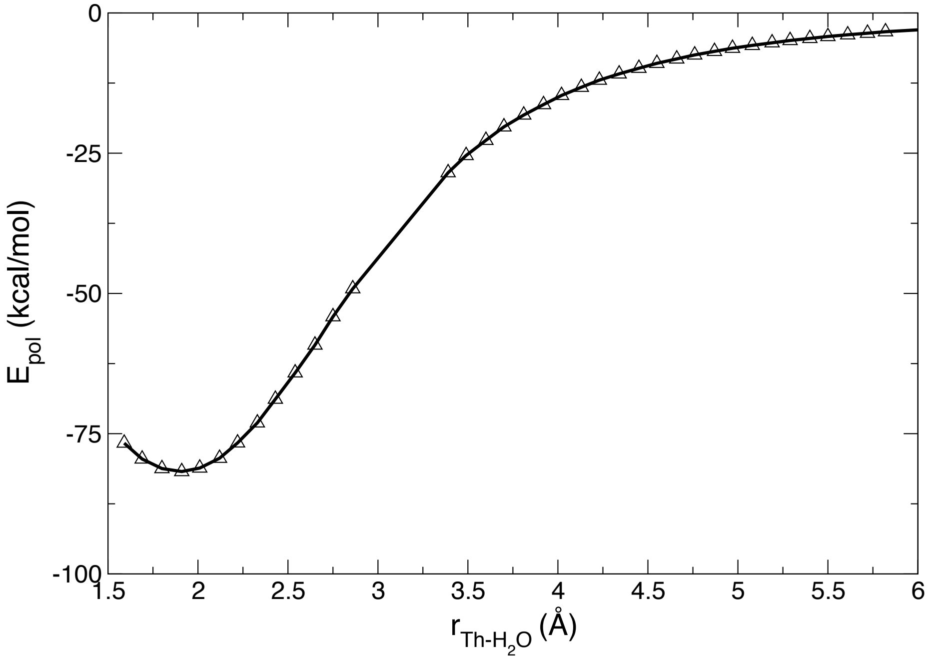
M. Masella and P. Cuniasse, *J. Chem. Phys.* **119**, 1866 (2003)

Polarizable force fields for ion-ligand interaction

$$U = U_{rep} + U_{elec} + U_{pol} + U_{CT}$$

Polarization

$$U_{pol} = \frac{1}{2}\sum_{j=1}^{N_\mu}\frac{p_j^2}{\alpha_j} - \sum_{j=1}^{N_\mu}\vec{p_j}.\vec{E_j^q} - \frac{1}{2}\sum_{i=1}^{N_\mu}\sum_{j=1;j\neq i}^{N_\mu}\vec{p_i}.T_ij.\vec{p_j}$$



- ✦ F.J. Vesely, *J. Comput. Phys.*, **24**, 361 (1977)
- ✦ B.T. Thole, *Chem. Phys.*, **59**, 341-350 (1981)
- ✦ M. Masella and P. Cuniasse, J. Chem. Phys., **119** 1866 (2003)

Polarizable force fields for ion-ligand interaction

$$U = U_{rep} + U_{elec} + U_{pol} + U_{CT}$$

Polarization

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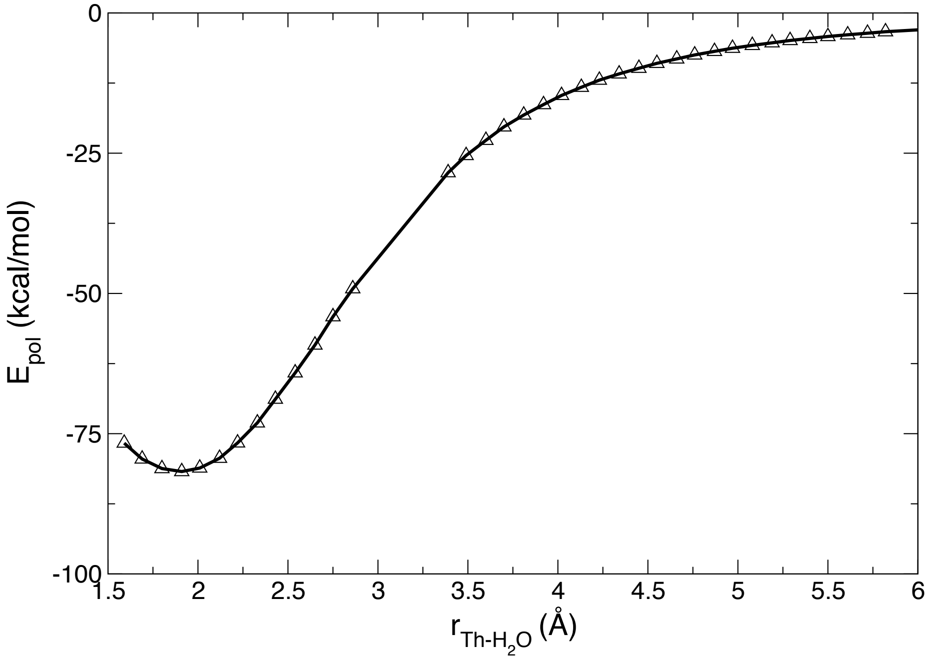

with $\vec{p_i} = \frac{\mu_{sat}}{E_i} L(\frac{3\alpha_i E_i}{\mu_{sat}})\vec{E_i}$

- F.J. Vesely, *J. Comput. Phys.*, **24**, 361 (1977)
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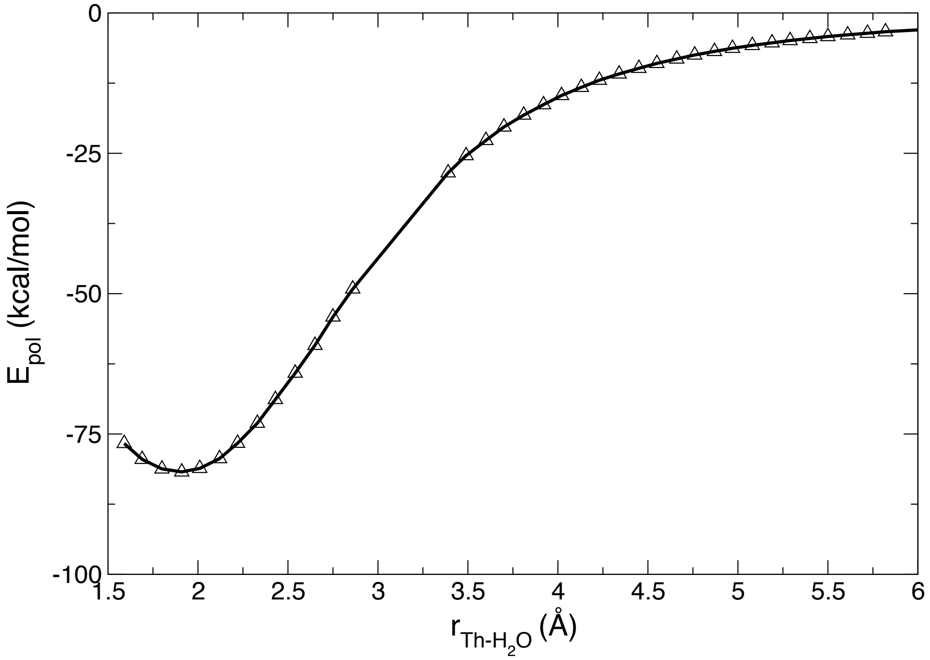
Polarizability

with $$\vec{p_i} = \frac{\mu_{sat}}{E_i}L\left(\frac{3\alpha_i E_i}{\mu_{sat}}\right)\vec{E_i}$$



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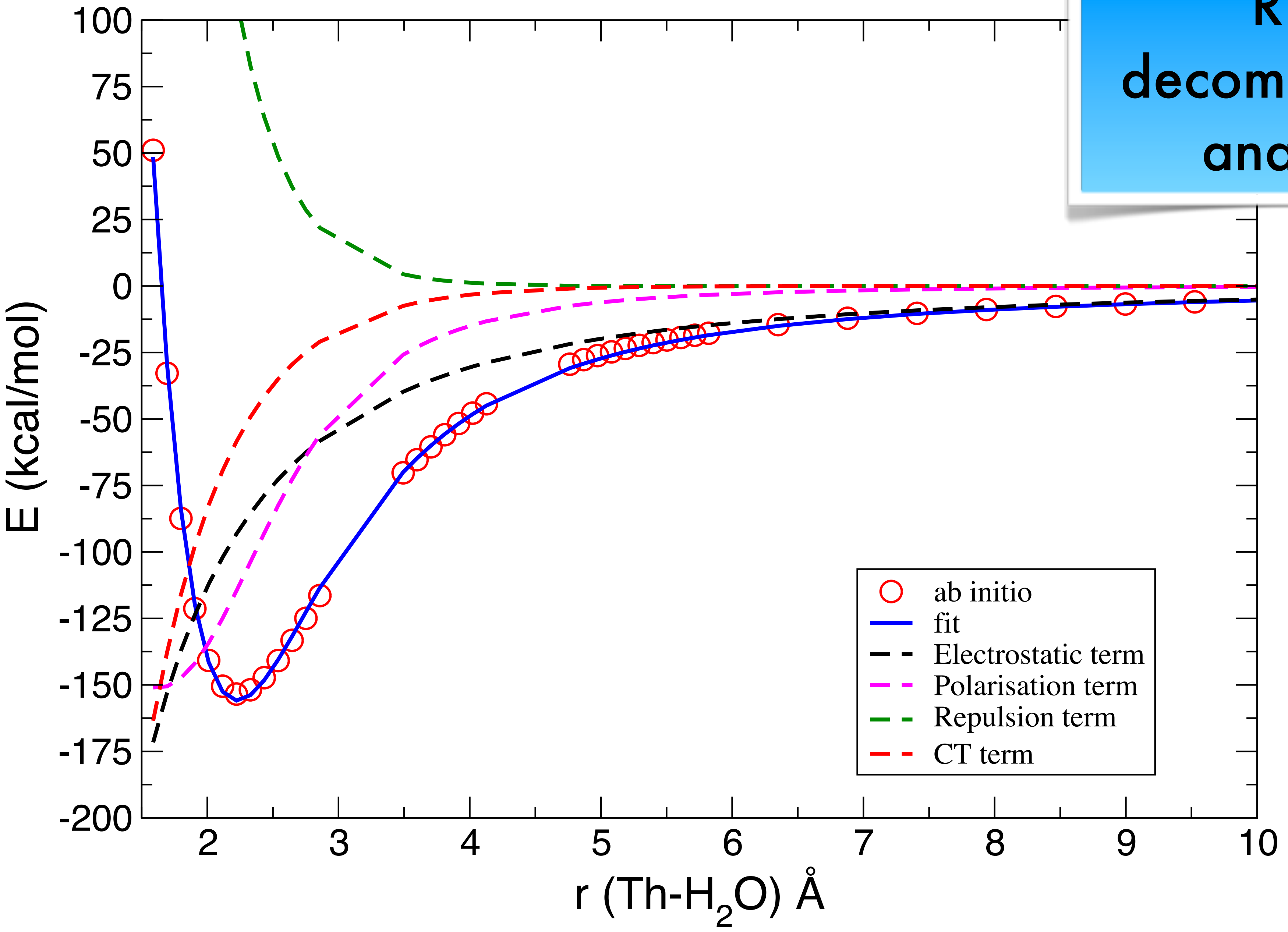
Polarizable force fields for ion-ligand interaction

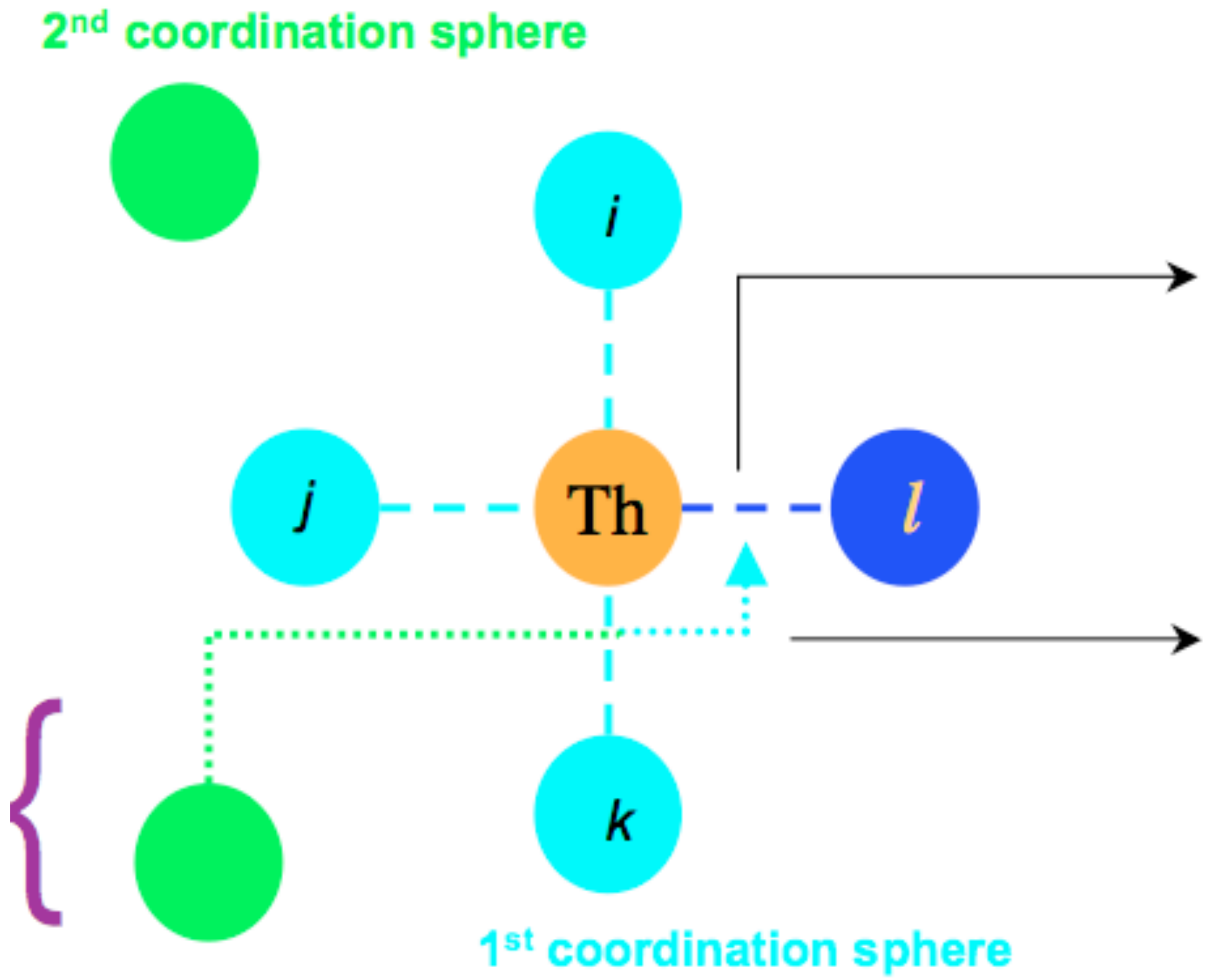
Metal-Oxygen bond
MetOx

$$U_{ct}^{2body} = \sum_i \boxed{d_i} exp(\boxed{-\beta} r_i)$$

RVS decomposition analysis



Polarizable force fields for ion-ligand interaction



Non-additivity of MetOx bond effects

Cooperative character of the MetOX contribution

$$U_{ct}^{3b} = \sum_{i>j} exp(-\beta_{\mathrm{ct}}^{3b} \cdot r_i) \times exp(-\beta_{\mathrm{ct}}^{3b} \cdot r_j) \times (a_1 \cdot r_{ij} + a_2).$$

Cooperative character of the MetOx bond contribution with an explicit 3-body term

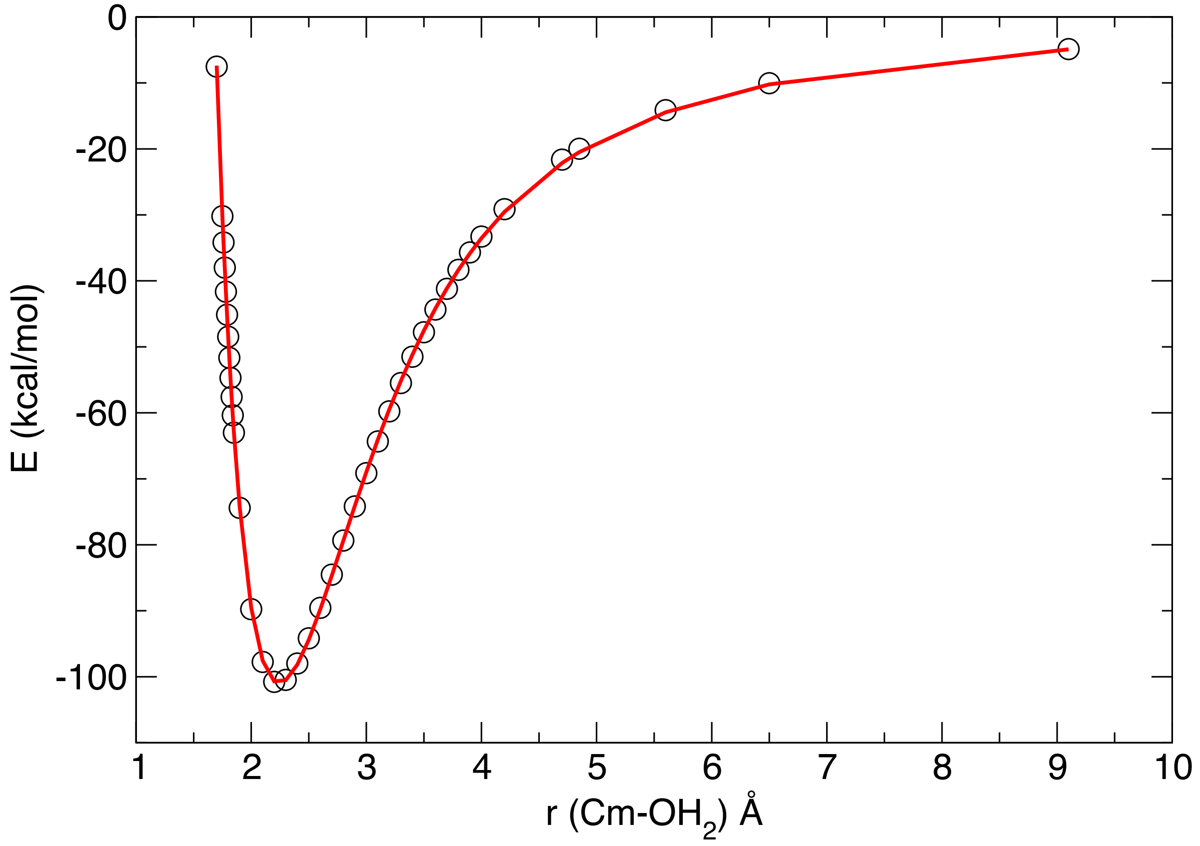
Damping factor of 2-body MetOX effects

$$U_{ct}^{coop} = \sum_i d_i exp(-\beta r_i) \left(1 - \zeta_i \sum_{j \neq i} \left(exp \left(\frac{2r_j - 2r_{min}}{r_{max} - r_{min}} + 1 \right)^{-1} \right) \right)$$

How to optimize force-field parameters?

- Need of a **large set of ab initio reference data** computed with the highest accuracy:

Metal-ligand interaction curve



How to optimize force-field parameters?

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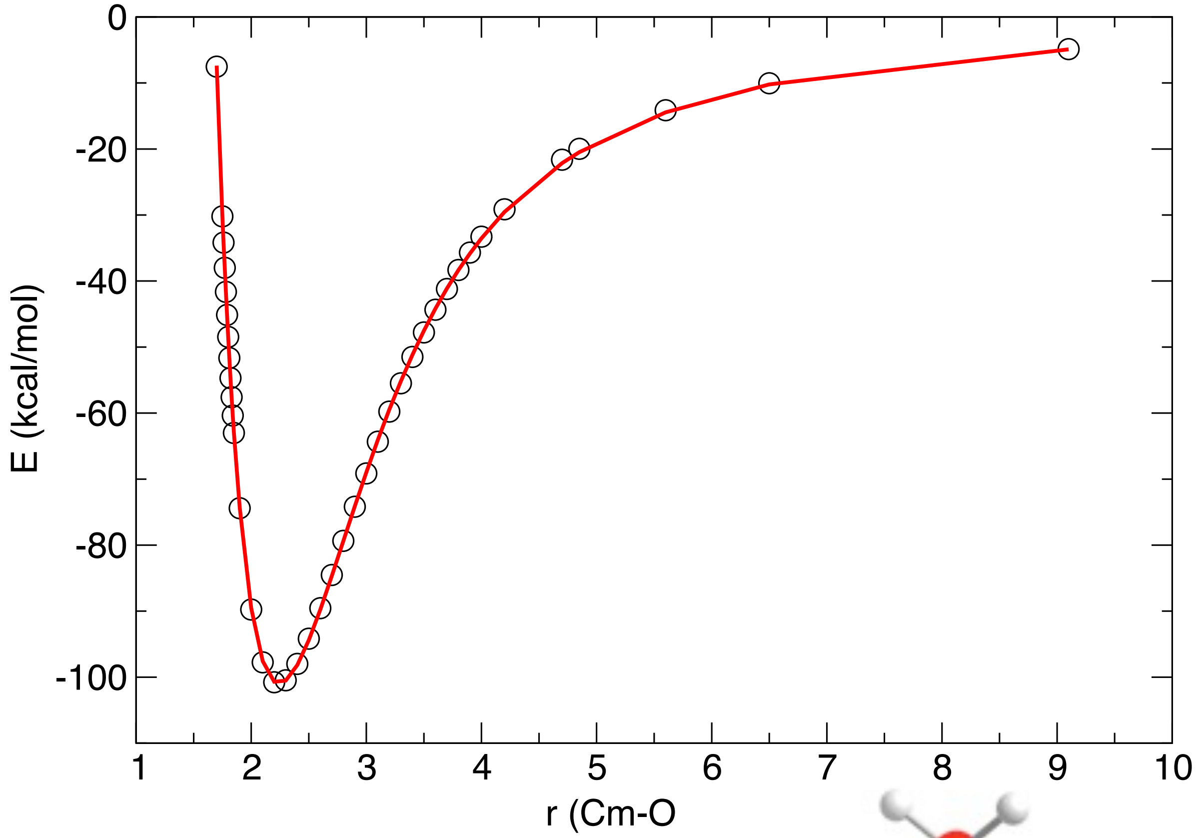
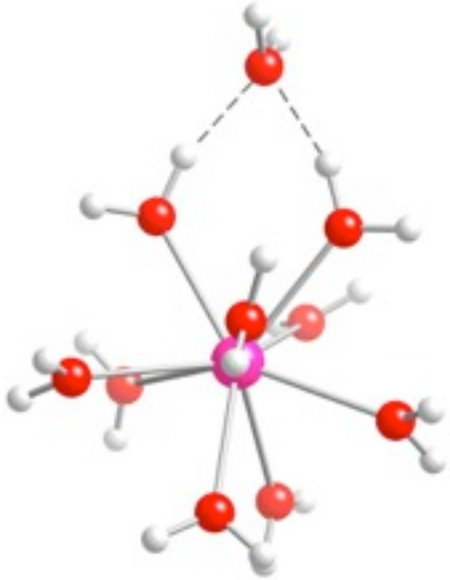
Metal-ligand interaction curve

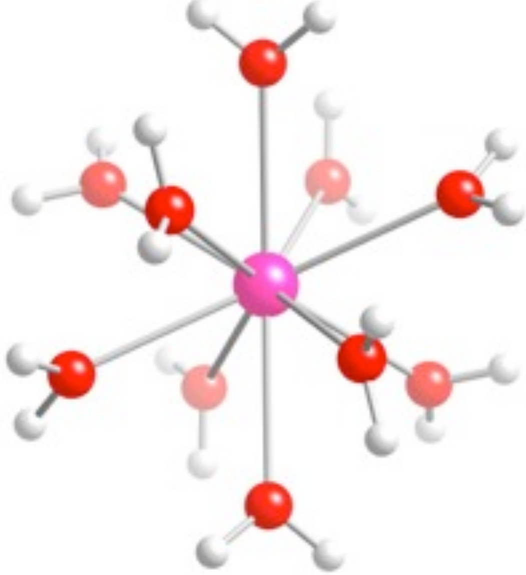
Metal-ligand clusters



$[Cm(H_2O)_8]^{3+},(H_2O)_2$



$[Cm(H_2O)_9]^{3+},(H_2O)$



$[Cm(H_2O)_{10}]^{3+}$

Choice of the ab initio method

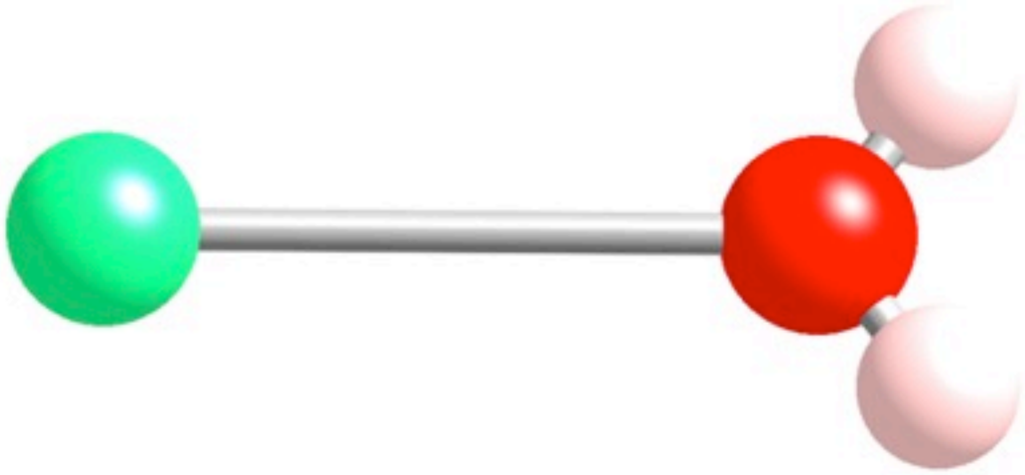


Table 3: Binding energies of the Th(IV)/water dimer in kcal/mol at 2.22 Å, computed with different multi-reference and single-reference correlated methods.

WFT				DFT				
HF	MP2	CCSD(T)	MRCI+DC	BP86	B3LYP	MX06-HF	MX06-L	MX06-2X
145	155	155	156	173	165	163	167	161

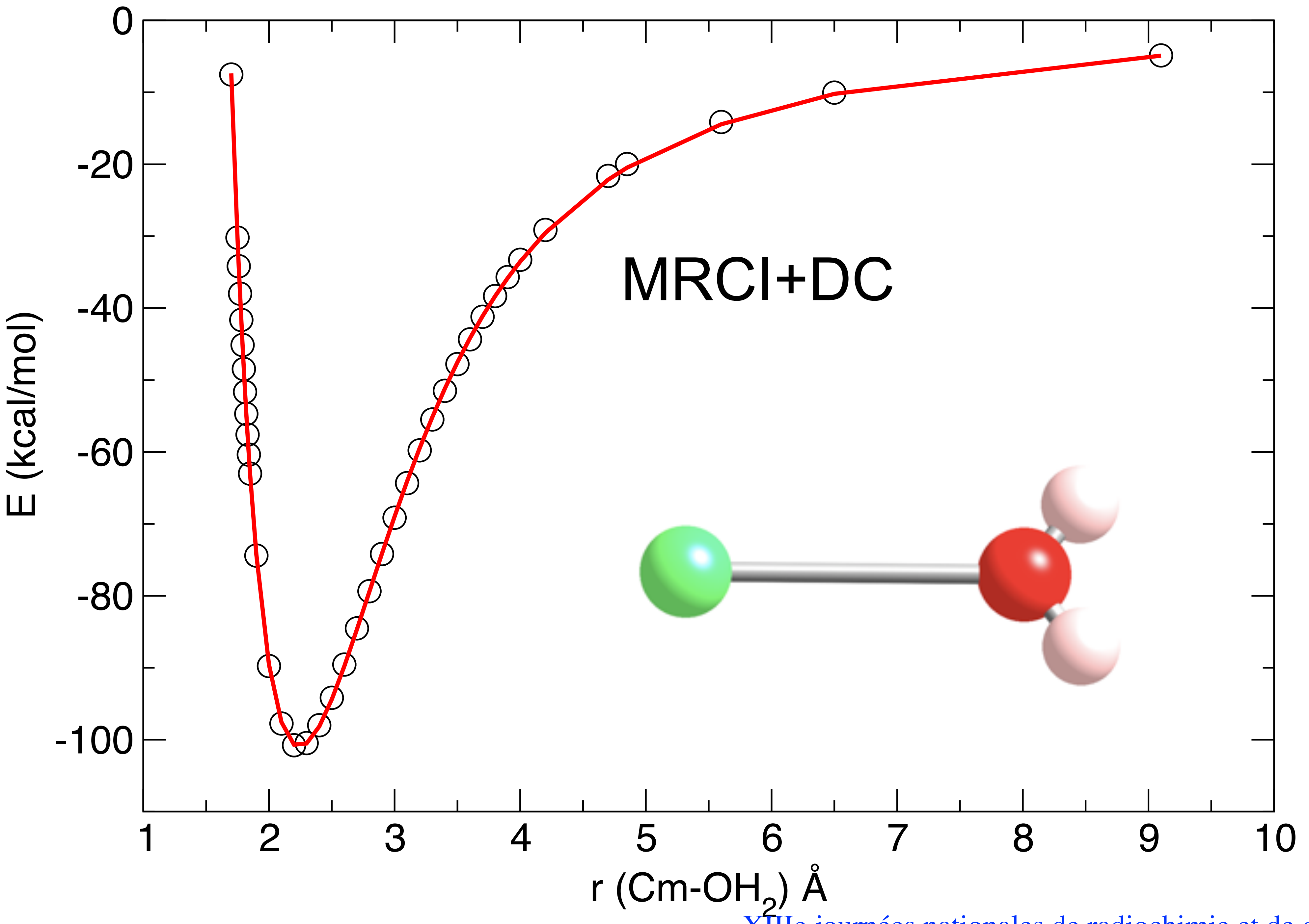
- K. E. Gutowski, D. A. Dixon, J. Phys. Chem. A, **110**, 8840-8856 (2006)
- P. Wahlin, et al. *J. Chem. Theory Comput.*, **4**, 569-577 (2008)
- J. P. Austin, et al. *Phys. Chem. Chem. Phys.*, **11**, 1143 (2009)

Ab initio An^{3+}-H_2O pair potential

Calibration of the fit

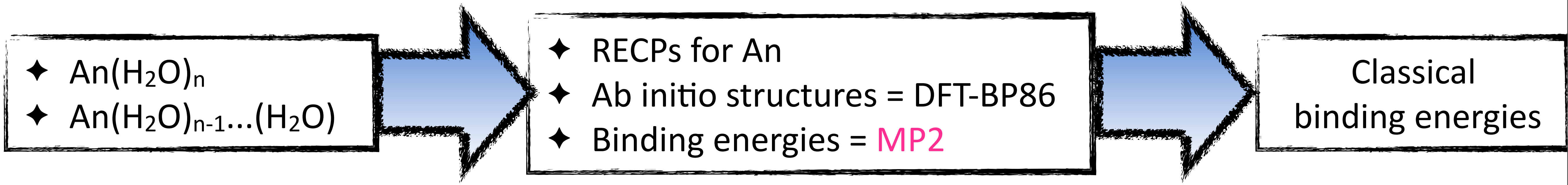
$\Delta E < 0.1$kcal/mol

Need for charge transfer term in the potential



Parameters adjusted on the clusters and accuracy of the fit

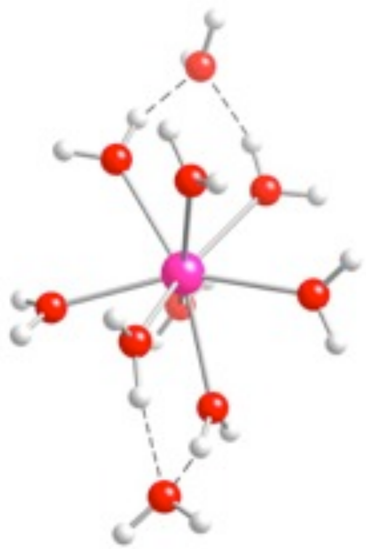
Adjustment of the many-body terms



- ✦ An$(H_2O)_n$
- ✦ An$(H_2O)_{n-1}$...(H_2O)

- ✦ RECPs for An
- ✦ Ab initio structures = DFT-BP86
- ✦ Binding energies = MP2

Classical
binding energies



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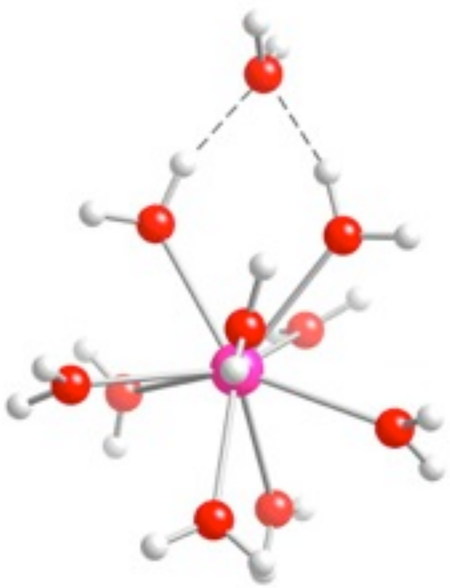

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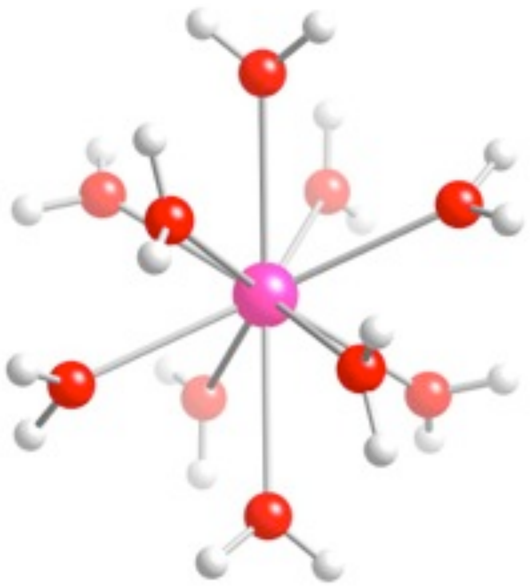
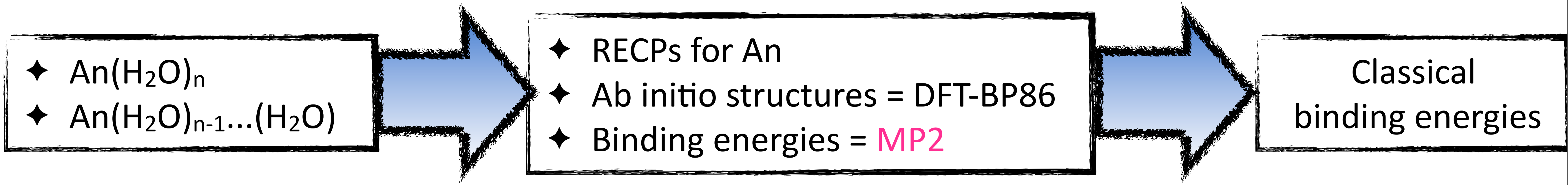


$[Cm(H_2O)_{10}]^{3+}$

Parameters adjusted on the clusters and accuracy of the fit

Adjustment of the many-body terms

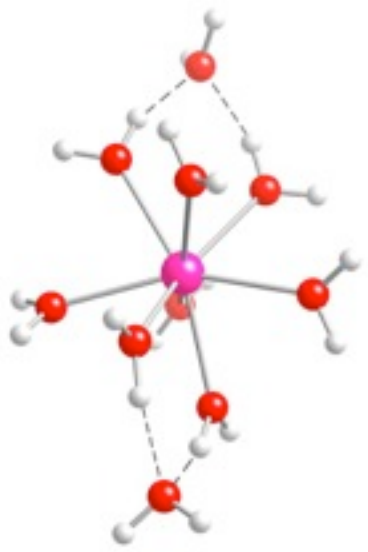


- $An(H_2O)_n$
- $An(H_2O)_{n-1}...(H_2O)$

- RECPs for An
- Ab initio structures = DFT-BP86
- Binding energies = MP2

Classical
binding energies

Error ≃ 2 kcal/mol
< 1% of the total binding energy



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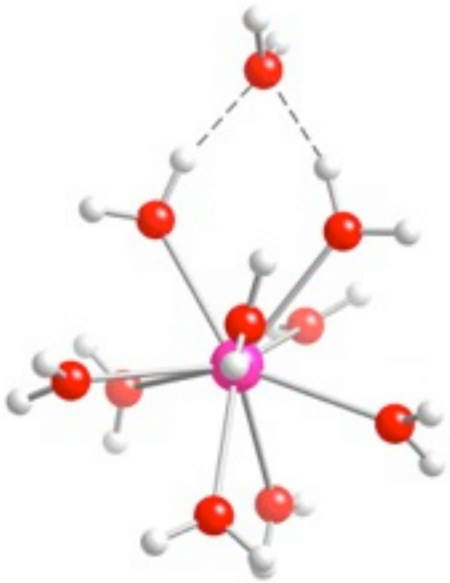

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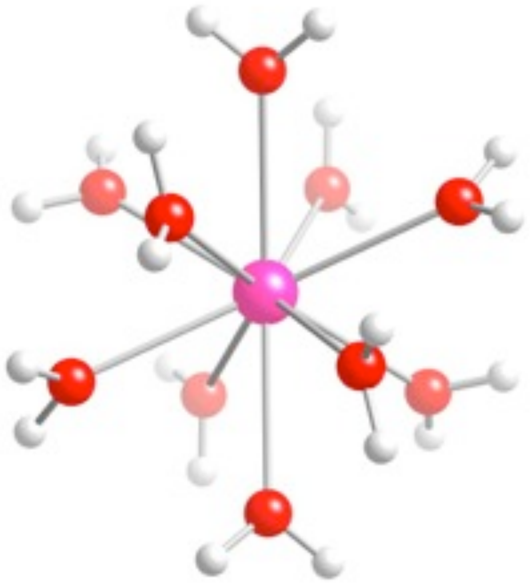
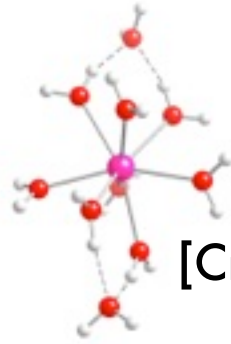


$[Cm(H_2O)_{10}]^{3+}$

Simulation protocol

- For each parameter set, 10 ns molecular dynamics with starting points



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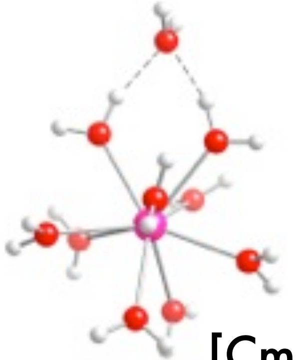

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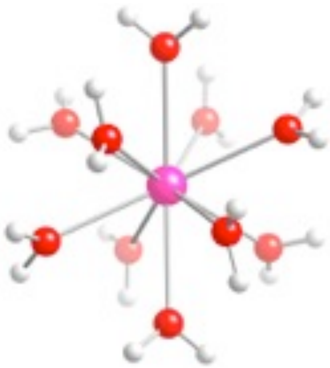


$[Cm(H_2O)_{10}]^{3+}$

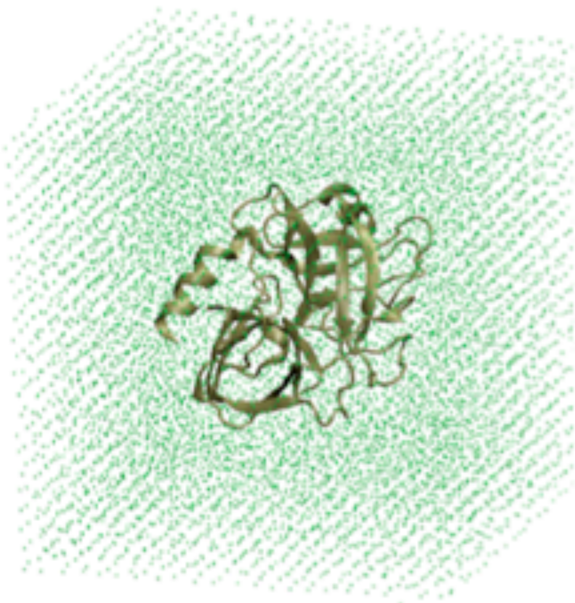
- Th(IV) and Cm(III) embedded in 1000 water molecules with periodic boundary conditions

« POLARIsation and Simulations (Molecular Dynamics) »

(>60 000 lines, MPI/FORTRAN95)

Polarisable force field TCPEp
Including short-range
many-body term
(J. Chem. Phys. 1997-2003)

Polarisable coarse grained
solvent approach
(J. Comput. Chem. 2008
and manuscript submitted)

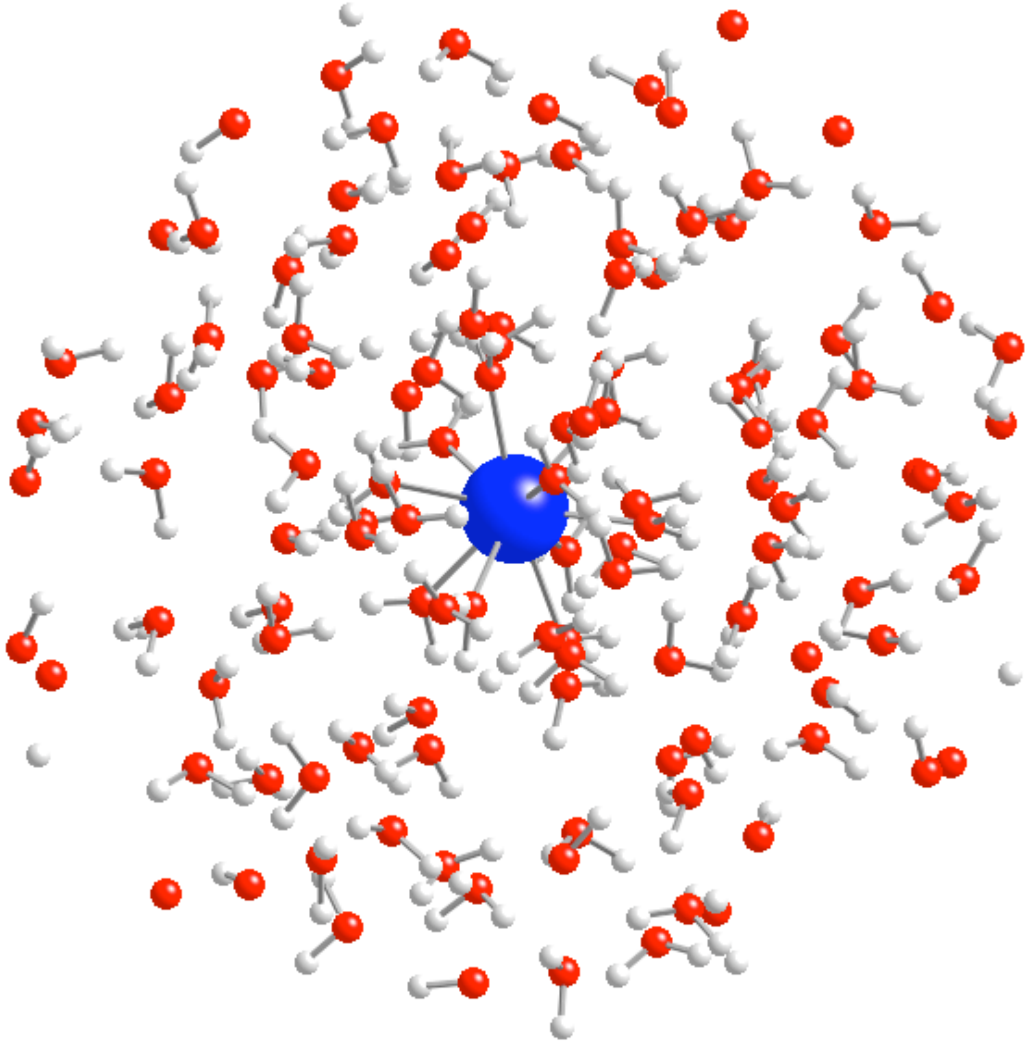


Multiple time steps algorithm
MD speed up up to x3
(Mol. Phys. - 2006)

Ewald summation techniques
NVT MD (GGMT thermostat)
NPT MD (isotropic cell fluctuations)

M. Masella (CEA Saclay)
Polaris Code

Thorium (IV) and Curium(III) aqua ions



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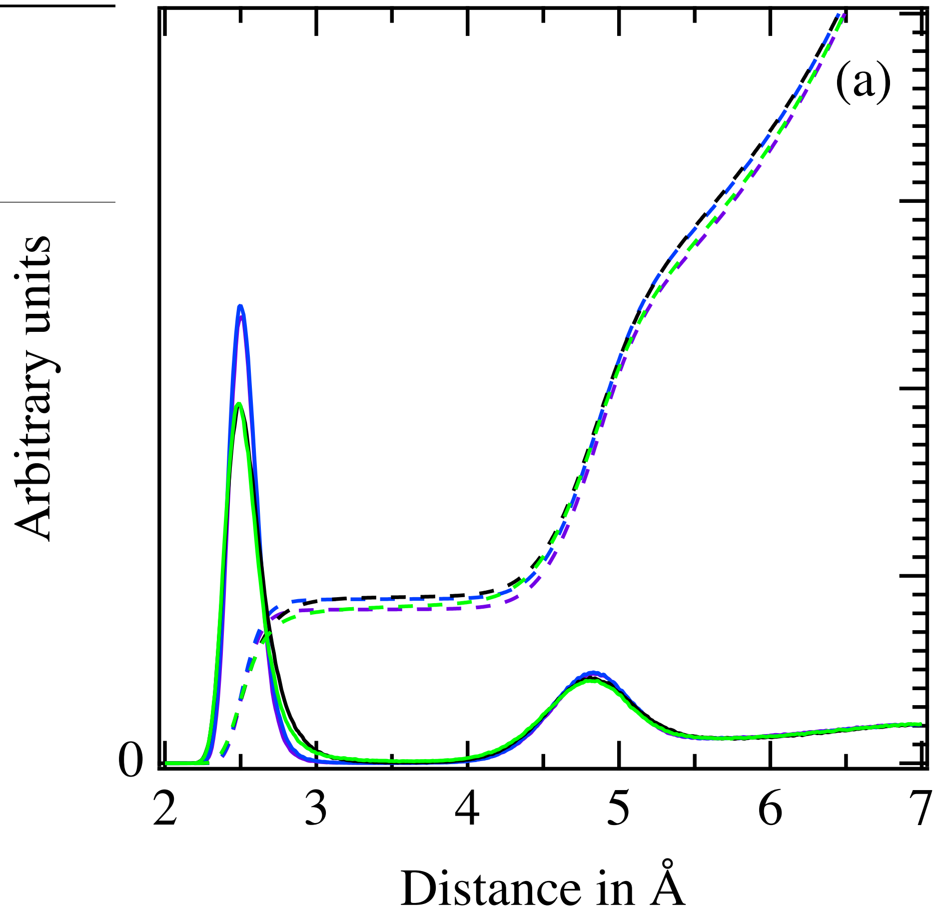
Coordination of Cm(III)

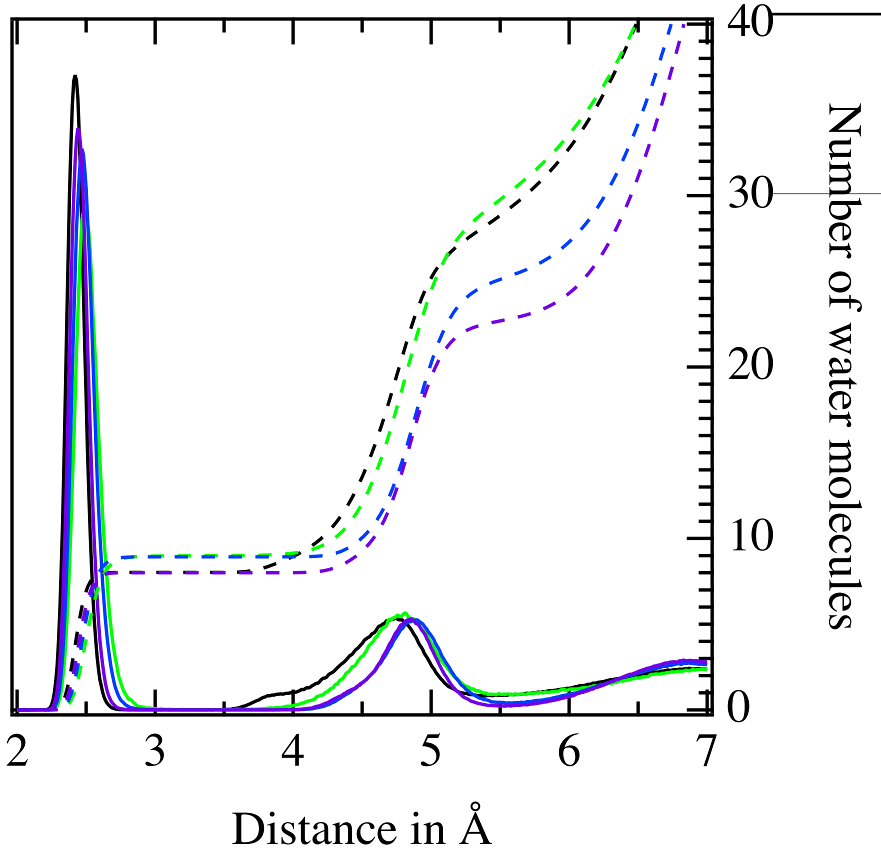
Parameter set	CN	r(Cm-O)	CN_2
M_{nocoop}	9.0	2.41	20.9
M_{dens}	8.9	2.49	19.7
M_{3body}	8.8	2.49	18.8
M_{dens}	8.4	2.49	20.4
M_{3body}	8.2	2.49	20.3
Average MD	8.6 ± 0.3	2.49	19.8 ± 0.6
Average Exp	8-9	2.45-2.48	13(4)



F. Réal et al. accepted to J. Comput. Chem.

Coordination of Th(IV)

Parameter set	CN	r(Cm-O)	CN_2
M_{nocoop}	10.0	2.43	17.5
M_{dens}	8.0	2.42	20.0
M_{3body}	8.0	2.44	14.6
M_{dens}	9.0	2.48	21.2
M_{3body}	9.0	2.47	16.3
Average MD	8.5 ± 0.25	2.45 ± 0.02	18.0 ± 2.0
Average Exp	8-12	2.45-2.51	



F. Réal et al. accepted to J. Comput. Chem.

Temporal properties

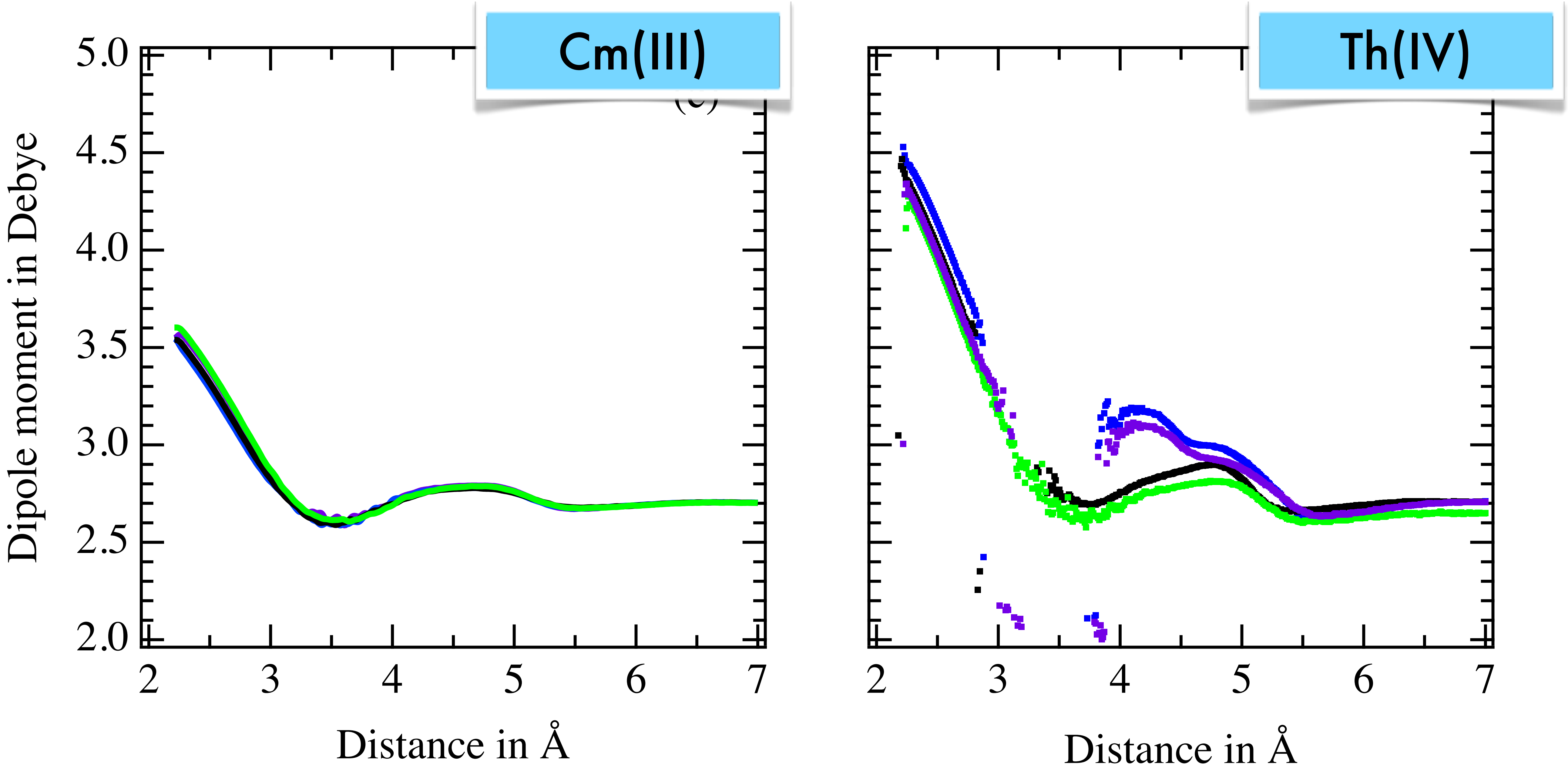
Parameter set	$\underline{M}_{coop}$	$\underline{M}_{3body}$	M_{coop}	M_{3body}	Average	Exp.
Cm(III)						
D_{Cm} (10^{-5} cm^2 s^{-1})	0.59	0.53	0.52	0.58	0.55 ± 0.03	0.6
mrt1 (ps)	140	510	240	670	520 ± 200	830, 940 for Gd(III)
mrt2 (ps)	7.7	8.7	7.5	9.9	8.5 ± 1.1	?
Th(IV)						
D_{Th} (10^{-5} cm^2 s^{-1})	0.70	0.54	0.58	0.59	0.60 ± 0.05	?
mrt1 (ns)	> 10	> 10	> 10	> 10	-	< 20 ns
mrt2 (ps)	17.7	15.6	18.6	29.6	20.5 ± 4.7	?

Atta-Fynn et al. J Phys, Chem A. 2011
For Cm^{3+}:

- AIMD mrt1 = ? not computed due to lack of statistic
- CMD 3b or LJ (no MetOx Bond) ≈ 3ps.

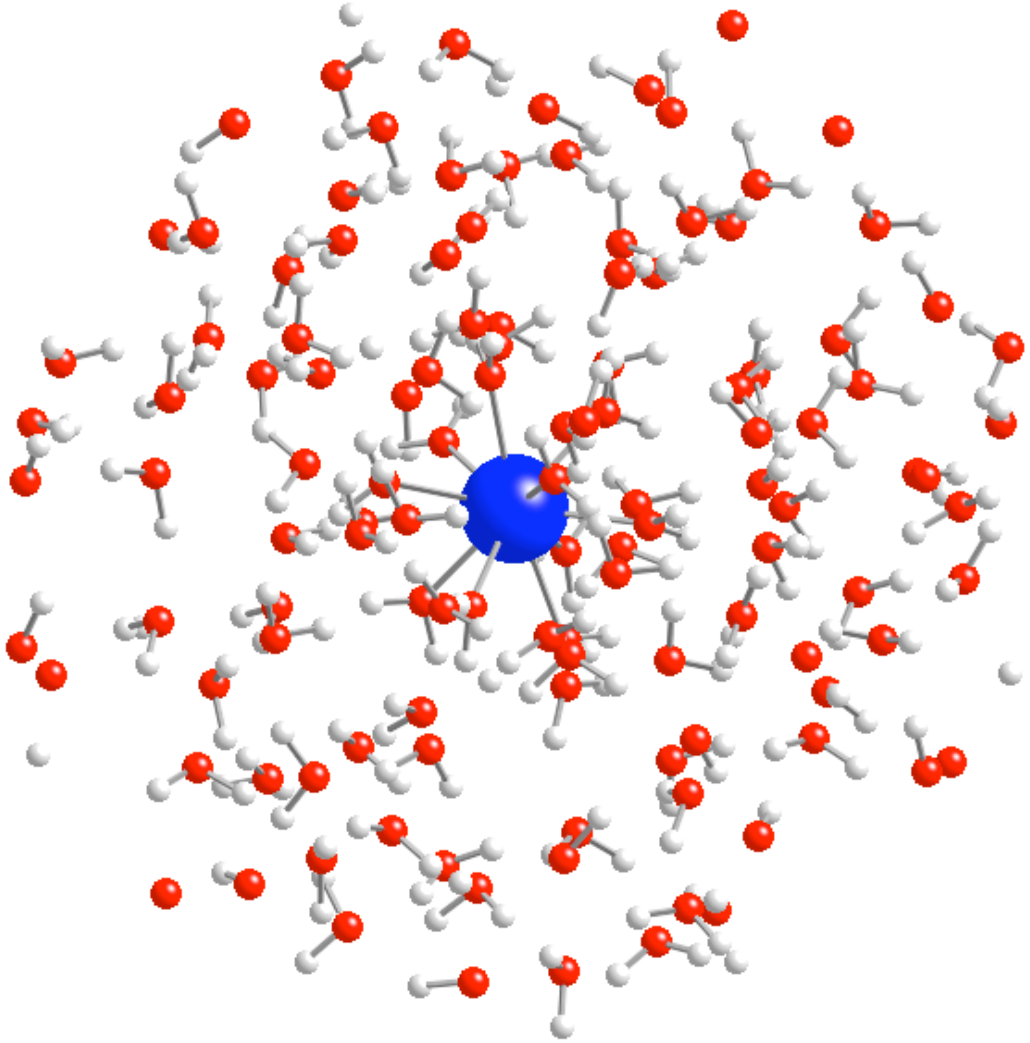
F. Réal et al. accepted to J. Comput. Chem.

Water polarization near the cation

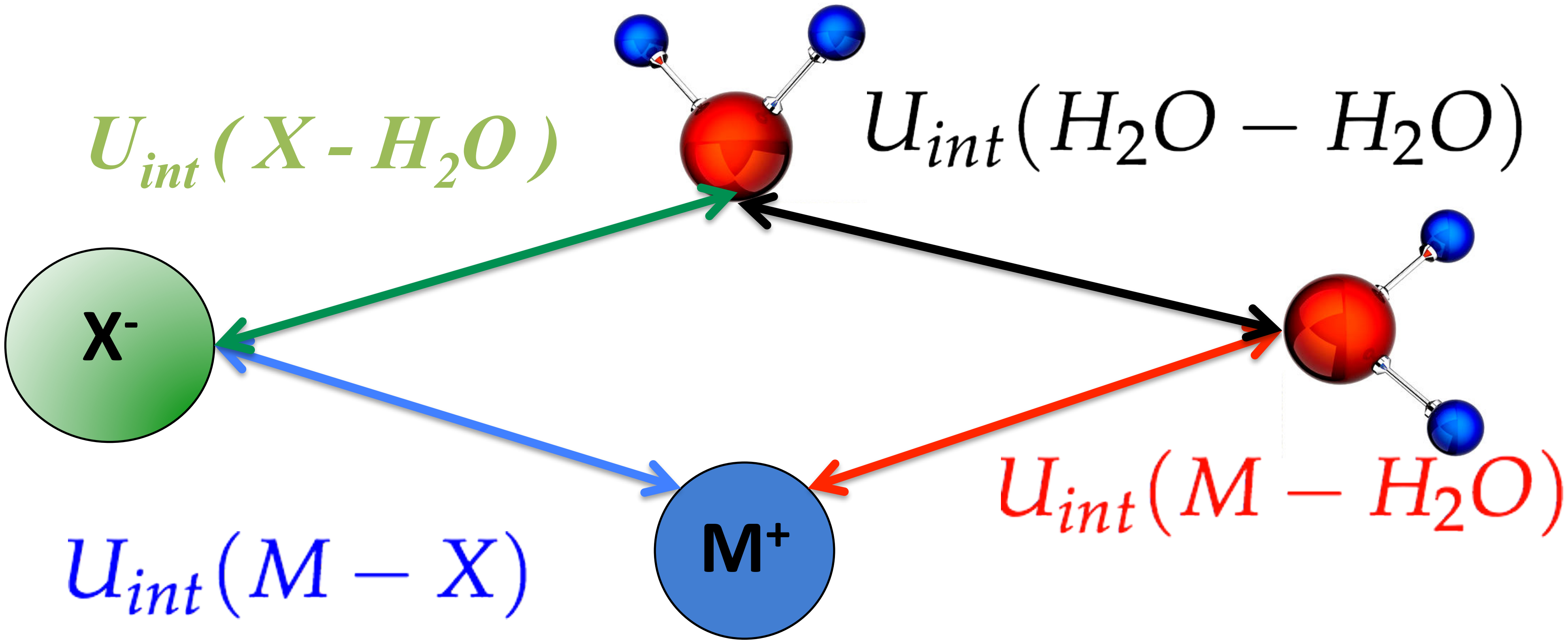


Need for polarizable force fields!

Modeling counter-ions effects(ex: halides)



Modeling counter-ions effects(ex: halides)



$U_{int}(X - H_2O)$

$U_{int}(H_2O - H_2O)$

X^-

M^+

$U_{int}(M - H_2O)$

$U_{int}(M - X)$

Accuracy the of Anion/Water polarisable potentials

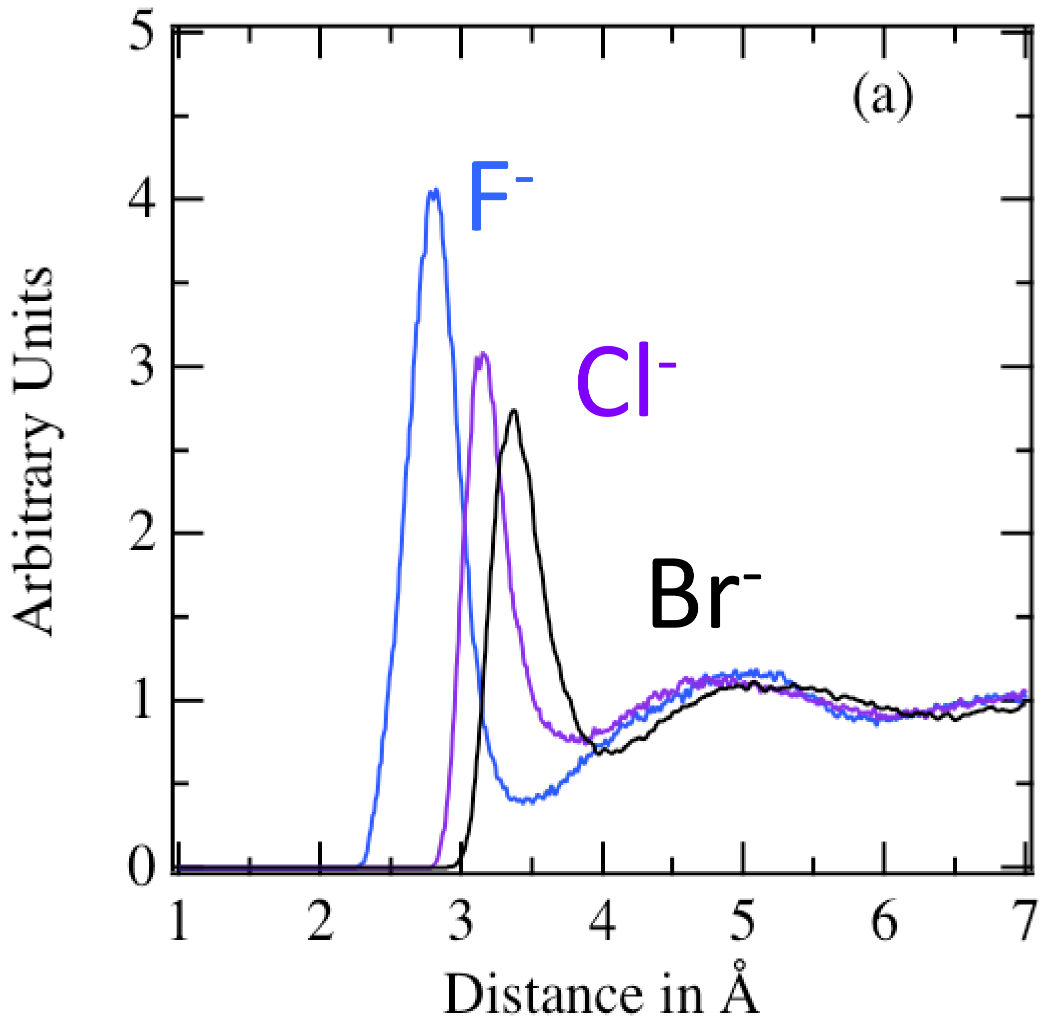
Same procedure for halides: X-H_2O interaction

Enthalpy for gas-phase reactions
$[X(H_2O)_{n-1}]^- + H_2O \rightleftharpoons [X(H_2O)_n]^-$

	F^-			Cl^-			Br^-		
n	QM	MM	exp.	QM	MM	Expt.	QM	MM	Expt.
1	27.9	26.8	23.3	14.4	13.7	13.1/14.7	12.4	12.4	12.6/11.7
2	19.3	20.0	16.6/19.2	12.9	12.5	12.7/13.0	11.9	10.9	12.3/11.6
3	16.9	17.0	13.7/15.3	13.4	12.9	11.7/11.8	13.1	12.8	11.5/11.4
4	13.2	13.2	13.5/13.9	11.3	12.0	11.1/10.6	12.6	12.0	10.9/11.0
5	10.1	9.9	13.2/12.3	7.6	8.5	9.5	8.0	7.9	10.8
6	9.9	8.2	10.9	8.8	5.4	8.8	6.8	7.0	10.3

M. Trumm et al. J. Chem. Phys. **136**, 044509 (2012)

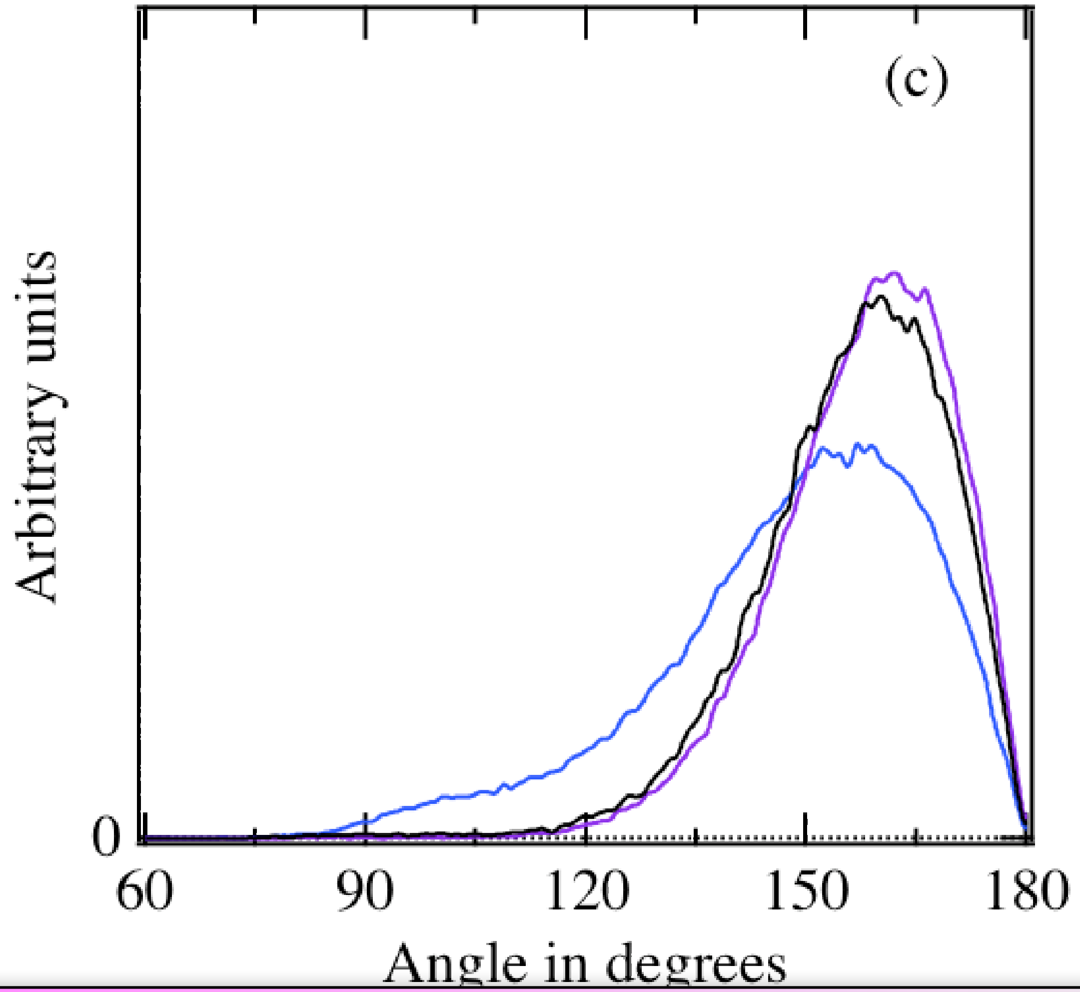
Anion hydration properties



F$^-$ (6.7 water) bidentate HBs

Cl$^-$ (7.0 water) monodentate HBs

Br$^-$ (7.6 water) monodentate HBs



Extend the study to the heavier halides. cf poster.

M. Trumm et al. J. Chem. Phys. **136**, 044509 (2012)

D. Laage and J. T. Hynes, J. Phys. Chem. B 112, 7697 (2008)

Accuracy the of Anion/Water polarisable potentials

Differences in free hydration energies kcal/mol

	MD	Exp
F^- to Cl^-	31.0	29-30
Cl^- to Br^-	9.5 ± 0.5	6 and 9

→ accurate modelling!!!

water time	MD	simulations
F^-	28.1 ps	
Cl^-	11.8 ps	6 ps
Br^-	10.4 ps	

M. Trumm et al. J. Chem. Phys. **136**, 044509 (2012)
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- Strong influence of second-shell Bromide counter ions
  - We need to understand how Br influence the hydration shell around the anion

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