DISTINCTIVE – Theme 3 Meeting

Computational investigations of the interaction of brucite surfaces with uranium and its fission products

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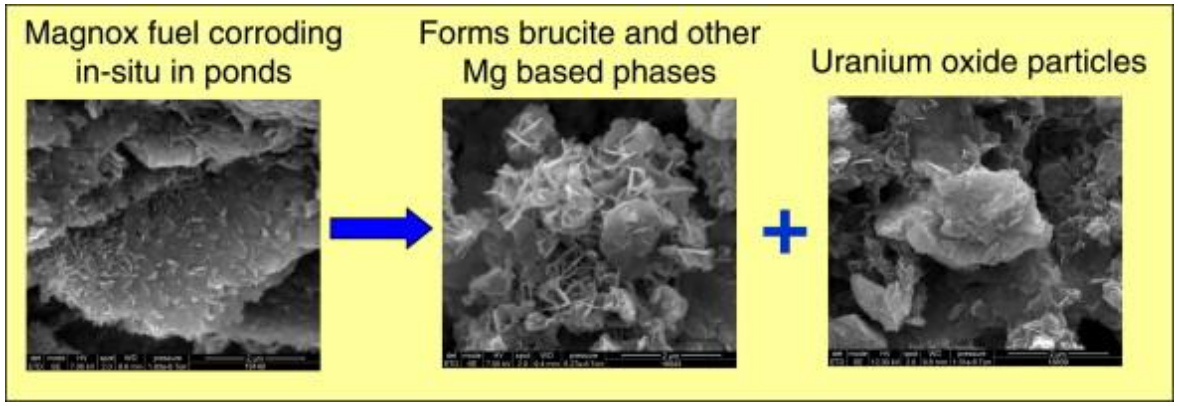
industrial supervisor: Dr Jonathan Austin

First generation British nuclear power reactors used Magnox as fuel cladding

- In the nuclear waste:
  - Highly reactive hydrated brucite ($Mg(OH)_2$ [0001])
  - Uranium oxide particles
  - UO_2^{2+} and its fission products in solution (Sr^{90}, I^{131}, Cs^{137}, Ba^{140})

Oldbury MAGNOX fuel element in graphite brick.
(Photo Credit: Prof. B Marsden, University of Manchester, NGRG)

First generation Magnox storage ponds
Sellafield Ltd. (http://www.sellafieldsites.com)



C.R. Gregson *et al. Journal of Nuclear Materials* **412** (2011) 145–156

1. OBJECTIVES

INITIAL OBJECTIVE:

Studying the interaction between the solvated UO_2^{2+}, Sr^{2+} and Cs^{+} ions and the hydrated brucite surface with quantum chemical methods

ACHIEVED OBJECTIVES:

Studied the hydrolysis of Sr^{2+} in aqueous phase

Using a combined model of explicit and implicit solvent, investigated the Sr^{2+} hydroxide complexes in water

Created a representation for the brucite ($Mg(OH)_2$) surface with an electrostatic embedded cluster method

Using Turbomole code and the implemented PEEC method, I created an embedded cluster of $Mg(OH)_2$

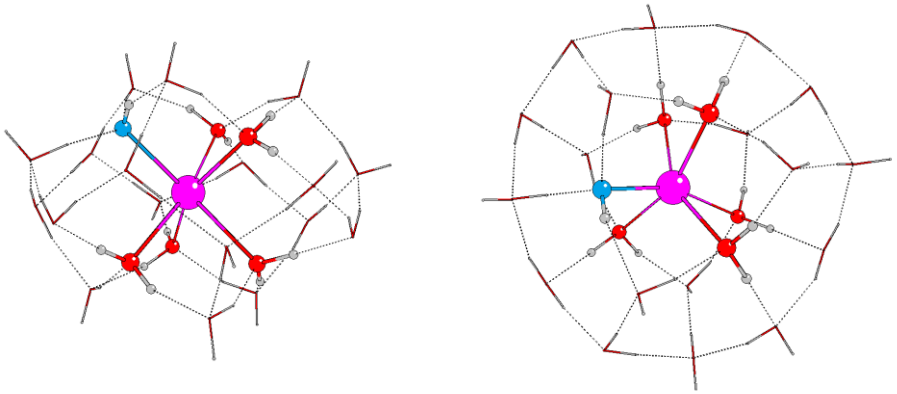
Used single ion adsorption and substitution to benchmark the reliability of the surface

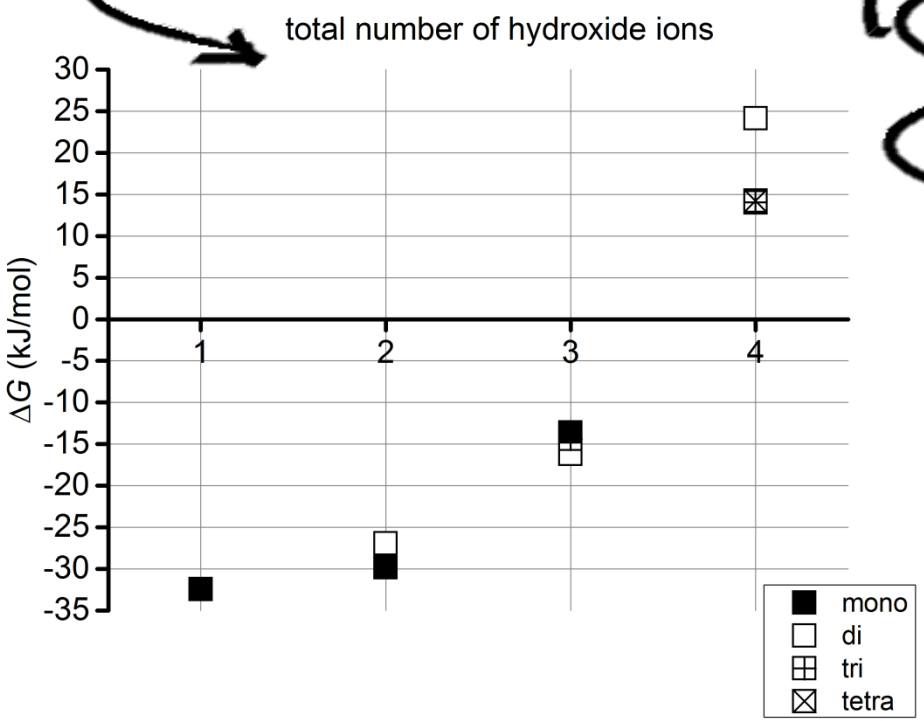
FUTURE OBJECTIVES:

Investigate the effects of the adsorbed Sr^{2+} complexes on the reactivity of the surface

Combined solvation model:

- 6.5 Turbomole code, DFT calculations
- TPSS/def2-TZVP (def2-ecp for Sr)
- COSMO continuum solvent model
- 2 explicit solvation shells





We are able to describe:

Relative stability of hydroxide complexes

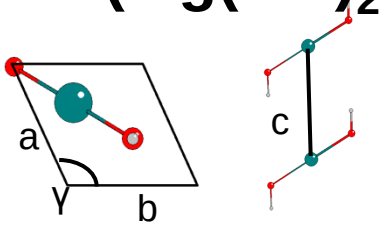
- Proton transfer mechanism

Sr^{2+} complex	ΔE_{SCF} (kJ/mol)	ΔG (kJ/mol)
Dihydroxide	0.0	0.0
Transition State	1.6	3.0
Monohydroxide	-3.0	-2.5

E. Makkos, A. Kerridge, N. Kaltsoyannis, *Dalton Trans.* **44** (2015) 11572

Representation of the brucite ($Mg(OH)_2$ [0001]) surface

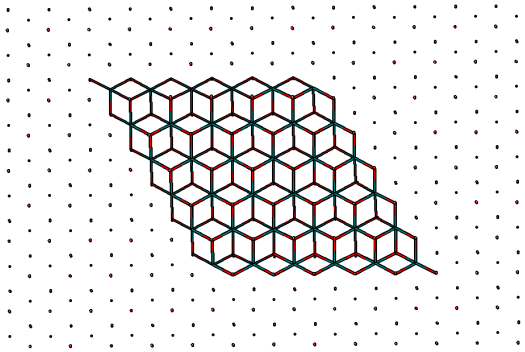
Hexagonal unit cell parameters
a=3.15 Å, b=3.15 Å, c=4.77 Å, α,β=90°, γ=120°



Periodic electrostatic embedded cluster method (PEECM)

- Finite sized (6x6 Mg) cluster
→ Quantum mechanically (QM) treated
- Infinite array of point charges (PC)
→ Representing the long-range electrostatic interactions

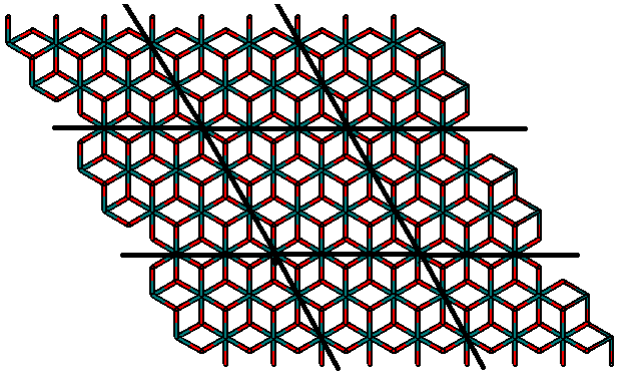
Turbomole code



Periodic DFT method

- Finite sized unit cell
- Repeated infinitely using symmetry operations
→ Whole system QM treated

Crystal code

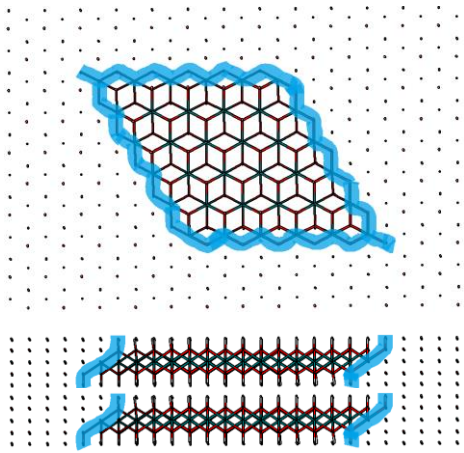


Representation of the brucite ($Mg(OH)_2$ [0001]) surface

PEECM

•**Advantages**
-The defects are isolated
-Charged systems can be studied
-Higher quality basis sets can be used

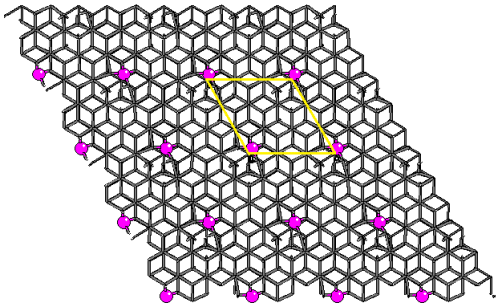
•**Disadvantages**
-Fixed boundary atoms, lot of constraints
-Limited size of the QM region
-Possible polarisation of the cluster



Periodic DFT method

•**Advantages**
-All atoms can relax
-Relatively easy to increase slab size in *z* direction
-Everything is QM treated

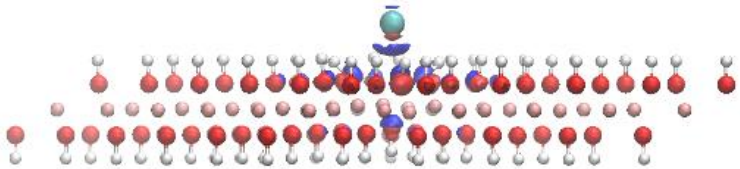
•**Disadvantages**
-Not completely isolated
-Studying charged systems is very difficult
-Limitation on the basis sets



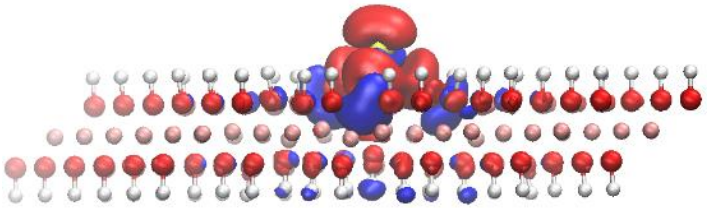
Single ion adsorption with PEECM

Studied system		Adsorption energy (kJ/mol)		Relative E_{ad} (kJ/mol)	
		def2-SVP	def2-TZVP	def2-SVP	def2-TZVP
Na^+	single	-131.0	-249.7	0.0	0.0
	ex2	-123.6	-212.1	7.4	37.6
Rb^+	single	-144.7	-112.7	0.0	0.0
	ex2	-135.1	-76.1	9.6	36.6
Cs^+	single	-118.0	-94.5	0.0	0.0
	ex2	-108.4	-57.9	9.7	36.6
Mg^{2+}	single	-1182.7	-1319.6	0.0	0.0
	ex2	-1199.2	-1272.5	-16.5	47.1
Sr^{2+}	single	-890.9	-835.4	0.0	0.0
	ex2	-896.9	-780.5	-5.9	54.9
Ba^{2+}	single	-717.9	-730.1	0.0	0.0
	ex2	-723.5	-674.1	-5.5	55.9

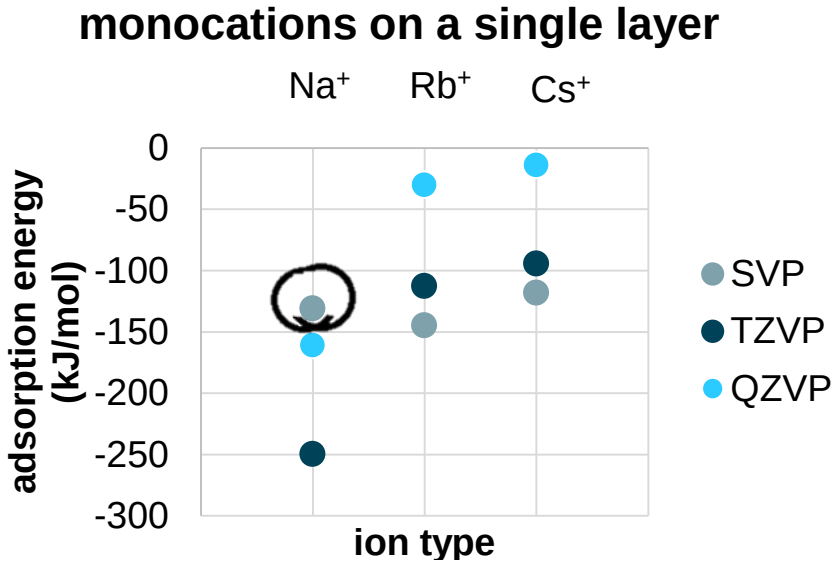
Cs^+

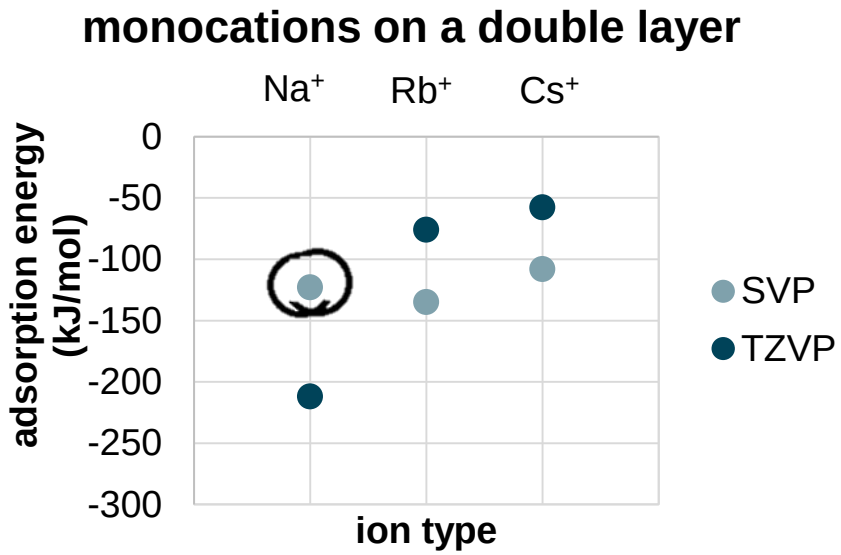


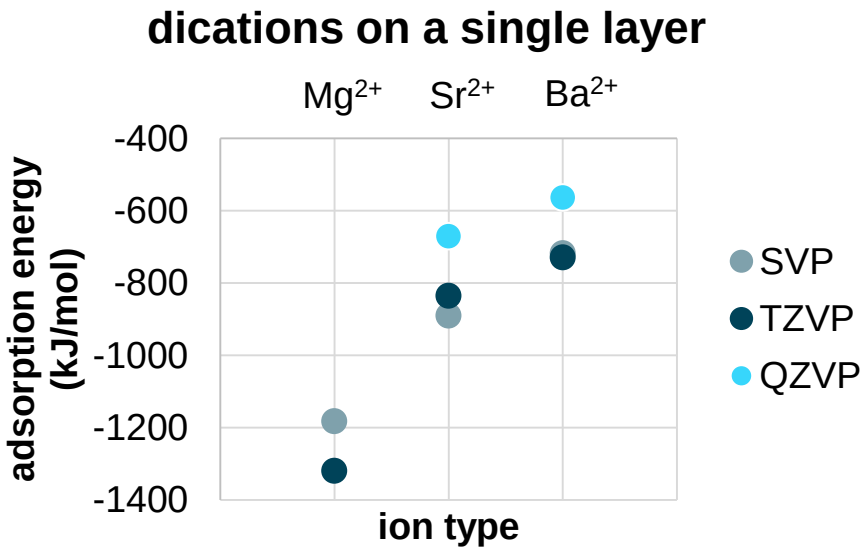
Sr^{2+}

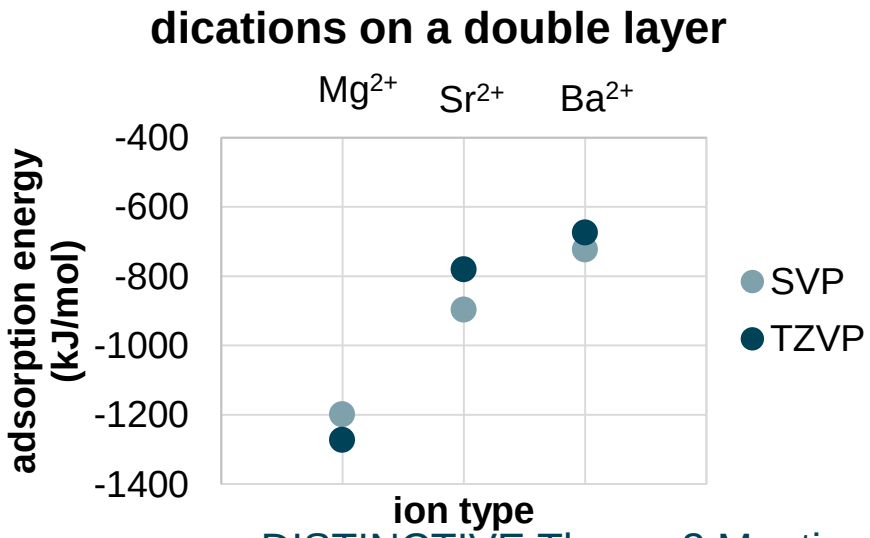


Basis set comparison









Benchmarking with substitution studies

Questions:

-Are there enough layers in the system?

-Is the QM cluster big enough?

-Are the results comparable between the two methods?

(similar geometries and energy differences)

Substitution is good for benchmarking:

-Single ion substitution has only one stable coordination

-The overall system is neutral

-used Be^{2+} Ca^{2+} and Sr^{2+} for benchmarking

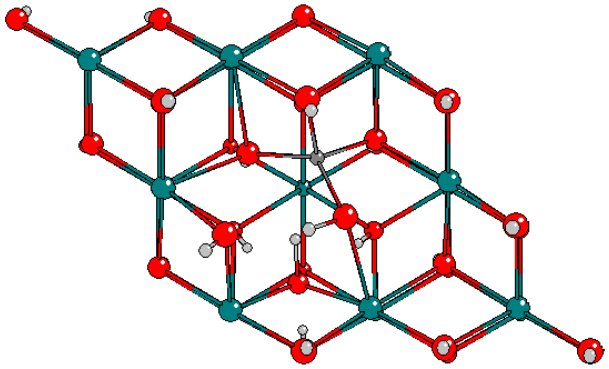
-Because the ionic radius of the chosen alkaline earth metals are in the following order:

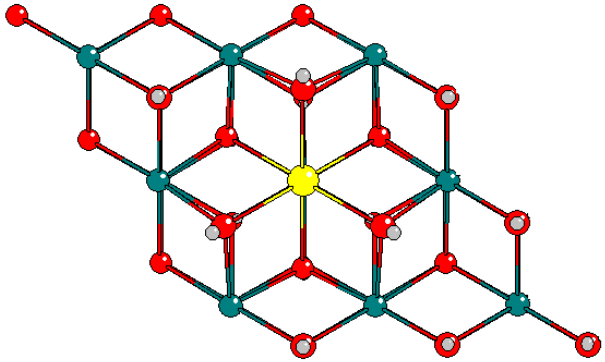
$$\mathbf{Be^{2+} < Mg^{2+} < Ca^{2+} < Sr^{2+}}$$

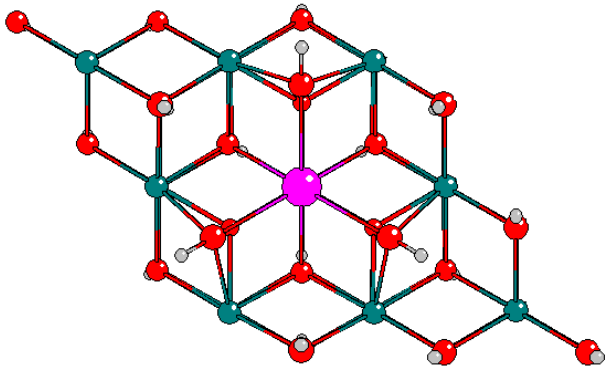
Benchmarking with substitution studies

Turbomole vs Crystal, PBE/TZVP* functional basis set

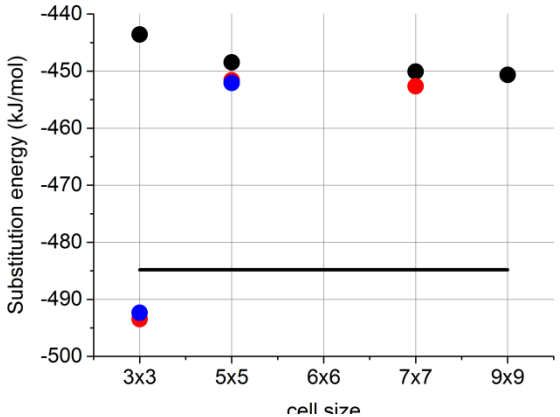
6x6 cluster for PEECM, 3x3, 5x5, 7x7 and 9x9 cell size for periodic DFT



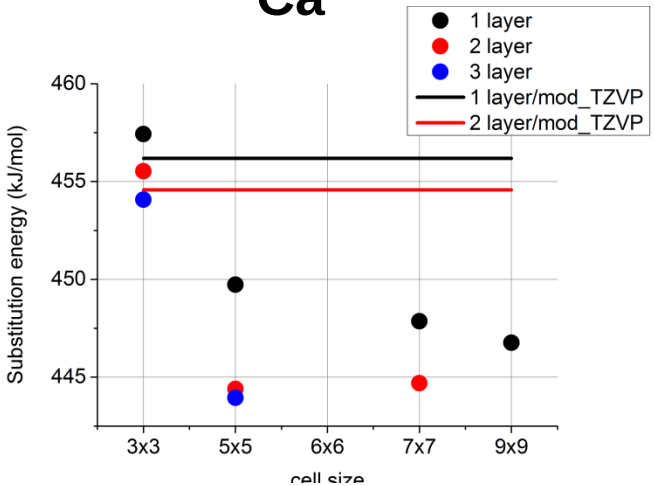




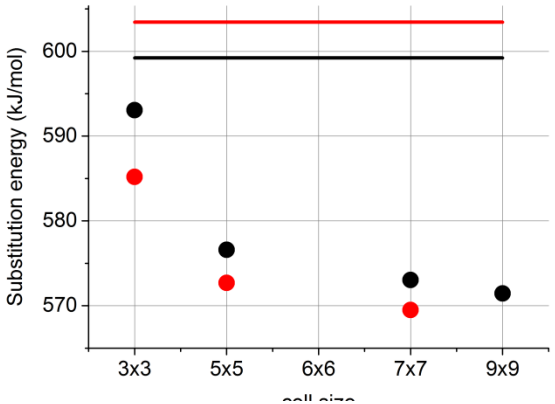
Be^{2+}



Ca^{2+}



Sr^{2+}



Benchmarking with substitution studies

-Including a third layer has only a small effect on the substitution energy

-The difference between 5x5 and 7x7 results is small for each case

-What about comparing the two methods?

(PBE/TZVP*)

1 layer		Be^{2+}		Ca^{2+}		Sr^{2+}	
Crystal	9x9	-450.7	%	446.8	%	571.5	%
Turbomole	Isolated	-484.8	(7.6)	456.2	(2.1)	599.2	(4.9)

2 layers		Be^{2+}		Ca^{2+}		Sr^{2+}	
Crystal	7x7+7x7	-452.7	%	444.7	%	569.5	%
Turbomole	Isolated			454.6	(1.7)	603.4	(5.6)

6. SUMMARY AND FUTURE PLANS

Conclusions:

Although the PEECM approach contains a lot a constraints, it is good enough to capture the important properties of the studied interactions:

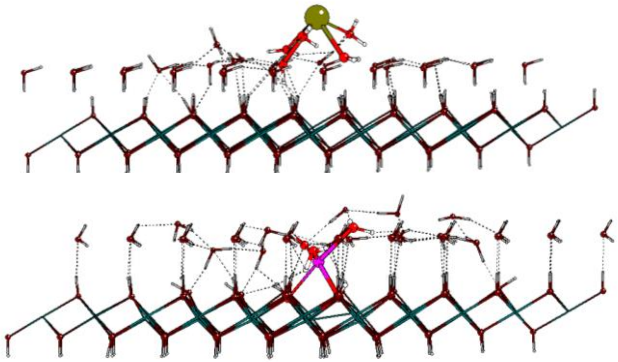
•We get the expected energy trends for the studied series of ions

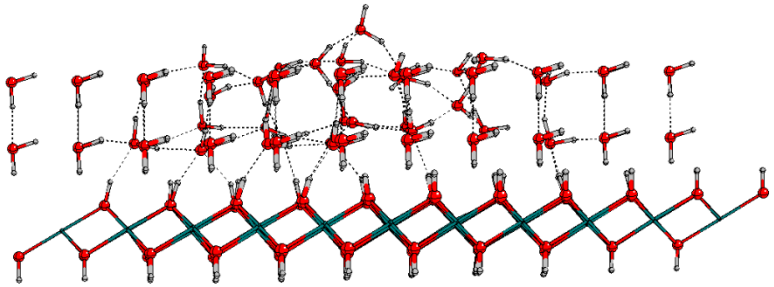
•The cluster contains the atoms which are affected by the interaction

Future plans:

•Adsorption of $Sr(OH)_2$ complexes with both methods

•Ion adsorption on a hydrated surface





Thank you for your kind attention!

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2. SOLVATION MODELS

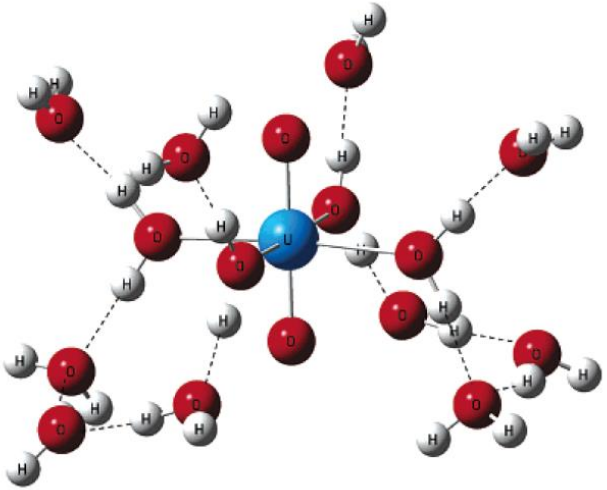
Explicit solvation model

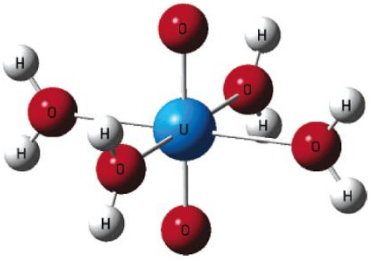
- Short-range interactions
  - Hydrogen bonds
  - Van der Waals interaction
  - Charge transfer effects
  - Solvent-solute dynamics
  - Hydrophobic effects

Implicit solvation model

- Long-range interactions
  - Polarisation
  - Dipole orientation

- Homogeneous polarisable medium
- Molecular shaped cavity





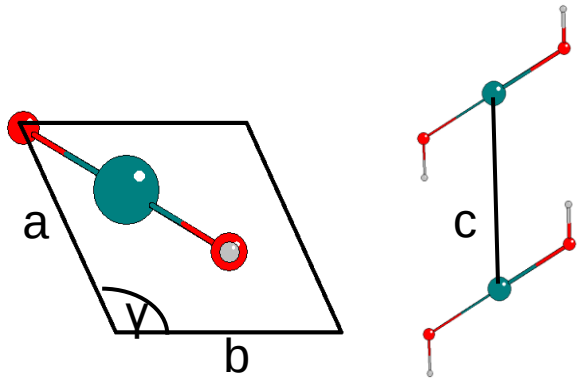
K. E. Gutowski and D. A. Dixon *J. Phys. Chem. A 110 (2006) 8840-8856*

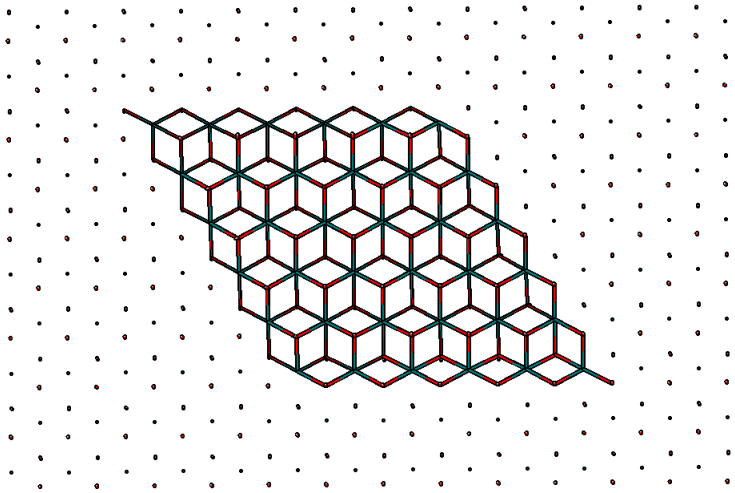
Representation of the brucite ($Mg(OH)_2$ [0001]) surface

Periodic embedded cluster method
Hexagonal unit cell
6x6 Mg sized cluster
fixed boundary atoms
TPSS/def2-SVP

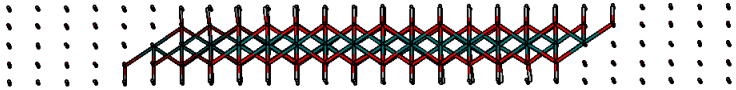
Point charges (PC) calculated
with Natural Population Analysis (NPA)

a=3.15 Å, b=3.15 Å, c=4.77 Å
α,β=90°, γ=120°

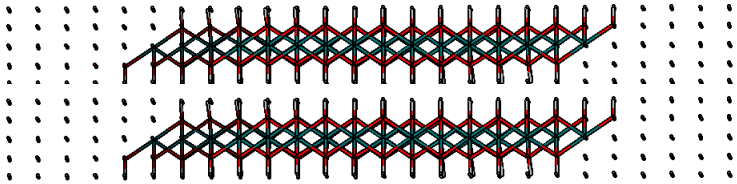




Single layer



Double layer



Single ion adsorption

Mono cations

Na^+

Rb^+

Cs^+

Di cations

Mg^{2+}

Sr^{2+}

Ba^{2+}

Different quality basis sets

Studied system		Adsorption energy (kJ/mol)	
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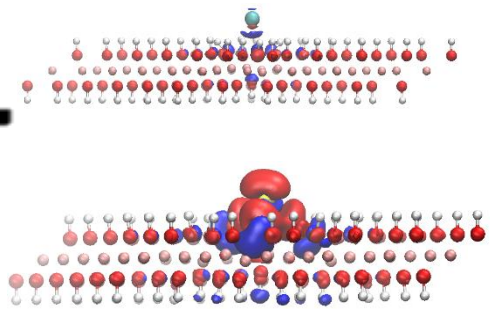

$$E_{adsorption} = E_{complex} - (E_{surface} + E_{ion})$$