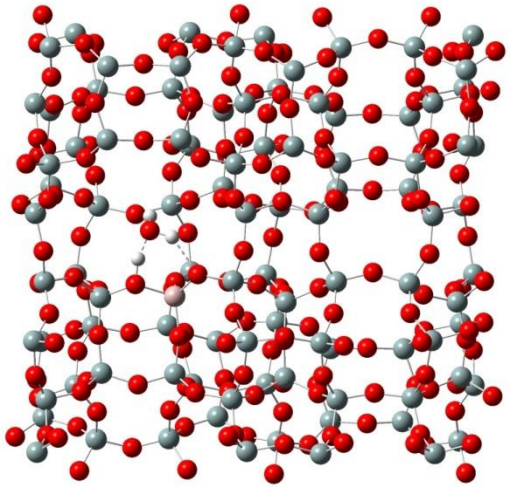
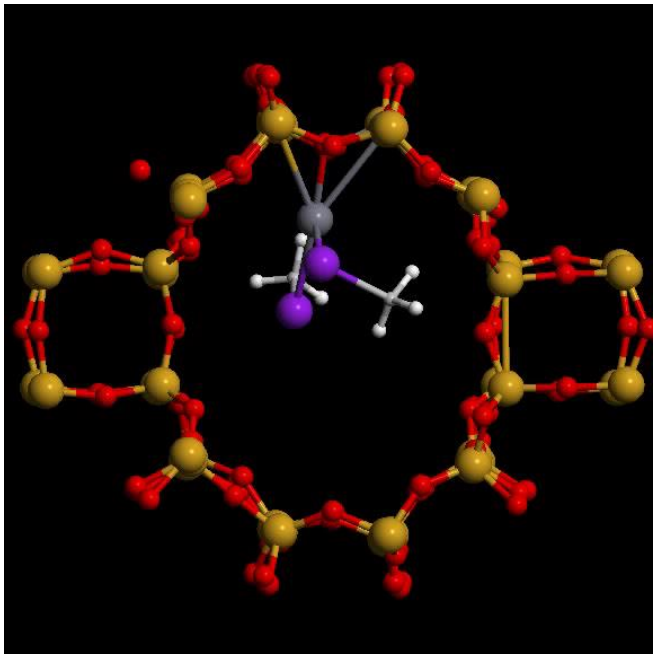
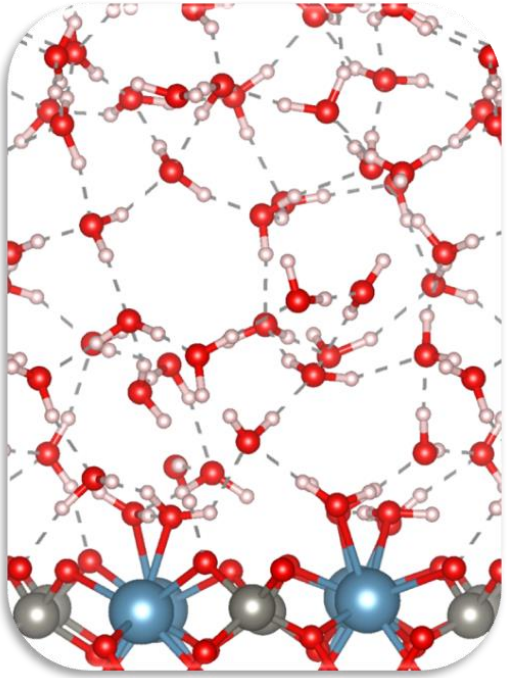
michael.badawi@univ-lorraine.fr

Ecole de l'Association Française de l'Adsorption
Modélisation à l'échelle moléculaire







Michaël Badawi

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Mercredi 26 Février 2022

Introduction

Introduction

Molecular Modeling is useful for what ?

Compute energy of a system (guest+host)

Structure	Thermodynamics	Dynamics
- Geometry - Stability under operating conditions -Frequency ➔ IR, Raman, RMN	- Nature of adsorption sites - Adsorption enthalpies -Adsorption capacities	- Diffusions, collisions

Better understanding of the adsorption system

Molecular Modeling

Quantum mechanical simulations (DFT)

$$\hat{H}_T \varphi(\vec{r}) = E\varphi(\vec{r})$$

$$E[\rho] = T[\rho] + J[\rho] + E_{ncl}[\rho] + \int V_{ne}(\vec{r})\rho(\vec{r})d\vec{r}$$

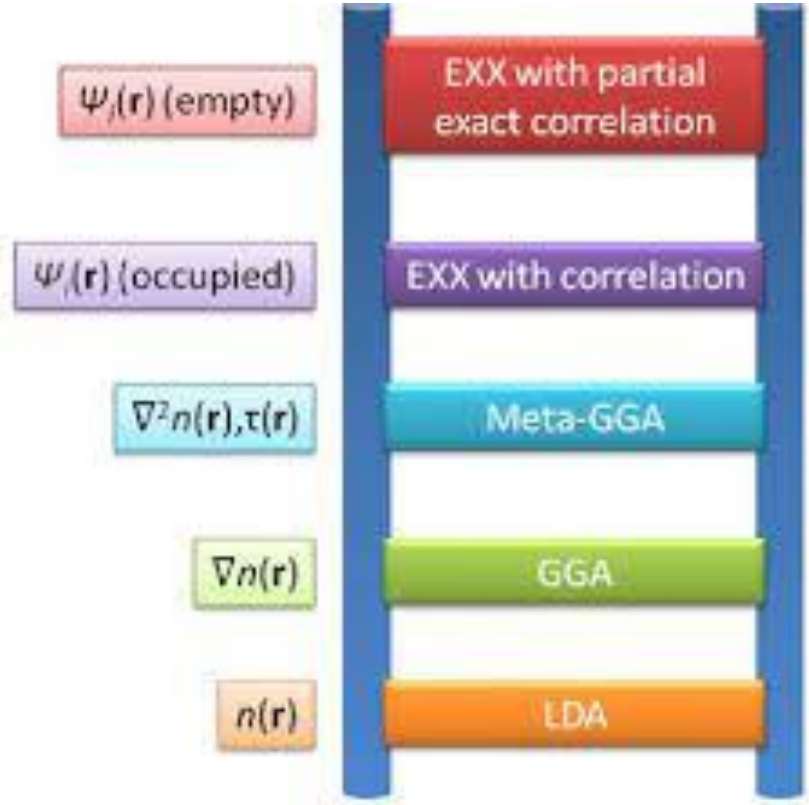
⇨ **Density Functional Theory (DFT)**

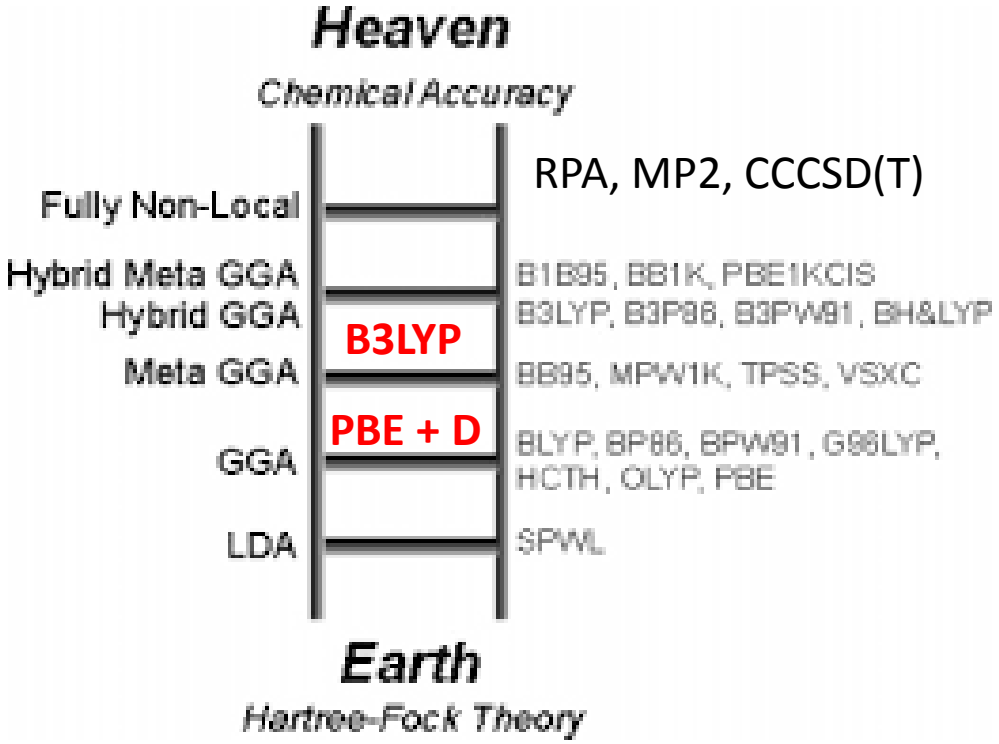
- No parameter (*ab initio*)
- Very good agreement with high precision experiments
- Up to 2000 atoms and 50 A^3 cells
- >15 000 papers including DFT published each year

Molecular Modeling

Quantum mechanical simulations (DFT)

Jacob's Ladder

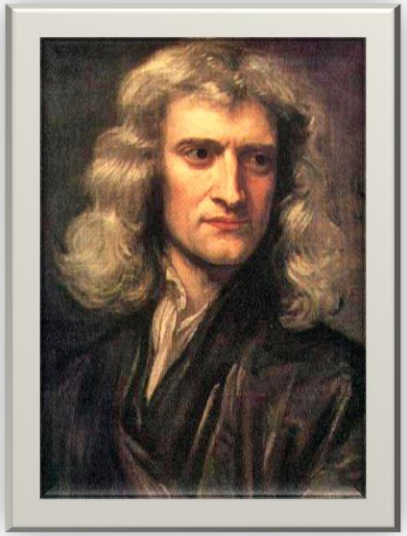




Molecular Modeling

Molecular dynamics simulations

$$m_i \frac{d^2 r_i}{dt^2} = f_i = -\frac{\partial}{\partial r_i} U(r_1, r_2, \ldots, r_n)$$

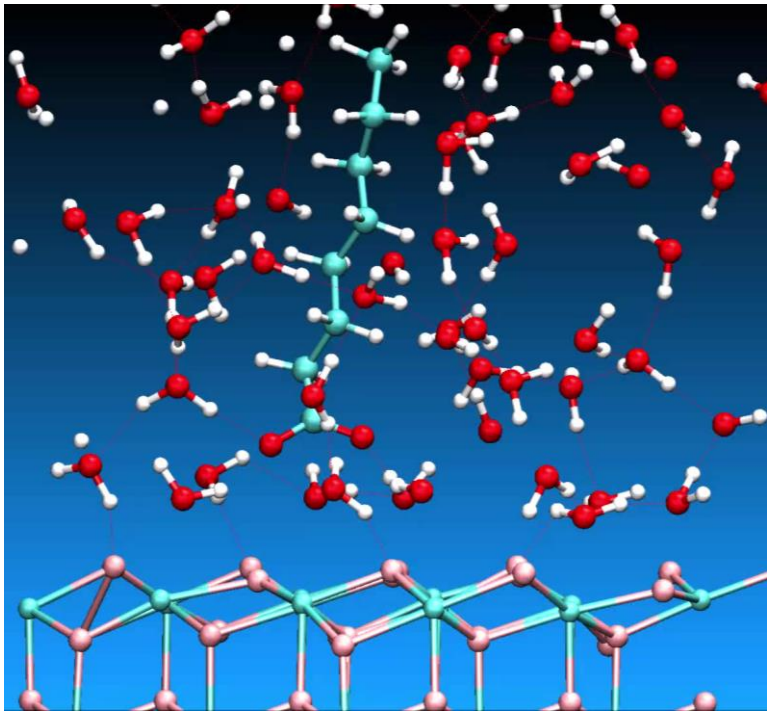


- N (number of particles), V (volume of the cell) constant
- E (energy), T (temperature), or P (pressure) can be kept constant
- Common time step: 1 fs (10^{-15} s)
- F_i (external forces) are calculated by means of:
  - Force fields, called « Classical Molecular Dynamics »
  - DFT, called « Ab Initio Molecular Dynamics »

Molecular Modeling

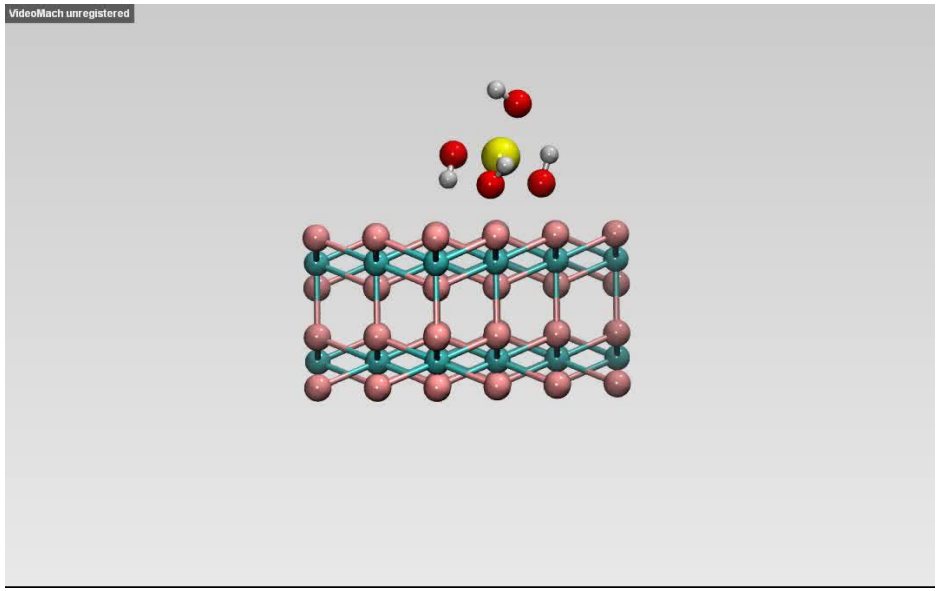
Ab initio molecular dynamics (AIMD) simulations

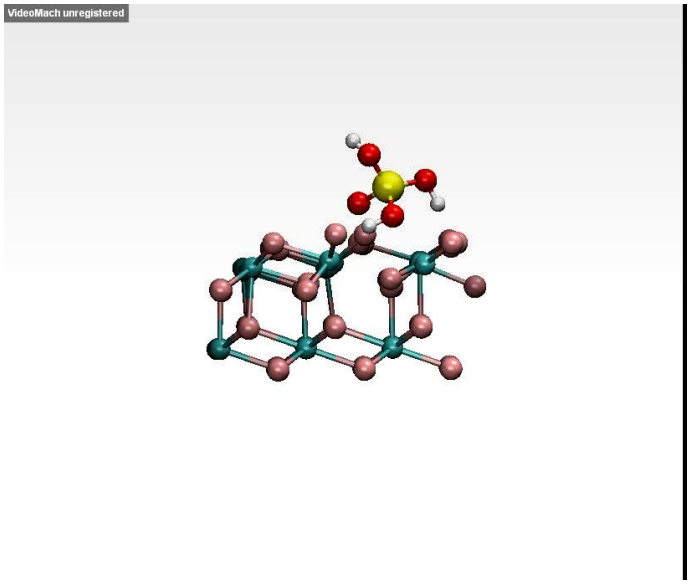
- At each time step, forces are calculated by DFT
- Associates the high precision of DFT and the temperature/pressure control of MD
- One of the most powerful method for energy and structure determination
- Allows to consider reactivity (bond creation/breakage)
- **Up to 100 ps and 500 atoms in the cells**
- Requires high performance computers



Molecular Modeling

Static DFT relaxation *vs* *MD simulation*





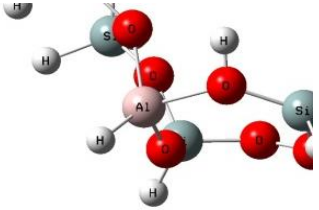
- From a guess, the energy and forces of the system are minimized to reach a minima of the Potential Energy Surface (PES)
- Only the final geometry has a physical meaning
- T = 0 K

- Propagation of a trajectory
- After equilibration period, all steps have a physical meaning
- T = 300 K (can be set to any T)

Molecular simulation techniques

Static	**Statistic**	**Dynamic**	
DFT	**MC**	**CMD**	**AIMD**
Density Functional Theory	Monte Carlo	Classical Molecular Dynamics	Ab initio Molecular Dynamics
Quantum mechanics *ab initio*	Classical mechanics Forcefields	Classical mechanics Forcefields	Quantum mechanics *ab initio*
Interaction energy at 0 K Low coverage Potential reactivity	Adsorption capacity High coverage	CMD Diffusion coefficients	AIMD Adsorption enthalpy at finite T

One short example on system sizing



- Zeolite = microporous aluminosilicate

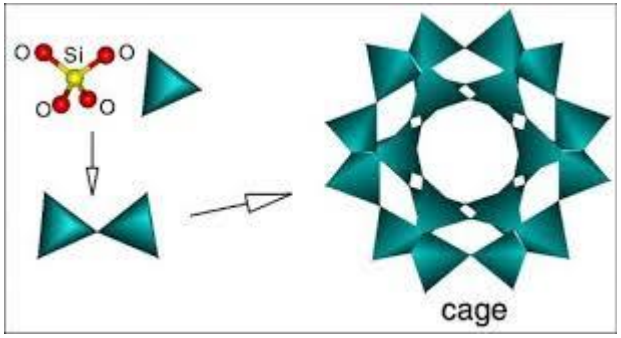
  $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedrons linked by O atoms

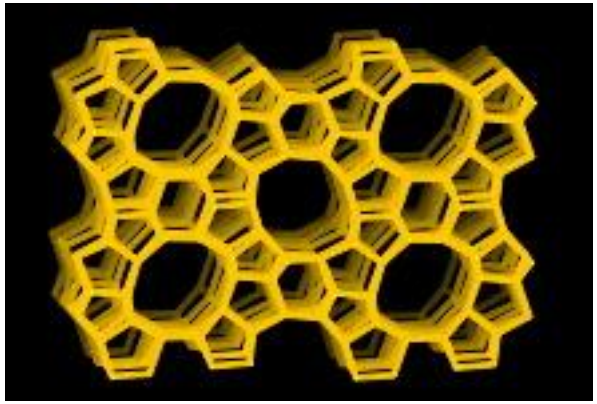
  Al insertion => negative charge compensated by cation incorporation

- Zeolites attractive for many applications:

  - thermal / mechanical stabilities

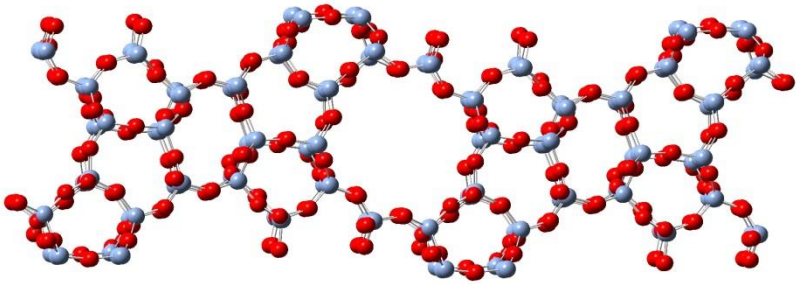
  - tunable properties (structure, cation, Si/Al ratio)



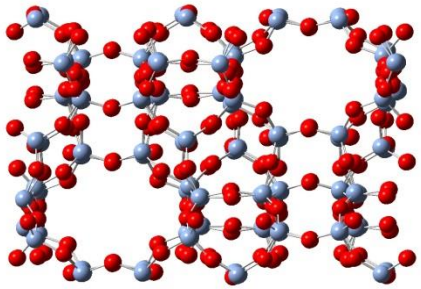


ZSM-5 structure

- ZSM-5 mainly used in automotive depollution processes
- Network of interconnected sinusoidal and straight channels
- Preferential adsorption at the channels intersection



ZSM-5 : 576 atoms unit cell to visualize a straight channel



ZSM5 : The same unit cell view of another angle (2 sinusoidal channels)

- Periodic model would be the most suitable : but unit cell too big, requires too large amount of CPU time

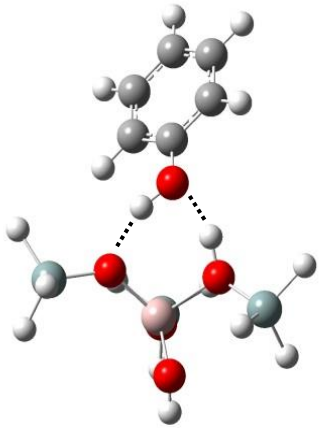
Zeolite models

Cluster model

+ User friendly
- Limited size of system (50 atoms max)
- Pb termination of the cluster

Package : Gaussian, Orca, Turbomole …

Al : pink
Si : blue
C : gray
O : red
H : white

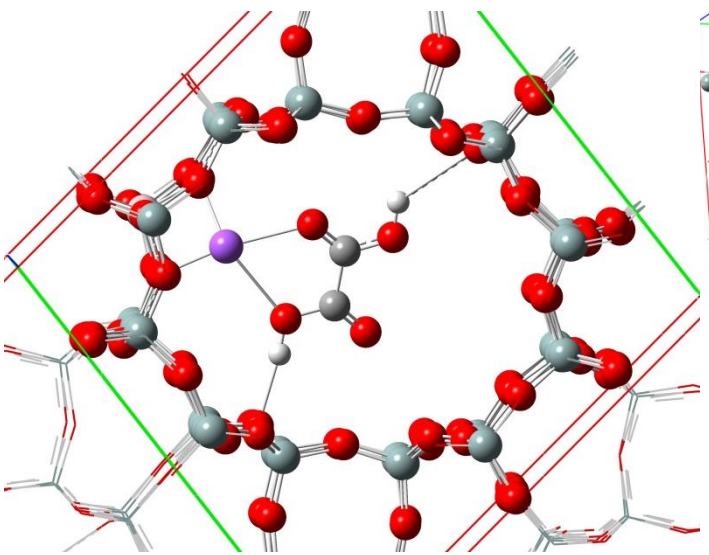


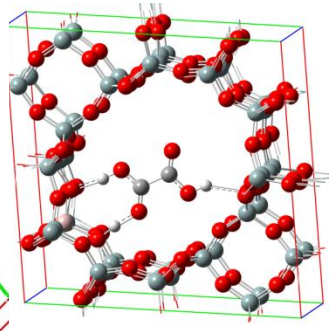
Cluster – Phenol adsorbed over a Brönsted Site- can represent any B sites of large pores zeolites(HY)

Periodic model

+ Treatment of biggers systems (up to 300 atoms)
- Less data accessible (bond order)

Package : VASP, CP2K, Quantum Espresso …0



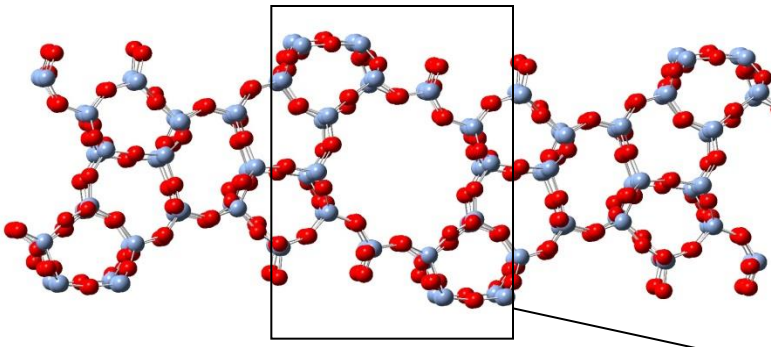


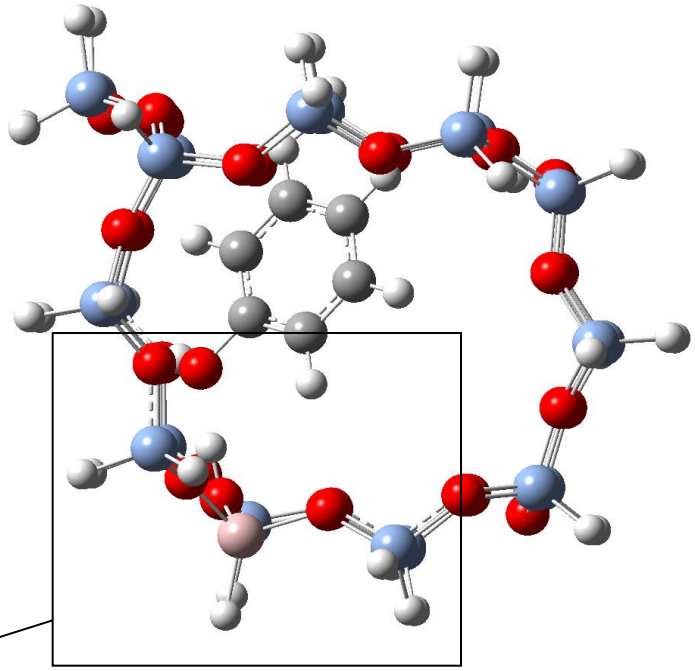
Mordenite : 144 atoms unit cell

Building of the model

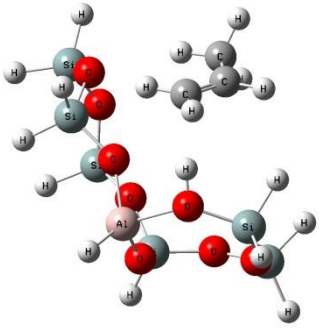
Periodic model

Large cluster model





Small cluster model



- Compromise : model size vs CPU time

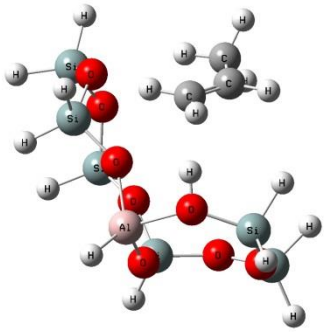
van Santen et al , J Phys Chem. C 113 (2009) 15307
I. Graça, J.M. Lopes, M.F. Ribeiro, M. Badawi, S. Laforge, P. Magnoux, F.R. Ribeiro, Fuel 94 (2012)

Computational methods for pre-screening

- DFT calculations (Gaussian 03)
  - Hybrid functionnal B3LYP,
  - atomic orbitals basis set 6-31g(d,p) for H, C, O, Al, Si, …
  - Stuttgart RSC 1997 basis set containing effective core potentials for transition metals
  - Spin multiplicity checked : lowest energy chosen

- Adsorption energy : $\Delta E_{ads} = E_{cluster+adsorbed\ molecule} - E_{cluster} - E_{molecule\ in\ gas\ phase}$ computed at 0 K : only useful for comparisons, try to give some clues
- Small 7T cluster

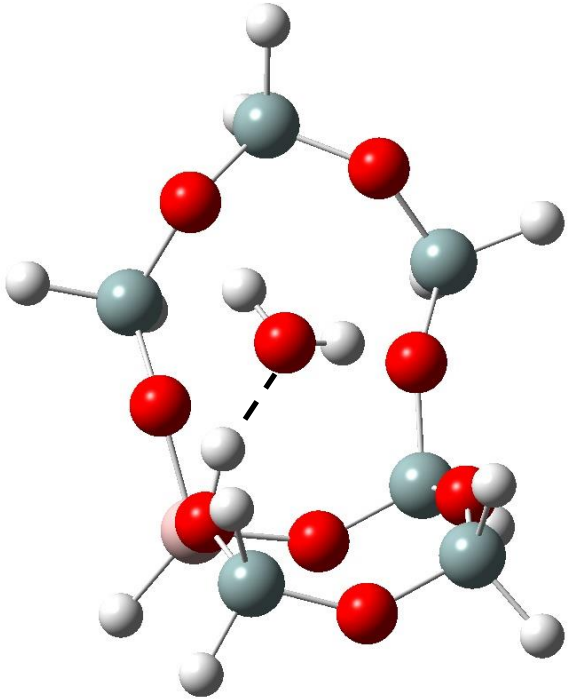
Al : pink
Si : blue
C : gray
O : red
H : white



Adsorption modes

- **Water** over small cluster :

Hydrogen bond between the O atom of water and the proton



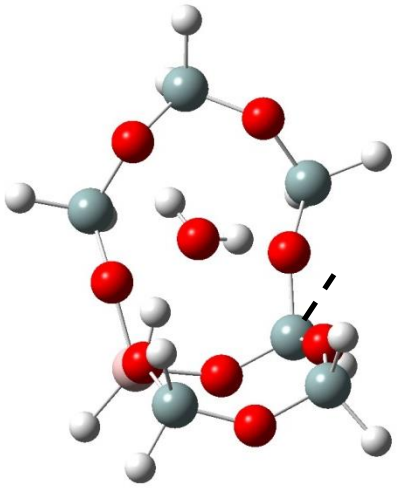
ΔE_{ads} = -66 kJ/mol

Al : pink
Si : blue
C : gray
O : red
H : white

Distance (Å)		
O_{mol}-$H_{structure}$	O_{struc}-H_{struc}	O_{mol}-H_{mol}
1.67	1.02	0.97

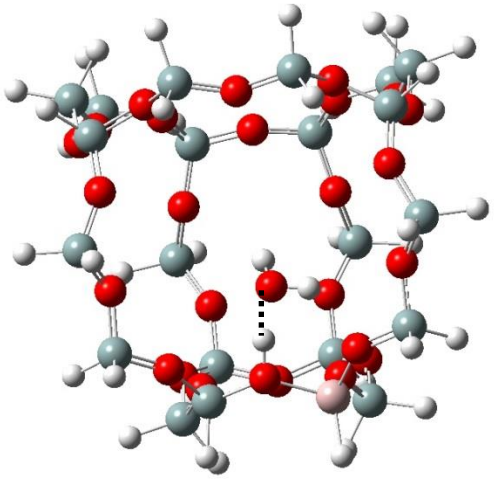
Water adsorption modes

– Small cluster (B3LYP) -Large cluster -Periodic model (PBE+D)



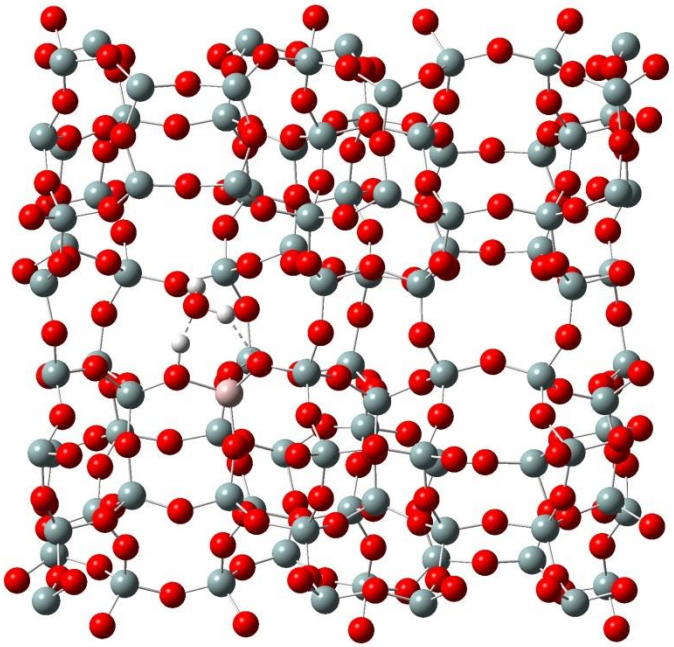
ΔE_{ads} = -66 kJ/mol

1 hydrogen bond (1,67 Å)



ΔE_{ads} = -93 kJ/mol

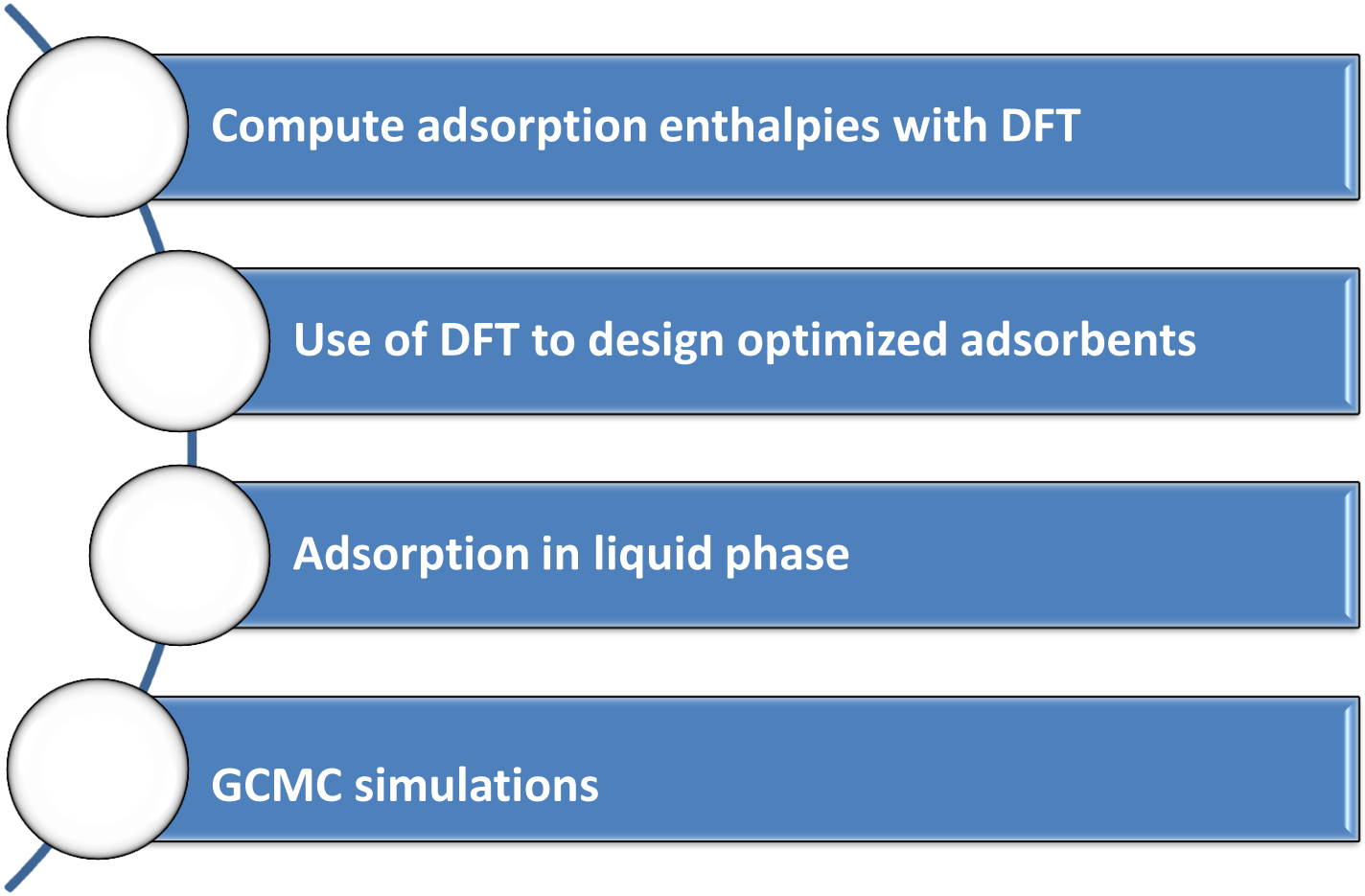
2 hydrogen bonds (1,47 et 2,00 Å



ΔE_{ads} = -101 kJ/mol

2 hydrogen bonds (1,34 et 1,92 Å)

- Be careful with the model size
- Here, the calculation cost for the periodic model is similar to the large cluster one


Compute adsorption enthalpies with DFT
Use of DFT to design optimized adsorbents
Adsorption in liquid phase
GCMC simulations

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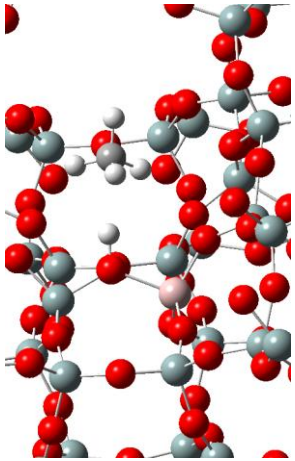
Part 1 - Method
How to compute accurate adsorption enthalpies of molecules onto materials in the frame of DFT ?

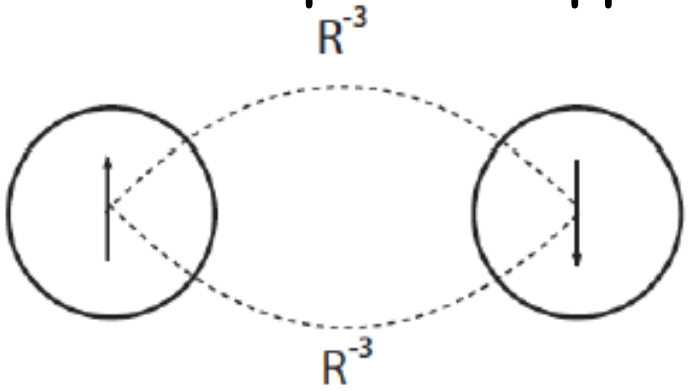
van der Waals interactions



thermal corrections

Dispersion interaction

- London dispersion forces (van der Waals for physicits): created by instantaneous induced dipoles
- decrease as R^6 at large distances
- always attractive within the pairwise approximation



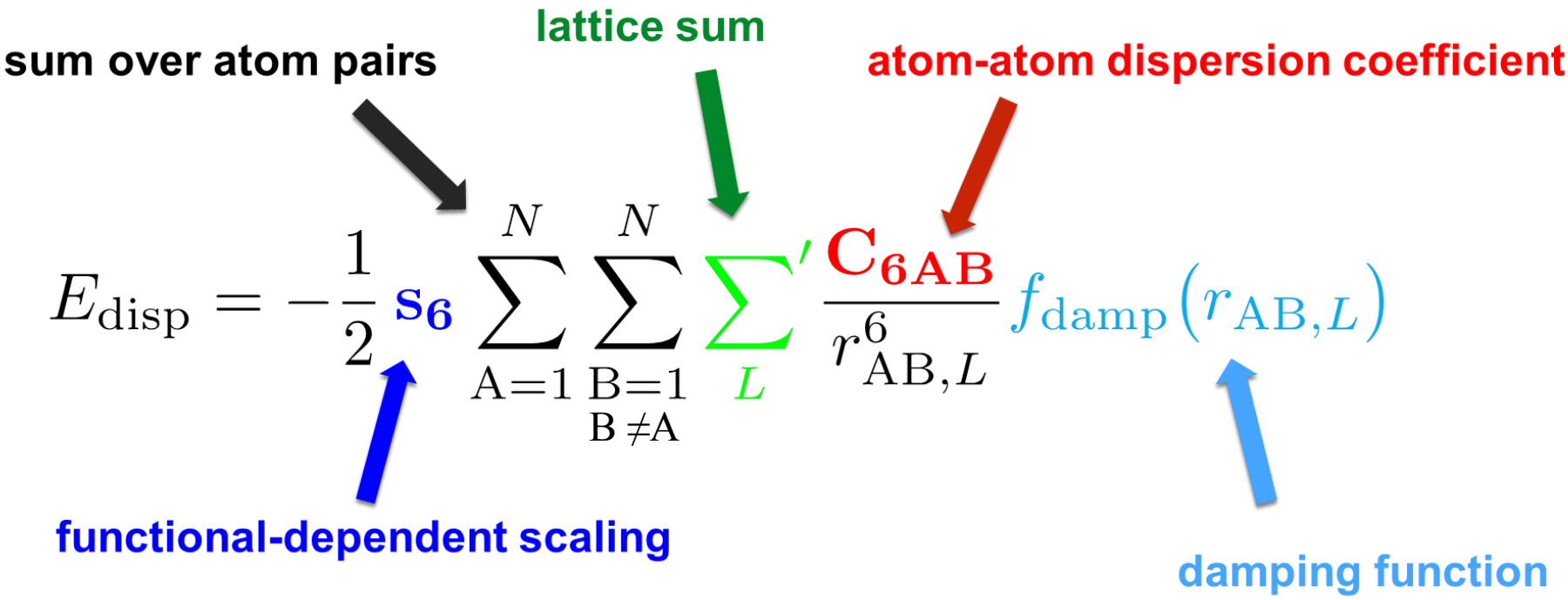
$$E_{\text{disp}} = -\frac{1}{2\pi}\int d\omega\, \alpha^{\text{A}}(i\omega)\, R_{\text{AB}}^{-3}\, \alpha^{\text{B}}(i\omega)\, R_{\text{AB}}^{-3} \sim C_6\, R\text{AB}^{-6}$$

- Long range dynamic correlation not included in DFT

General form of dispersion energy correction

Conventional Kohn-Sham calculation corrected by a dispersion term:

$$E_{\text{DFT-D}} = E_{\text{KS-DFT}} + E_{\text{disp}}$$



- Several methods determine C_6 by various ways : D2 (Grimme) vs TS methods

T. Bucko, S. Lebègue, J. Hafner and J.G. Ángyán, Phys. Rev. B 87 (2013) 064110

TS method (Tkatchenko-Scheffler, 2009)

- Free atom dispersion coefficients $C_{6\mathrm{AA}}^{\mathrm{free}}$ and static polarizabilities $\alpha_{\mathrm{AA}}^{\mathrm{free}}$ from OEP-SIC calculations of Chu and Dalgarno, 2004

- In-molecule polarizabilities and dispersion coefficients scaled by the atom-in-molecule vs. free-atom volume ratio

$$\alpha_{\mathrm{A}} = \left(\frac{V_{\mathrm{A}}}{V_{\mathrm{A}}^{\mathrm{free}}}\right)\alpha_{\mathrm{A}}^{\mathrm{free}} \qquad C_{6\mathrm{AA}} = \left(\frac{V_{\mathrm{A}}}{V_{\mathrm{A}}^{\mathrm{free}}}\right)^2 C_{6\mathrm{AA}}^{\mathrm{free}}$$

- Volume ratio through the **Hirshfeld-partitioning** weights $w_A(\mathbf{r})$

$$\left(\frac{V_{\mathrm{A}}}{V_{\mathrm{A}}^{\mathrm{free}}}\right) = \frac{\langle r_A^3 \rangle}{\langle r_A^3 \rangle_{\mathrm{free}}} = \frac{\int r^3\, w_A(\mathbf{r}) n(\mathbf{r})\, d\mathbf{r}}{\int r^3\, n_{\mathrm{A}}^{\mathrm{free}}(\mathbf{r})\, d\mathbf{r}}$$

Density-dependent dispersion coefficients

Some dispersion correction methods

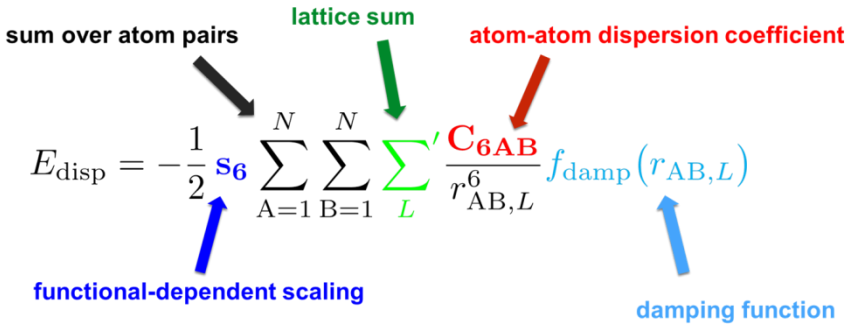
… implemented now in the VASP Package

	Method	C6	Polarizability	Damping	Functional	Remark
Semi-empirical C_6 tabulated	D2	London	Static/atomic	Fermi-type	PBE	IP from exp.
	D3	Casimir-Polder	Dynamic/model molecule	Chai—Head-Gordon	PBE	Coordination number
	D3-BJ	Casimir-Polder	Dynamic/model molecule	Becke-Johnson	PBE	3-body term added
Ab initio C_6 on fly … … + Ionicity + Many Body	TS	London Volume scaled	Atomic/Screened	Fermi-type	PBE	Hirshfeld vol.
	TS/HI	London Volume scaled	Atomic/Screened	Fermi-type	PBE	Iterative Hirshfeld
	MBD-TS/HI	London Volume scaled	Atomic/Screened	Erf+Fermi-type	PBE	Many-body; HI
specific density functionals	vdW-D2	n.a.	n.a.	n.a.	rev-PBE	nonlocal
	optB86b-vdW	n.a.	n.a.	n.a.	optB86b	nonlocal

D2 T. Bučko J. Hafner, S. Lebègue, J.G. Ángyán, J. Phys. Chem. A 114, 11814 (2010).
TS T. Bučko, S. Lebègue, J. Hafner, J.G. Ángyán, Phys. Rev. B 87 (2013) 064110.
TS/HI T.Bučko, S. Lebègue J. Hafner, J.G. Ángyán. J. Chem. Theory Comput. 9, 4293 (2013).
MBD T. Bučko, S. Lebègue, T. Gould, J.G. Ángyán, J. Phys.: Condens. Matter 28, 045201 (2016).
FI-MBD T. Gould, S. Lebègue, J.G. Ángyán, T. Bučko, J. Chem. Theory Comput. 12, 5920 (2016).

Methodology

- Periodic DFT calculations : VASP package
  - ✓ Chabazite (SSZ-13) : 36 atoms per cell or ZSM-5 : 288 atoms per cell
  - ✓ PBE + vdW scheme (van der Waals interactions taken into account)*
  - ✓ PAW pseudopotentials



- Interaction energies computed from 3 calculations :
  - ✓ The bare zeolite structure : Z
  - ✓ The isolated adsorbate molecule : X
  - ✓ The adsorption complex : X.Z

$$\Delta E_{int} = E(Z.X) - E(Z) - E(X)$$

*T. Bucko, S. Lebègue, J. Hafner, J.G. Angyan, J. Chem. Theory Comput. 9 (2013) 4293.
T. Bucko, S. Lebègue, J.G. Angyan, J. Hafner, J. Chem. Phys. 141 (2014) 034114.

Thermodynamic analysis

ΔE_{ads} (0K) ⟹ ΔH^0_{ads} (T)

To take into account the effect of temperature on the adsorption, the enthalpies $\Delta_r H_{ads}$ are equal by definition to:

$$\Delta_r H_{ads} = H_{FAU-X} - H_{FAU} - H_X \quad (3)$$

Given the partition functions, each enthalpy term is expressed as the summation of electronic energy and the contributions from partition functions of vibration, translation and rotation [49].

$$H_i = E_i + ZPVE + H_{vib} + H_{trans} + H_{rot} \quad (4)$$

With:

$$ZPVE = R \sum_{i=1}^{3N-6} \frac{h\nu_i}{2k} \quad (5)$$

$$H_{vib} = R \sum_{i=1}^{3N-6} \frac{h\nu_i}{k} \frac{1}{e^{h\nu_i/kT} - 1} \quad (6)$$

$$H_{trans} = \frac{5}{2}RT \quad (7)$$

$$H_{rot} = \frac{3}{2}RT \text{ for non linear molecule or } H_{rot} = RT \text{ for linear molecule} \quad (8)$$

Where R is the constant of perfect gas, h is the Planck constant, k is the Boltzmann constant, ν_i is a vibration frequency computed with the harmonic approximation, T is the temperature.

ZPVE is the zero point energy, H_{vib} is the contribution from molecules that are not in the vibrational ground state, depending on temperature.

Therefore we can express:

$$\Delta_r H_{ads} = \Delta E_{ads} + \Delta ZPVE + \Delta H_{vib} + \Delta H_{trans} + \Delta H_{rot} \quad (9)$$

Thermal corrections based on frequency calculations (harmonic approximation)

vs

Dynamic approach

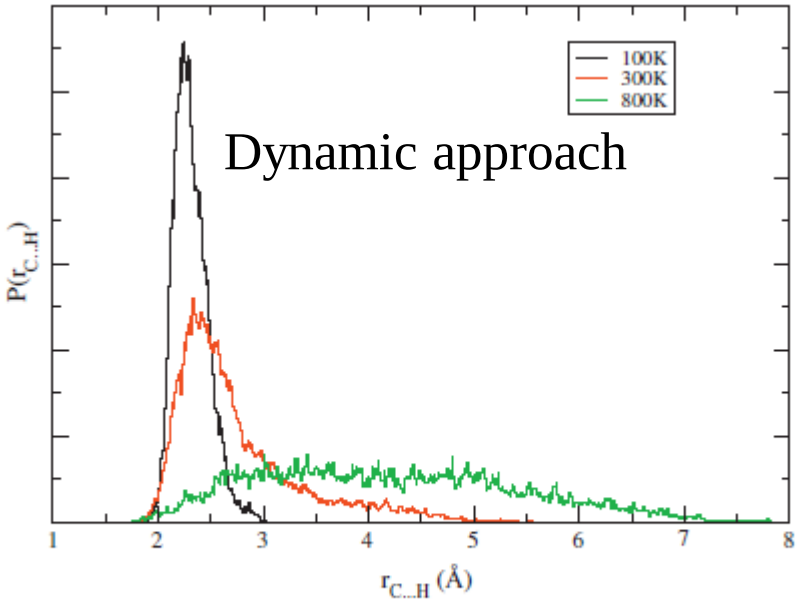


Fig. 4. Distribution function for the distance between proton and the nearest carbon atom of propane ($P(r_{C...H})$) computed for three different temperatures.

T. Bučko, L. Benco, J. Hafner, J.G. Ángyán, J. Catal. 279 (2011) 220

M. Badawi, J.F. Paul, S. Cristol, E. Payen, Catal. Commun. 12 (2011) 901

M. Chebbi, S. Chibani, J.-F. Paul, L. Cantrel, M. Badawi, Micro. Meso. Mater. 239 (2017) 111

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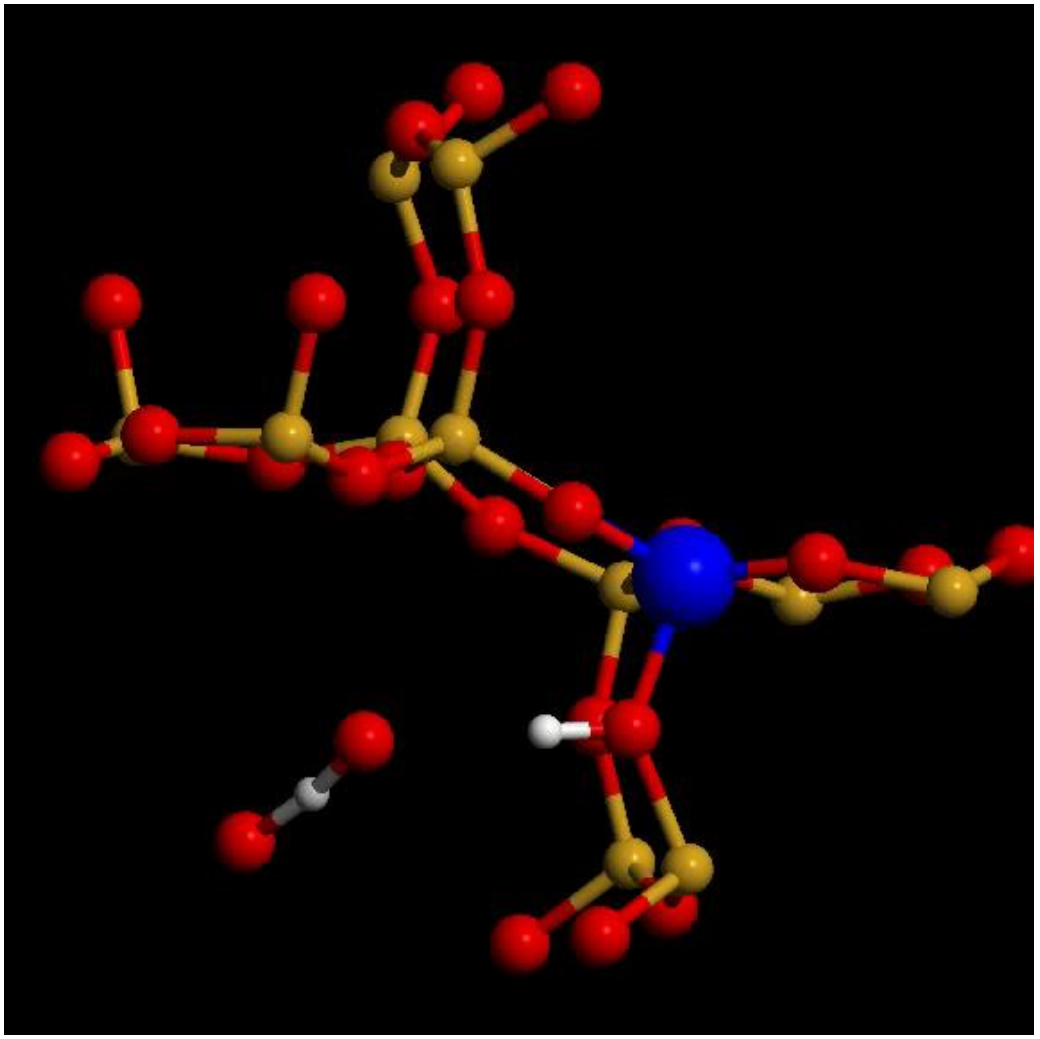
Ab initio Molecular Dynamics

- NVT ensemble (T= 300 K)
- Andersen thermostat
- Integration step: Δt = 1 fs
- Simulation time : 200 ps



Thermal correction

To take into account the effect of temperature on the adsorption, the enthalpies $\Delta_r H_{ads}$ are equal by definition to:

$$\Delta_r H_{ads} = H_{FAU-X} - H_{FAU} - H_X \quad (3)$$

Given the partition functions, each enthalpy term is expressed as the summation of electronic energy and the contributions from partition functions of vibration, translation and rotation [49].

$$H_i = E_i + ZPVE + H_{vib} + H_{trans} + H_{rot} \quad (4)$$

With:

$$ZPVE = R \sum_{i=1}^{3N-6} \frac{h\nu_i}{2k} \quad (5)$$

$$H_{vib} = R \sum_{i=1}^{3N-6} \frac{h\nu_i}{k} \frac{1}{e^{h\nu_i/kT} - 1} \quad (6)$$

$$H_{trans} = \frac{5}{2}RT \quad (7)$$

$$H_{rot} = \frac{3}{2}RT \text{ for non linear molecule or } H_{rot} = RT \text{ for linear molecule} \quad (8)$$

Where R is the constant of perfect gas, h is the Planck constant, k is the Boltzmann constant, ν_i is a vibration frequency computed with the harmonic approximation, T is the temperature.

ZPVE is the zero point energy, H_{vib} is the contribution from molecules that are not in the vibrational ground state, depending on temperature.

Therefore we can express:

$$\Delta_r H_{ads} = \Delta E_{ads} + \Delta ZPVE + \Delta H_{vib} + \Delta H_{trans} + \Delta H_{rot} \quad (9)$$

Thermal corrections based on frequency calculations (harmonic approximation)

ΔE_{ads} (0K) ⟹ ΔH^0_{ads} (T)

vs

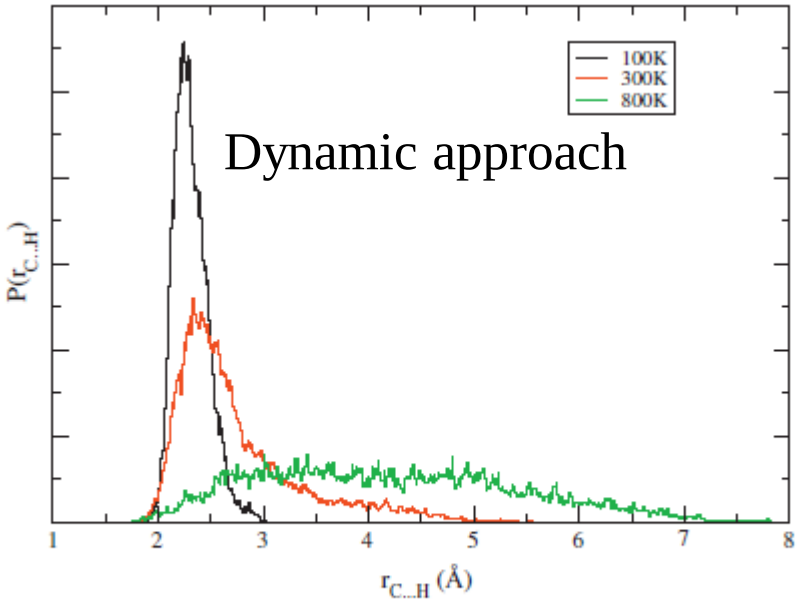


Fig. 4. Distribution function for the distance between proton and the nearest carbon atom of propane ($P(r_{C...H})$) computed for three different temperatures.

T. Bučko, L. Benco, J. Hafner, J.G. Ángyán, J. Catal. 279 (2011) 220

M. Badawi, J.F. Paul, S. Cristol, E. Payen, Catal. Commun. 12 (2011) 901

M. Chebbi, S. Chibani, J.-F. Paul, L. Cantrel, M. Badawi, Micro. Meso. Mater. 239 (2017) 111

Revover CO_2 ΔH_{ads} at 300K ?

- **Adsorption enthalpy of CO_2 in siliceous chabazite :**

Experimental values -22.5[a] / -24[b] kJ/mol at 300 K (microcalorimetry)

- **Interaction energies computed by ab initio MD (PBE +D2)**

Temperature	ΔE_{DFT}	ΔE_{disp}	ΔU_{ads}	ΔH_{ads}
0 K (DFT)	-2.8	-23.7	-26.5	-
300 K (AIMD)	+0.8	-19.8	-19.0	-21.5

$\Delta H_{ads} = \Delta U_{ads} - RT$ (ideal gas approximation)

- **What about other vdW correction schemes?**

[a] H. Fang, P. Kamakoti, J. Zang, S. Cundy, C. Paur, P. I. Ravikovitch, D.S. Sholl, Prediction of CO_2 Adsorption Properties in Zeolites Using Force Fields Derived from Periodic Dispersion-Corrected DFT Calculations, J. Phys. Chem. C 116 (2012) 116, 10692−10701

[b] T.D. Pham, M.R. Hudson, C.M. Brown, R.F. Lobo, Molecular Basis for the High CO2 Adsorption Capacity of Chabazite Zeolites, ChemSusChem 7 (2014) 3031 – 3038

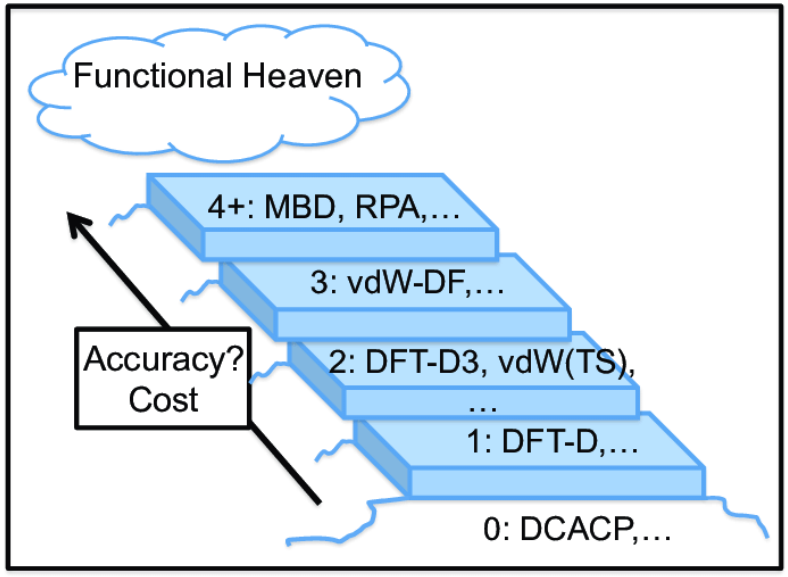
Revover CO_2 ΔH_{ads} at 300K ?

- **Adsorption enthalpy of CO_2 in siliceous chabazite :**

Experimental values -22.5 / -24 kJ/mol at 300 K (microcalorimetry)

- **From PBE+D2 : ΔH_{ads} *300K* – ΔU_{tot} *0K = 5 kJ/mol***

Method	Specificity	ΔH_{ads} *300K*
PBE + D2	C_6 tabulated	-21.5
PBE + TS/HI	C_6 computed on fly, ionicity	*-21.9*
PBE + MBD	C_6 on fly, many body	*-24.1*
RPA	vdW directly included	-16.8



- **TS/HI and MBD may provide best agreement**
- **RPA underestimates enthalpy**

Revover CO_2 ΔH_{ads} at 300K ?

- **Adsorption enthalpy of CO_2 in protonated chabazite (Si/Al=12)**

Experimental value -35.2[c] kJ/mol at 300 K (isotherms)

- **Interaction energies computed by ab initio MD (PBE +D2)**

Temperature	ΔE_{DFT}	ΔE_{disp}	ΔU_{ads}	ΔH_{ads}
0 K (DFT)	-11.6	-24.9	-36.5	-
300 K (AIMD)			-37.8	-40.3

- **Brönsted site contribute around 10 kJ/mol**
- **From PBE+D2 : ΔH_{ads} *300K* – ΔU_{tot} *0K = 3.8 kJ/mol***

[c] T.D. Pham, Q. Liu, R.F. Lobo, Langmuir 29 (2013) 832–839.

- Adsorption enthalpy of CO_2 in protonated chabazite (Si/Al=11)

Experimental value **-35.2**[c] kJ/mol at 300 K (isotherms)

- From PBE+D2 : ΔH_{ads} *300K* – ΔU_{tot} *0K = 3.8 kJ/mol*

Method	Specificity	ΔH_{ads} *300K*
PBE + D2	C_6 tabulated	-32.8
PBE + TS/HI	C_6 computed on fly, ionicity	*-32.5*
PBE + MBD	C_6 on fly, many body	*-35.2*

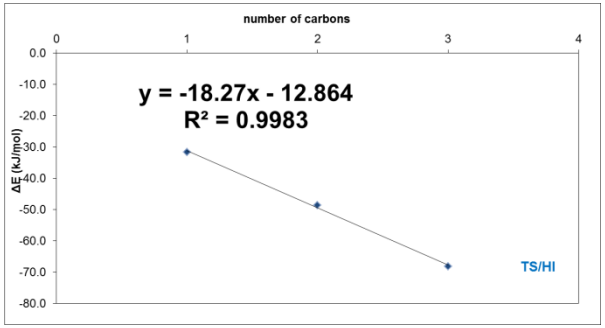
- MBD provide perfect agreement
- More sophisticated prediction methods now available: Machine Learning Perturbation Theory (see Mauricio Chagas Da Silva talk at the end of the AFA days this Friday)

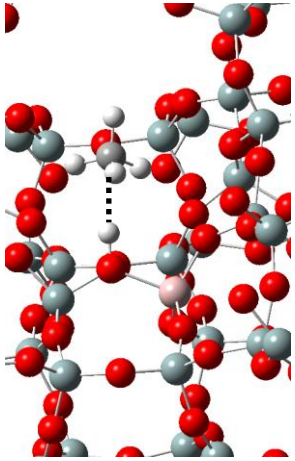
B. Chehaibou, M. Badawi, T. Bučko, T. Bazhirov, D. Rocca,, **Journal of Chemical Theory and Computation** 15 (2019) 6333−6342
https://doi.org/10.1021/acs.jctc.9b00782

Contribution of dispersion forces

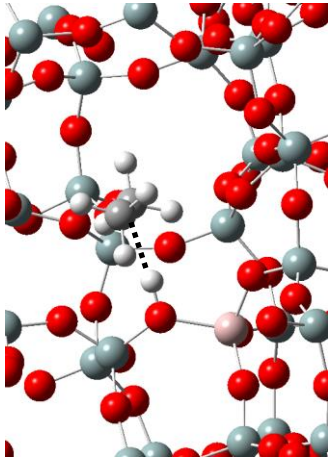
- Contribution of H-bond and van der Waals interactions to the adsorption of alkanes in H-ZSM-5 zeolite. PBE + TS-HI level of theory (kJ/mol)
- ΔE int (total interaction) = **ΔE H-bond** + **ΔE vdW**

Molecule	ΔE H-bond	**ΔE vdW**	ΔE int
methane	-10.6	**-20.9**	-31.5
ethane	-9.8	**-38.7**	-48.5
propane	-9.5	**-58.6**	-68.1

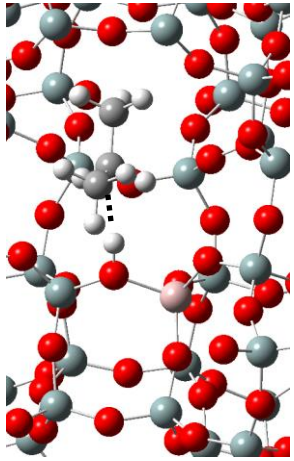




methane



ethane

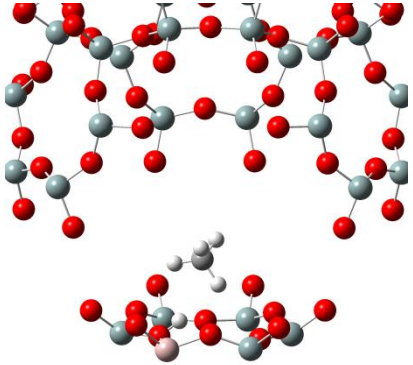


propane

Effect of structure

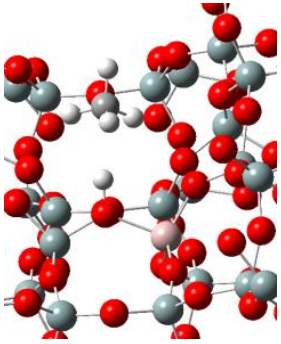
H-FAU	E_{DFT}	E_{disp}	E_{tot}
methane	-0.2	-15.9	-16.1
ethane	-1.3	-24.4	-25.7
propane	-2.5	-33.8	-36.3

Adsorption energy exclusively due to London dispersion, of about 12 kJ/mol per carbon atom.
Steric hindrance of favorable alkane-proton interactions leads to almost negligible PBE interaction energy.



H-ZSM-5	E_{DFT}	E_{disp}	E_{tot}
methane	-10.6	-20.9	-31.6
ethane	-9.8	-38.7	-48.5
propane	-9.5	-58.6	-68.1

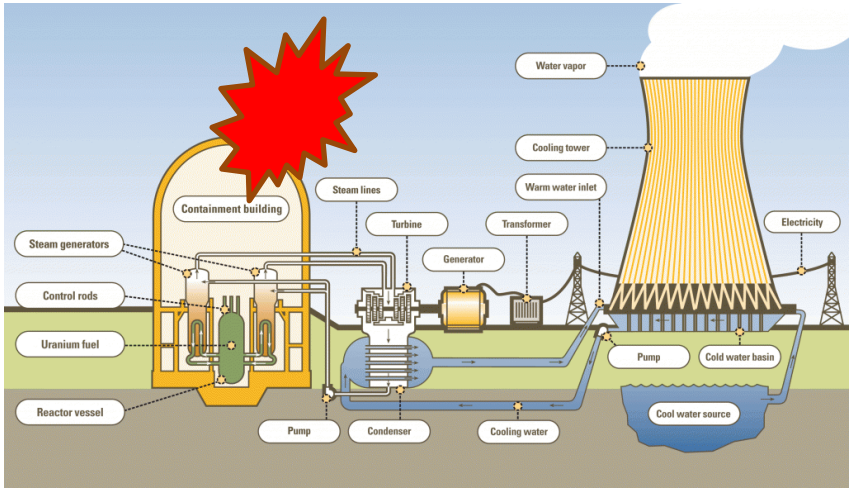
Almost constant PBE interaction energy of about 10 kJ/mol (H-bond).
Stronger dispersion contribution of about 20 kJ/mol per carbon atom in the denser ZSM5 structure.



- In silico design of adsorbents for what?

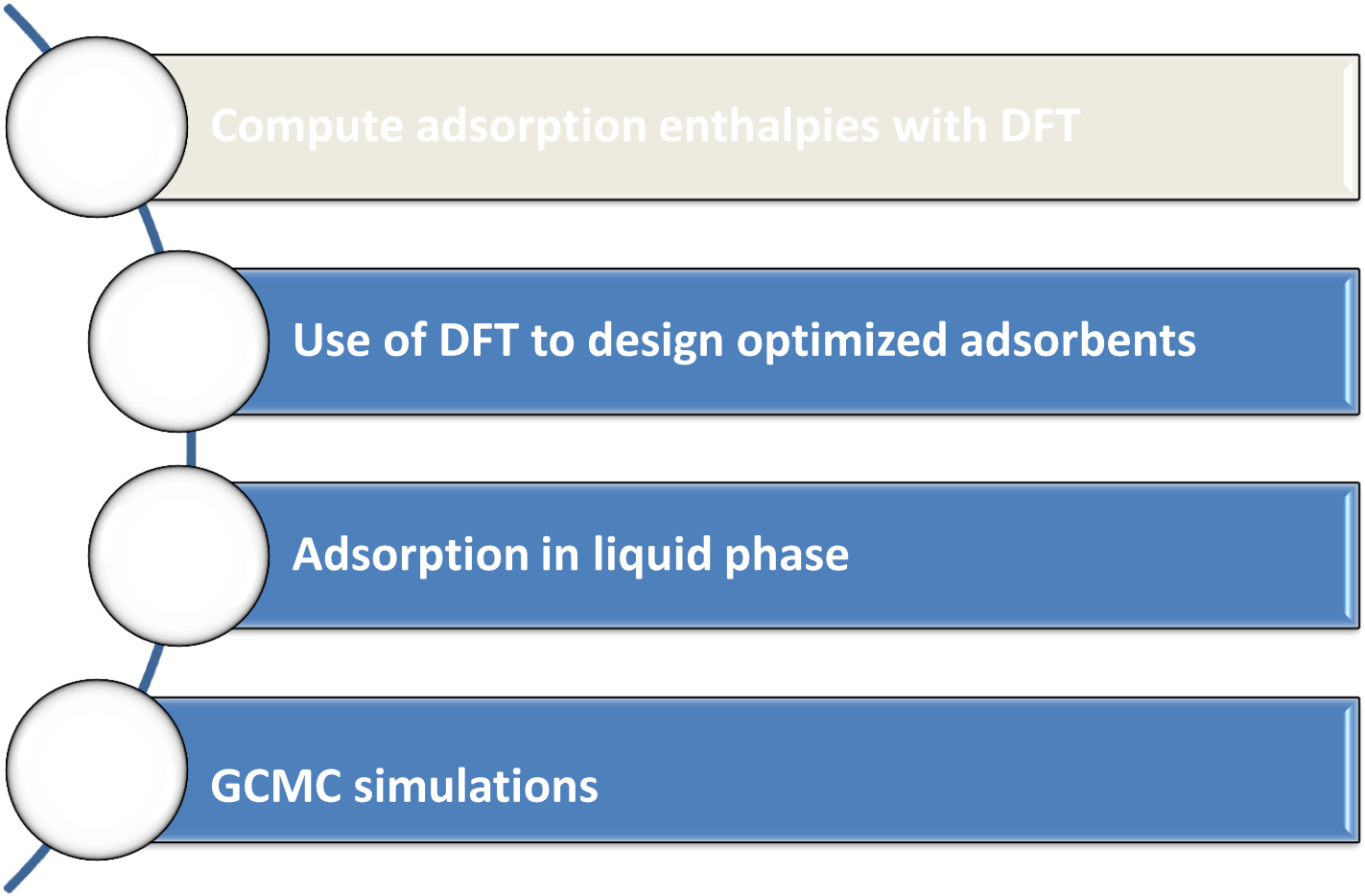
Air depollution

Example of nuclear accident

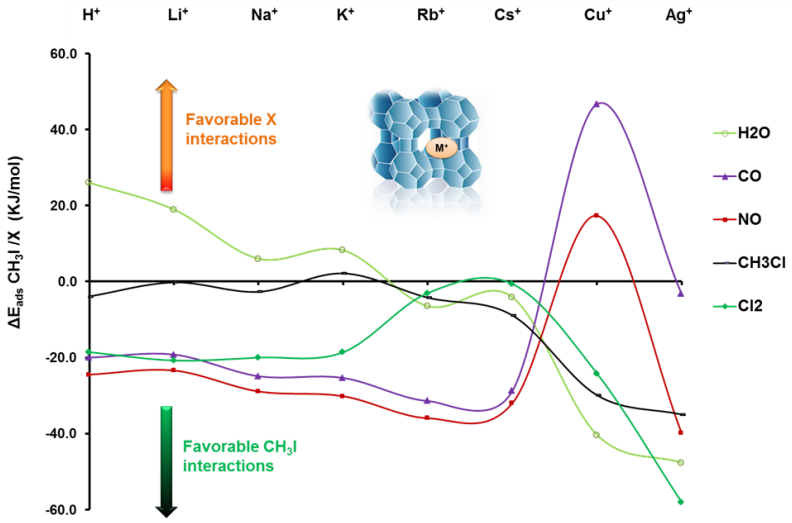


Energy production

separation of gases, …


Compute adsorption enthalpies with DFT
Use of DFT to design optimized adsorbents
Adsorption in liquid phase
GCMC simulations

Part 2- Use of density functional theory to design optimized adsorbents Case example of selective capture iodine species in case of nuclear severe accident



Motivation

- iodine compounds are among the most dangerous effluents of nuclear facilities

- iodomethane is formed by reaction of I_2 with organic impurities dissolved in water or with painted surfaces [1]

- efficient sorbents must be developed

- Gas flow contains H_2O, CO, …. in case of nuclear severe accident

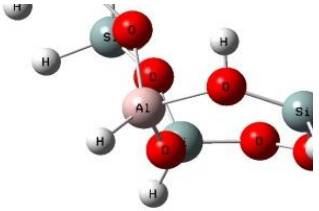
I_2 & CH_3I

Fukushima 2012
(source: http://themjreport.blogspot.sk/)

- Limited understanding of underlying processes at atomic-level → computer simulations

[1] B. Clement et al., OCDE Report, NEA/CSNI/R, p. 11.

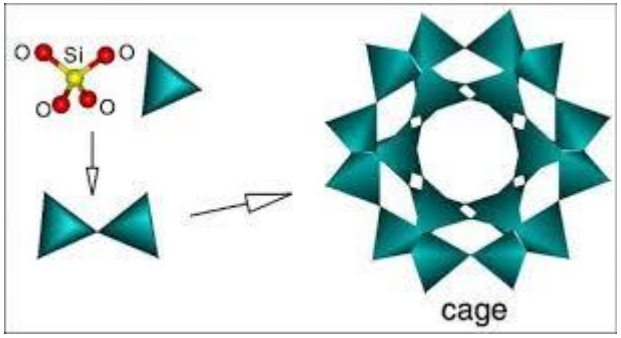
Trapping Materials : Zeolites



- Zeolite = microporous aluminosilicate

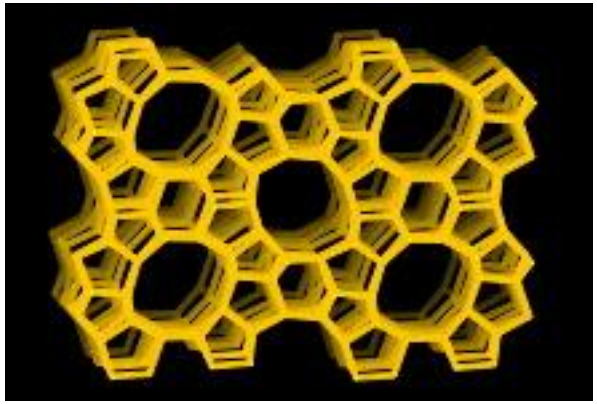
  $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedrons linked by O atoms

  Al insertion => negative charge compensated by cation incorporation



- Zeolites attractive for this application :

  - thermal / mechanical stabilities
  - tunable properties (structure, cation …)
  - resistant to irradiation



- **2 key parameters:**

Si/Al ratio (cation loading)

Nature of the cation

Objectives

- Trap **iodine compounds, I_2 and CH_3I**, over zeolites under severe accident conditions :
  T around 100°C, **contaminants**: H_2O, CO, NO, Cl_2 …

- **Find a cation where contaminants will be less adsorbed than I_2 and CH_3I**

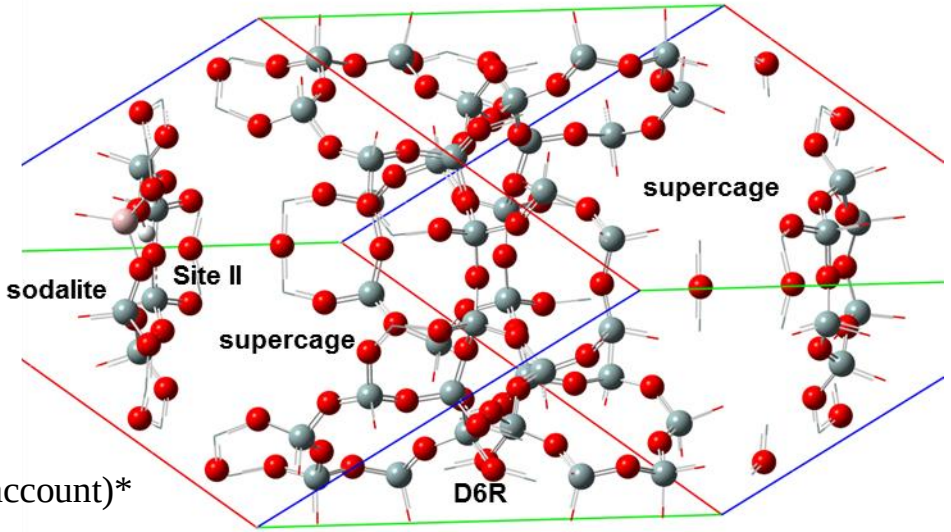
- Two zeolite structures are investigated : FAU and MOR

- DFT & thermodynamic calculations

Methodology

- Periodic DFT calculations : VASP
  - ✓ PAW pseudopotentials
  - ✓ K point 1x1x1
  - ✓ 144 atoms per cell, Si/Al = 47

  → monovalent cations



  - ✓ PBE + TS/HI (van der Waals interactions taken into account)*

sum over atom pairs — lattice sum — atom-atom dispersion coefficient

$$E_{\mathrm{disp}} = -\frac{1}{2} s_6 \sum_{A=1}^{N} \sum_{B=1}^{N} \sum_{L}{}' \frac{C_{6AB}}{r_{AB,L}^6} f_{\mathrm{damp}}(r_{AB,L})$$

functional-dependent scaling — damping function

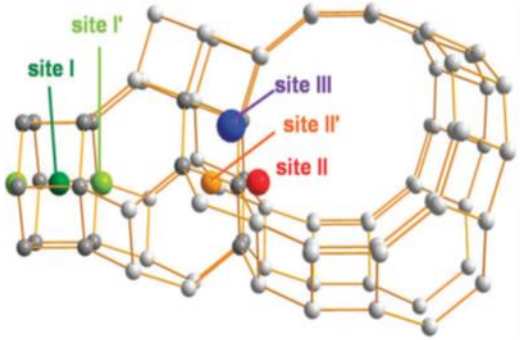
- Adsorption energies computed from 3 calculations :
  - ✓ The bare zeolite structure : Z
  - ✓ The isolated adsorbate molecule : X
  - ✓ The adsorption complex : X.Z

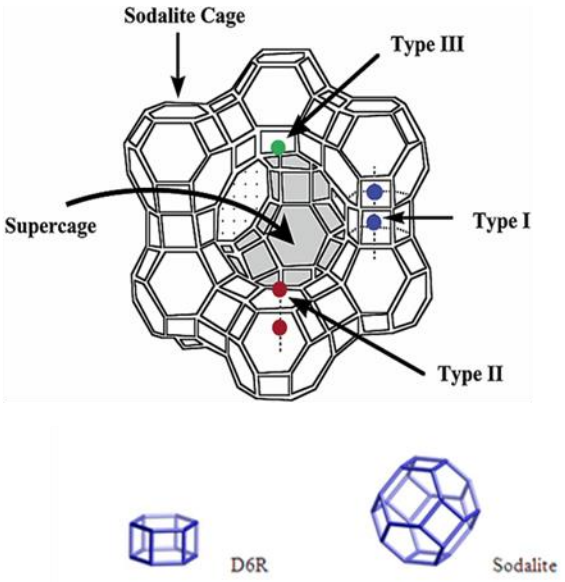
→ $\Delta E_{ads} = E(Z.X) - E(Z) - E(X)$

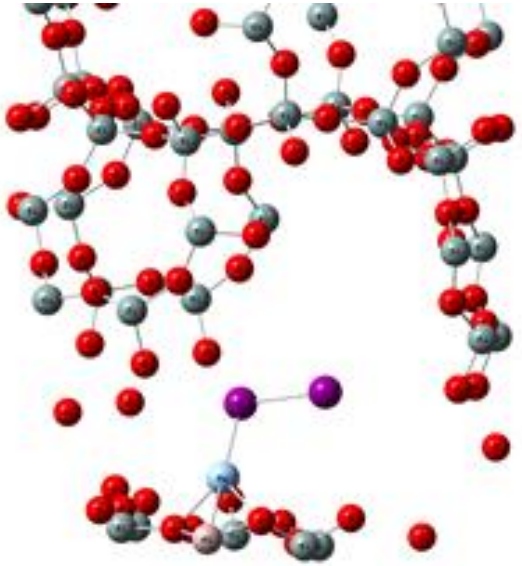
*T. Bucko, S. Lebègue, J. Hafner, J.G. Angyan, J. Chem. Theory Comput. 9 (2013) 4293.
T. Bucko, S. Lebègue, J.G. Angyan, J. Hafner, J. Chem. Phys. 141 (2014) 034114.

Faujasite (FAU) structure

- Three type of cavities
  - Supercage
  - Sodalite cage
  - D6R connection







- ✓ Site II can be occupied by all the considered extraframework cations
- ✓ Site II : site of interest to study the adsorption thanks to its accessibility by the studied adsorbates

Only one adsorption site considered in FAU

Al : pink
Si : blue
I : purple

Cationic screening

- Large choice of cation to incorporate into zeolite frameworks (ionic exchange, impregnation, ….) :
  - Columns I, II and transition metals in the periodic classification of elements

alkalines

Couche	Période	I	II											III	IV	V	VI	VII	VIII
K	1	$^{1}_{1}H$ Hydrogène 1,01																	$^{4}_{2}He$ Hélium
L	2	$^{7}_{3}Li$ Lithium 6,94	$^{9}_{4}Be$ Béryllium 9,01											$^{11}_{5}B$ Bore 10,8	$^{12}_{6}C$ Carbone 12,0	$^{14}_{7}N$ Azote 14,0	$^{16}_{8}O$ Oxygène 16,0	$^{19}_{9}F$ Fluor 19,0	$^{20}_{10}Ne$ Néon 20,2
M	3	$^{23}_{11}Na$ Sodium 23,0	$^{24}_{12}Mg$ Magnésium 24,3	transition metals										$^{27}_{13}Al$ Aluminium 27,0	$^{28}_{14}Si$ Silicium 28,1	$^{31}_{15}P$ Phosphore 31,0	$^{32}_{16}S$ Soufre 32,1	$^{35}_{17}Cl$ Chlore 35,5	$^{40}_{18}Ar$ Argon 39,9
N	4	$^{39}_{19}K$ Potassium 39,1	$^{40}_{20}Ca$ Calcium 40,1	$^{45}_{21}Sc$ Scandium 45,0	$^{48}_{22}Ti$ Titane 47,9	$^{51}_{23}V$ Vanadium 50,9	$^{52}_{24}Cr$ Chrome 52,0	$^{55}_{25}Mn$ Manganèse 54,9	$^{56}_{26}Fe$ Fer 55,8	$^{59}_{27}Co$ Cobalt 58,9	$^{58}_{28}Ni$ Nickel 58,7	$^{63}_{29}Cu$ Cuivre 63,5	$^{64}_{30}Zn$ Zinc 65,4	$^{69}_{31}Ga$ Gallium 69,7	$^{74}_{32}Ge$ Germanium 72,6	$^{75}_{33}As$ Arsenic 74,9	$^{80}_{34}Se$ Sélénium 79,0	$^{79}_{35}Br$ Brome 79,9	$^{84}_{36}Kr$ Krypton 83,6
O	5	$^{85}_{37}Rb$ Rubidium 85,5	$^{88}_{38}Sr$ Strontium 87,5	$^{89}_{39}Y$ Yttrium 88,9	$^{90}_{40}Zr$ Zirconium 91,2	$^{93}_{41}Nb$ Niobium 92,9	$^{98}_{42}Mo$ Molybdène 95,9	$^{}_{43}Tc$ Technétium 99,0	$^{102}_{44}Ru$ Ruthénium 101,1	$^{103}_{45}Rh$ Rhodium 102,9	$^{106}_{46}Pd$ Palladium 106,4	$^{107}_{47}Ag$ Argent 107,9	$^{114}_{48}Cd$ Cadmium 112,4	$^{115}_{49}In$ Indium 114,8	$^{120}_{50}Sn$ Etain 118,7	$^{121}_{51}Sb$ Antimoine 121,6	$^{128}_{52}Te$ Tellure 127,5	$^{127}_{53}I$ Iode 126,9	$^{129}_{54}Xe$ Xénon 131,3
P	6	$^{133}_{55}Cs$ Césium 132,9	$^{138}_{56}Ba$ Baryum 137,3	57 à 71 lanthanides	$^{180}_{72}Hf$ Hafnium 178,5	$^{181}_{73}Ta$ Tantale 180,9	$^{184}_{74}W$ Tungstène 183,9	$^{185}_{75}Re$ Rhénium 186,2	$^{192}_{76}Os$ Osmium 190,2	$^{193}_{77}Ir$ Iridium 192,2	$^{195}_{78}Pt$ Platine 195,1	$^{197}_{79}Au$ Or 197,0	$^{202}_{80}Hg$ Mercure 200,6	$^{205}_{81}Tl$ Thallium 204,4	$^{208}_{82}Pb$ Plomb 207,2	$^{209}_{83}Bi$ Bismuth 209,9	$^{210}_{84}Po$ Polonium 210	$^{218}_{85}At$ Astate 210	$^{222}_{86}Rn$ Radon 222
Q	7	$^{223}_{87}Fr$ Francium 223	$^{226}_{88}Ra$ Radium 226,1	89 à 103 actinides															

Find a cation : adsorption of iodine > contaminants

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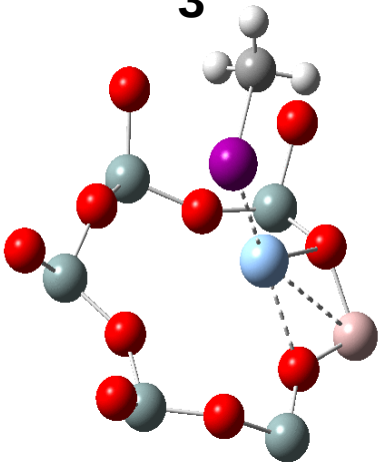
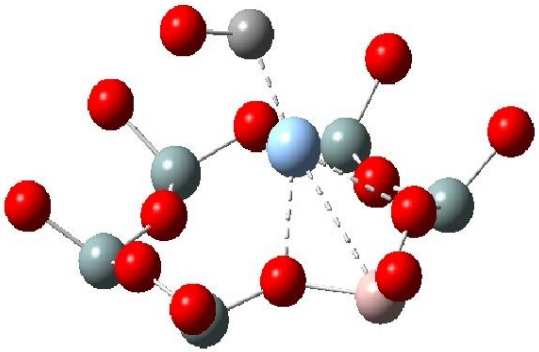
Adsorption modes of selected molecules (Ag-FAU)

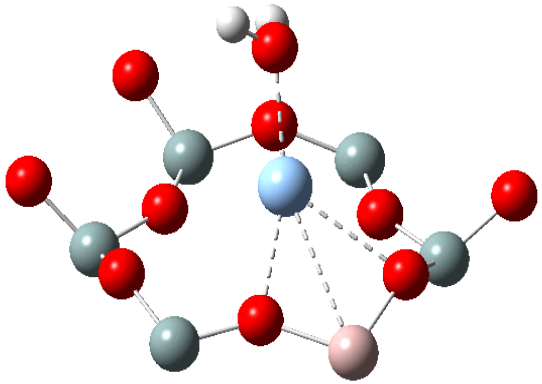
CH_3I



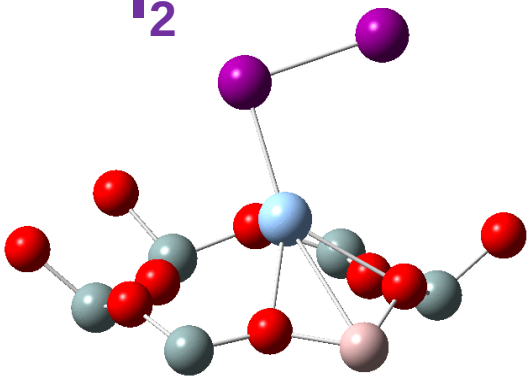
CO



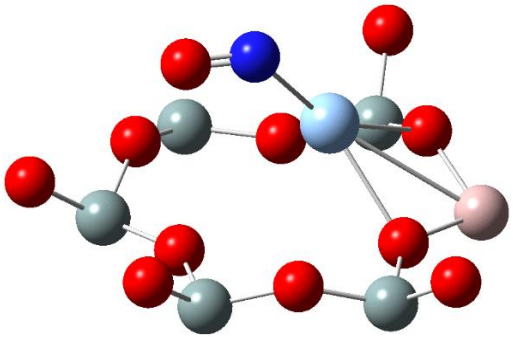
H_2O



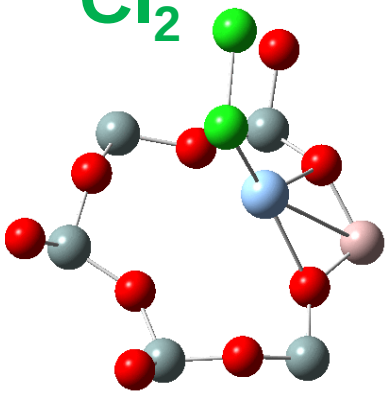
I_2



NO



Cl_2



Assessment of the Methodology

- Very few experimental data available. Data given in kJ/mol

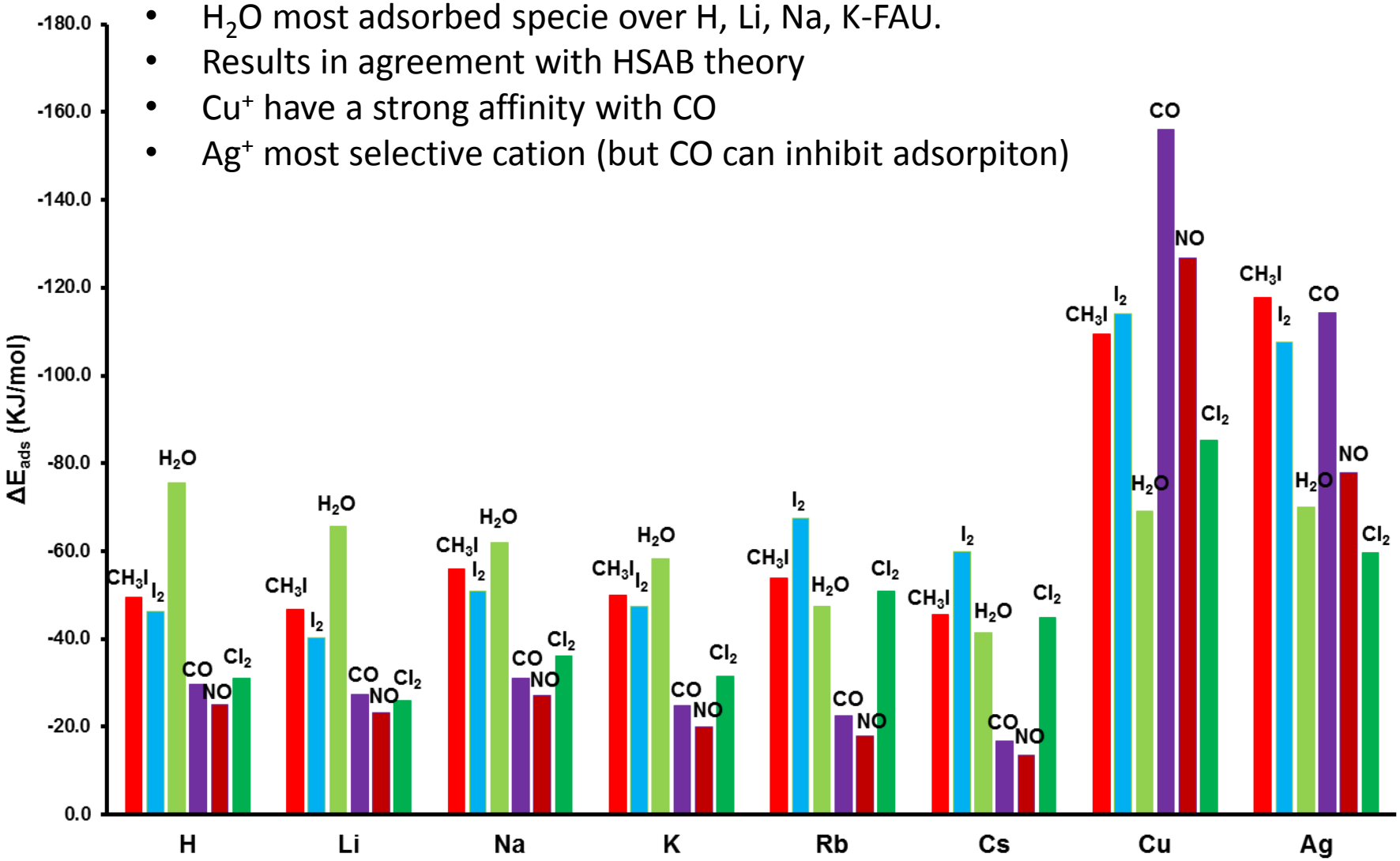
Si/Al ratio	47		2.5		
	ΔE_{ads} at 0K Theor.	ΔH_{ads} at 300K Theor.	ΔH_{ads} Litterature Exp.	Method and operating conditions	References
Li/CO	-35.2	-32	-28	microcalorimetry at 173 K	[1]
Na/CO	-30.7	-27.5	-27	Microcalorimetry at 298 K	[2]
Na/CO	-30.7	-27.5	-27	VTIR, T= 207-264 K	[3]
Na/H_2O	-62.8	- 58.0	-67	Microcalorimetry, T = 293 K	[4]
Na/CO_2	-34.4	-31.2	-29.5	Microcalorimetry, T = 307 K	[5]

Computed values for Si/Al = 47 in nice agreement with experiment for Si/Al = 2.5 due to the small size of the molecules

[1] P. Cicmanec, R. Bulanek, E. Frydova, Adsorption 19 (2013) 381-389
[2] T. A. Egerton and F. S. Stone, Trans. Faraday Soc. 66 (1970) 2364
[3] P. Nachtigall, M.R. Delgado, D. Nachtigallova, C.O. Arean, Phys. Chem. Chem. Phys. 14 (2012) 1552–1569.
[4] G. Whiting, D. Grondin, S. Bennici, A. Auroux, Solar Energy Materials and Solar Cells 112 (2013) 112–119.
[5] G. Maurin, P.L. Llewellyn, R. G.Bell J. Phys. Chem B 109 (2005) 16084-16091

FAU- cationic screening results

- H_2O most adsorbed specie over H, Li, Na, K-FAU.
- Results in agreement with HSAB theory
- Cu^+ have a strong affinity with CO
- Ag^+ most selective cation (but CO can inhibit adsorpiton)

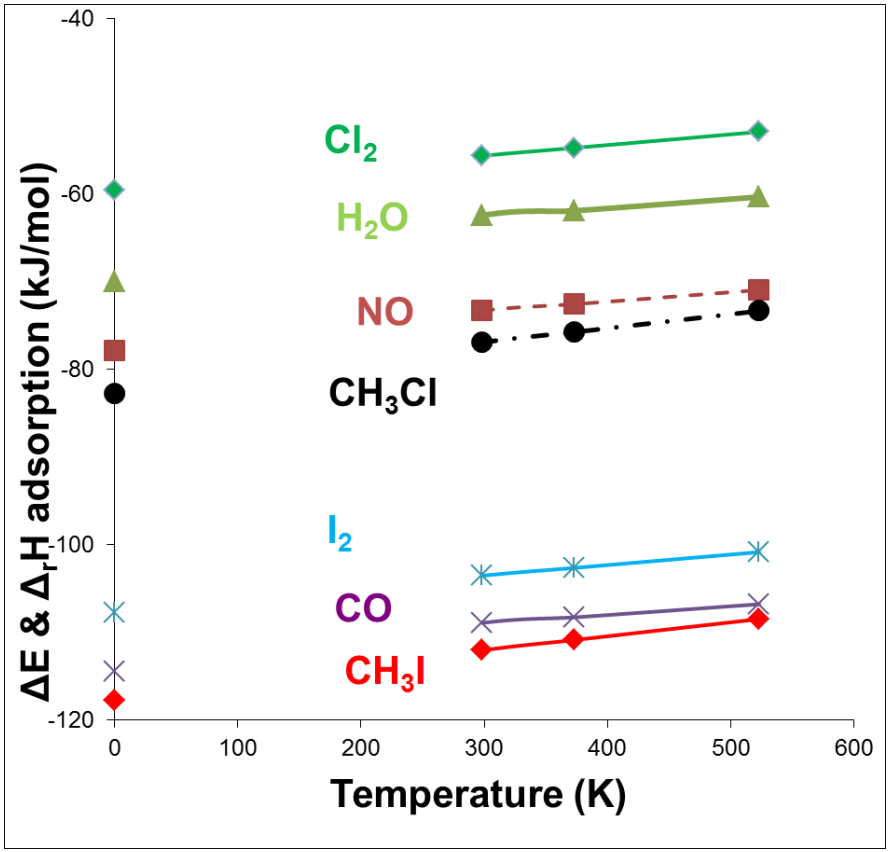


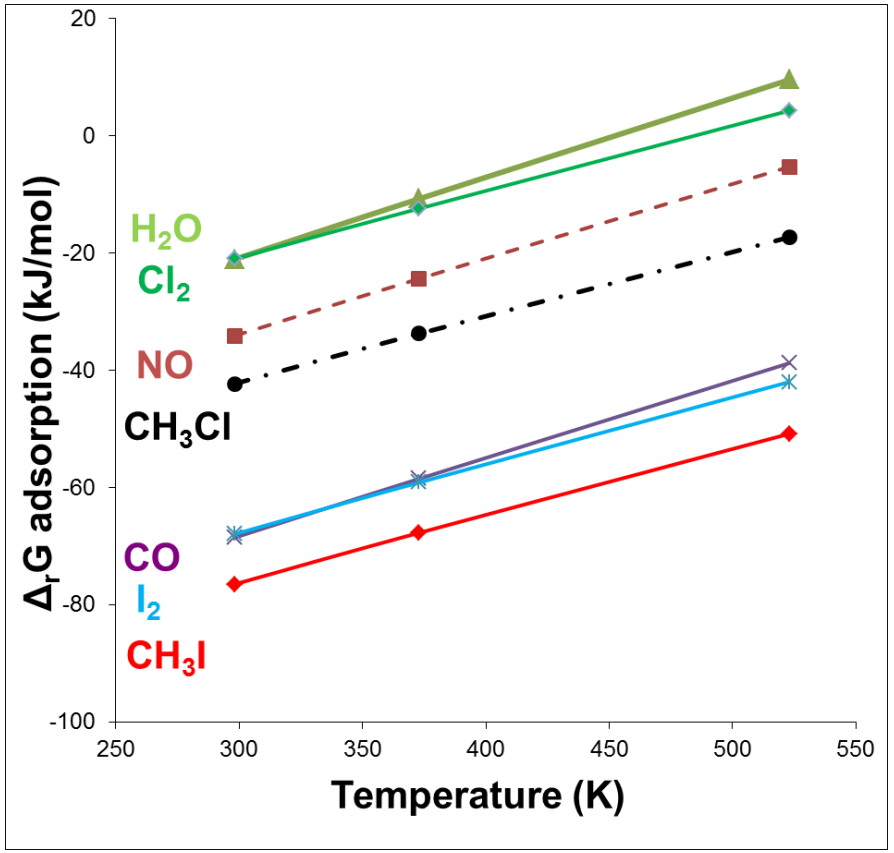
M. Chebbi, S. Chibani, J.-F. Paul, L. Cantrel, M. Badawi, *Evaluation of volatile iodine trapping in presence of contaminants: a periodic DFT study on cation exchanged-faujasite*, Micro. Meso. Mater. 239 (2017) 111

Thermodynamic analysis

- ΔE_{ads} (0K) * ⇒ ΔH^0_{ads} (T) ΔG^0_{ads} (T)

Ag-FAU



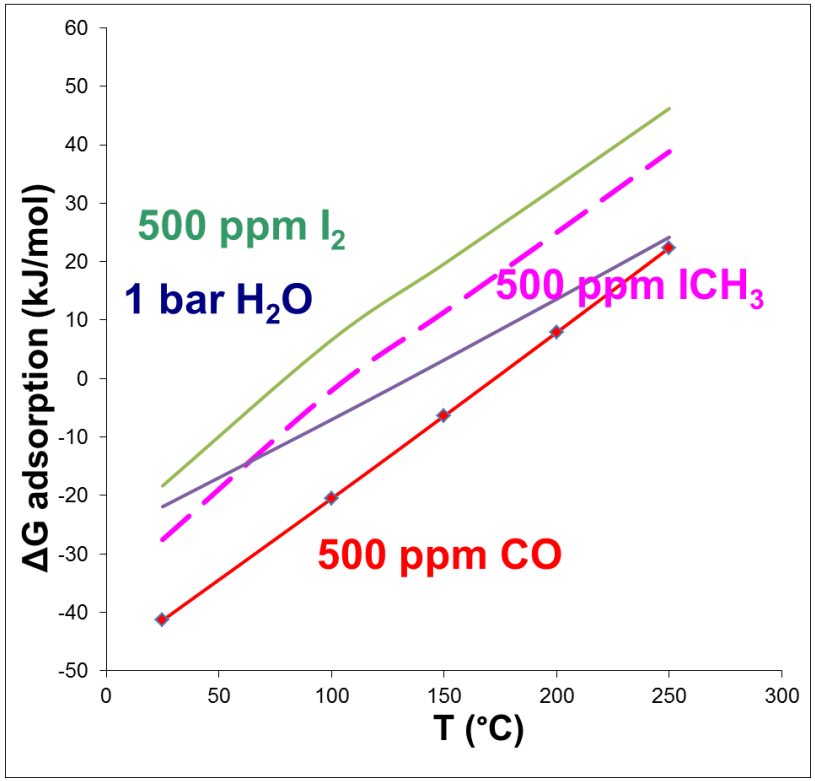


- Limited inhibiting effect of water expected.
- CO presents the most potential inhibitor effect.

*M. Badawi, J.F. Paul, S. Cristol, E. Payen, Catal. Commun. 12 (2011) 901

Thermodynamic corrections : Ag-FAU

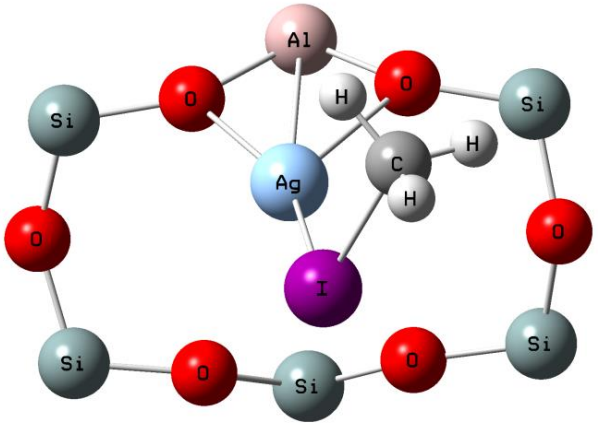
- Practical example
  - Total pressure 5 bar, 1000 ppm iodine compounds
  - 20% water in the feed (1 bar) or 10% water in the feed (0.5 bar)

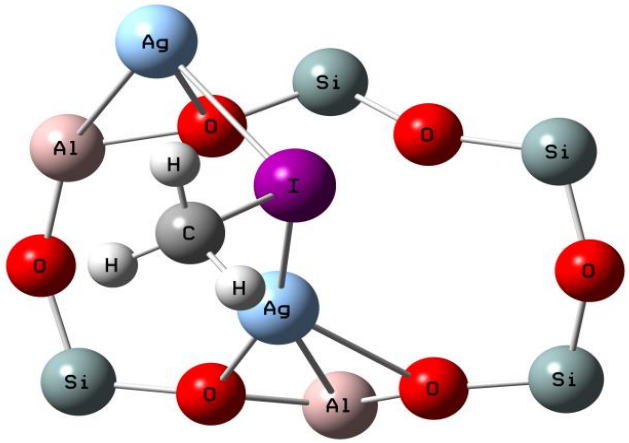


- Limited inhibiting effect of water expected.
- CO still presents the most potential inhibitor effect.

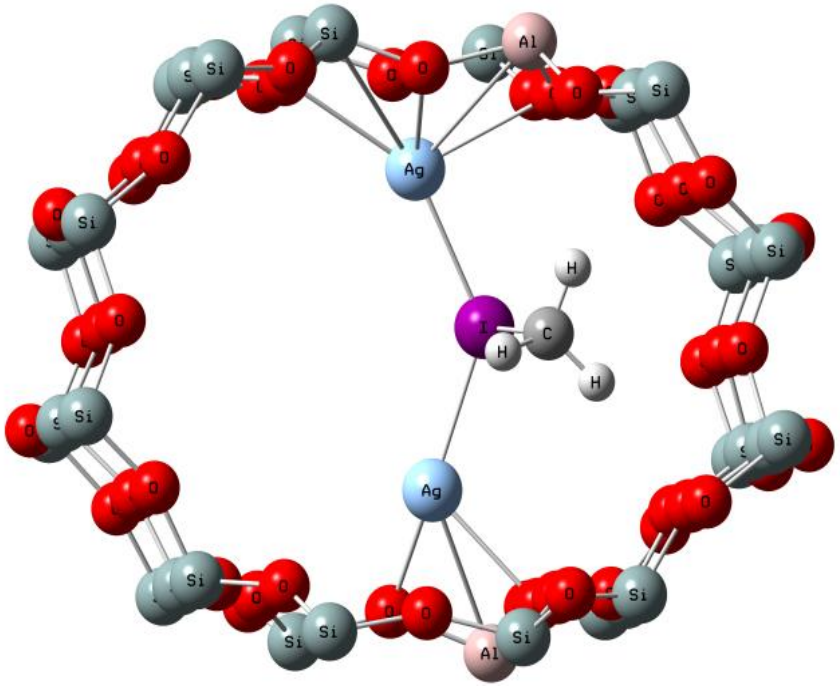
Ag-MOR: Effect of the Si/Al ratio

Calculation made for Si/Al 47 whereas commercial samples have ratio between 5 and 15





New adsorption modes



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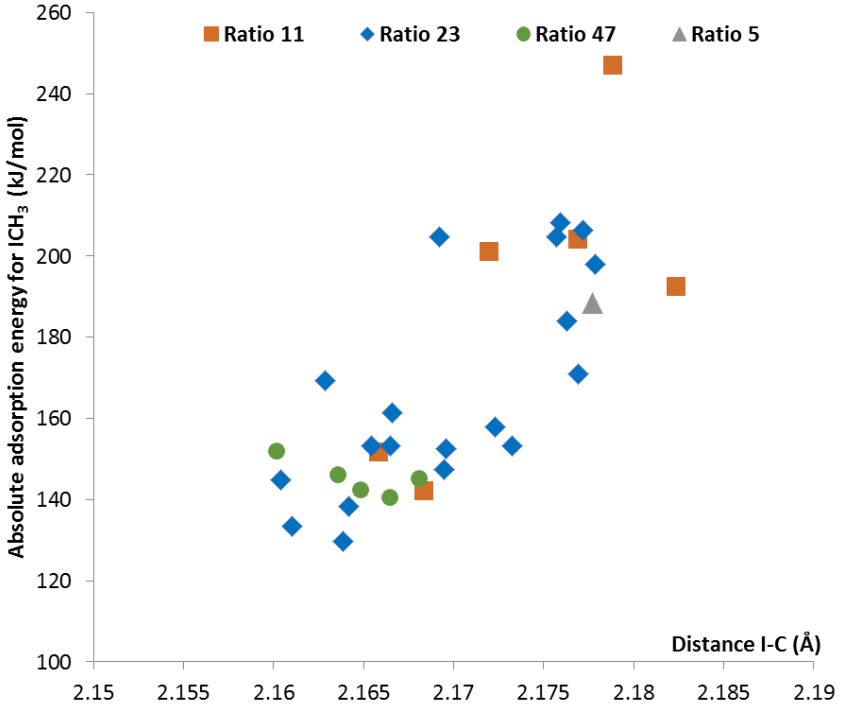
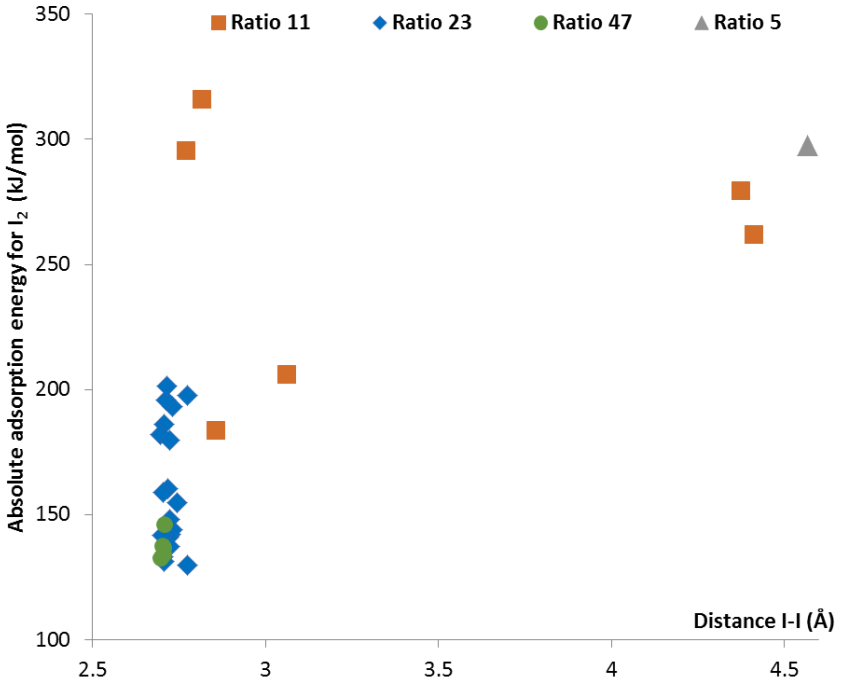
Ag-MOR: Effect of the Si/Al ratio

bond activation to … spontaneous dissociation



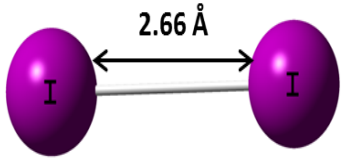
ICH_3

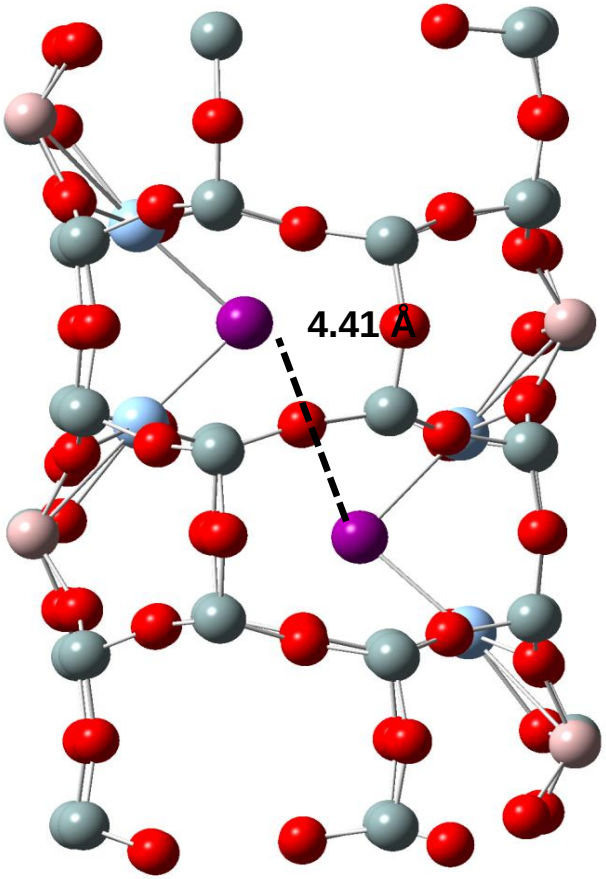


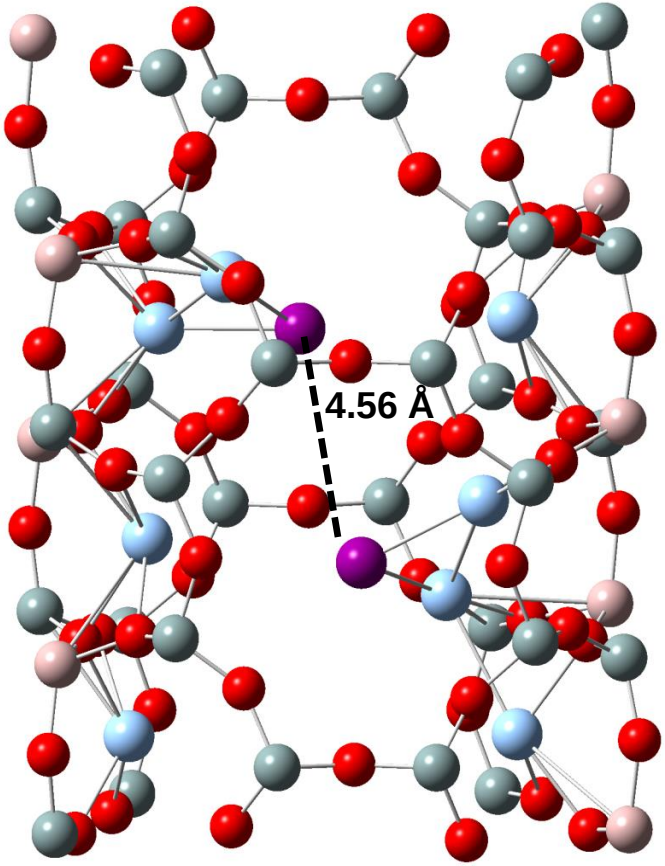
I_2

S. Chibani, M. Chebbi, S. Lebègue, L. Cantrel, M. Badawi, *Impact of the Si/Al ratio on the selective capture of iodine compounds in silver-mordenite: a periodic DFT study*, Phys. Chem. Chem. Phys. 18 (2016) 25574

Effect of the Si/Al ratio in Ag-MOR : Dissociation of I_2



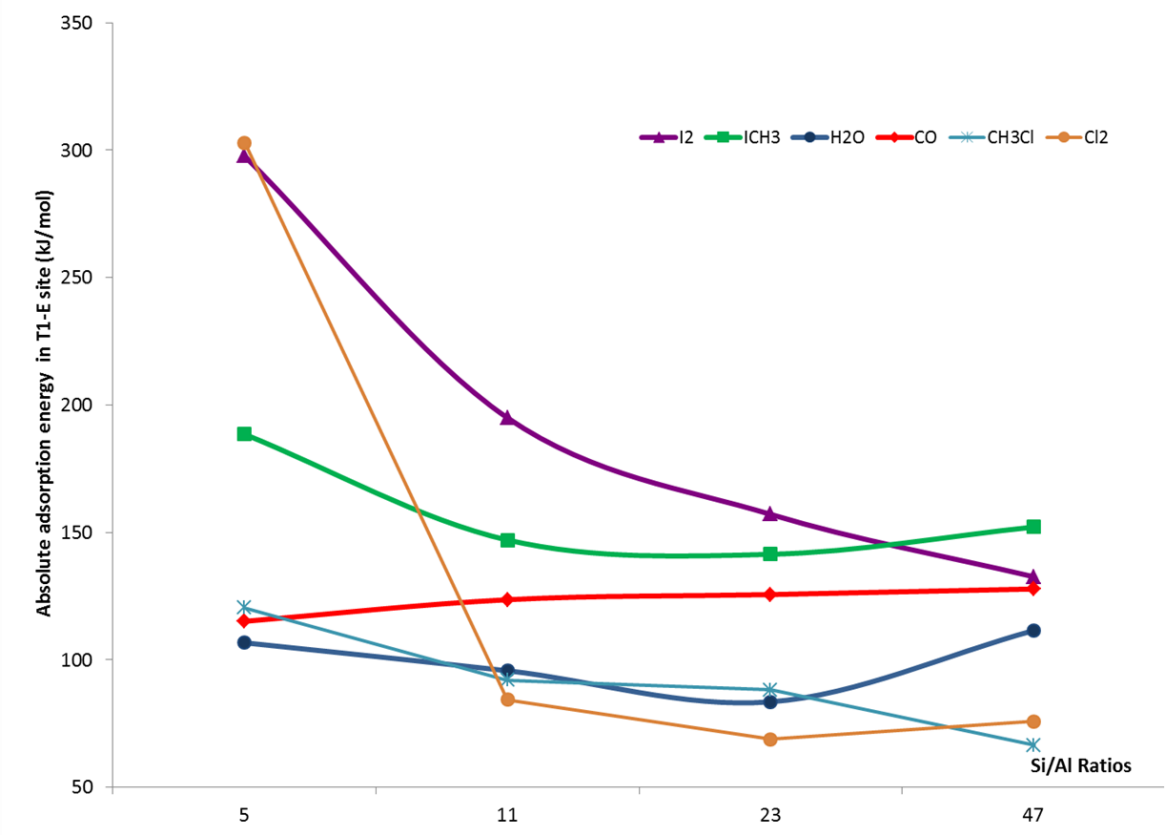




Si/Al = 11 **Si/Al = 5**

S. Chibani, M. Chebbi, S. Lebègue, L. Cantrel, M. Badawi, *Impact of the Si/Al ratio on the selective capture of iodine compounds in silver-mordenite: a periodic DFT study*, Phys. Chem. Chem. Phys. 18 (2016) 25574

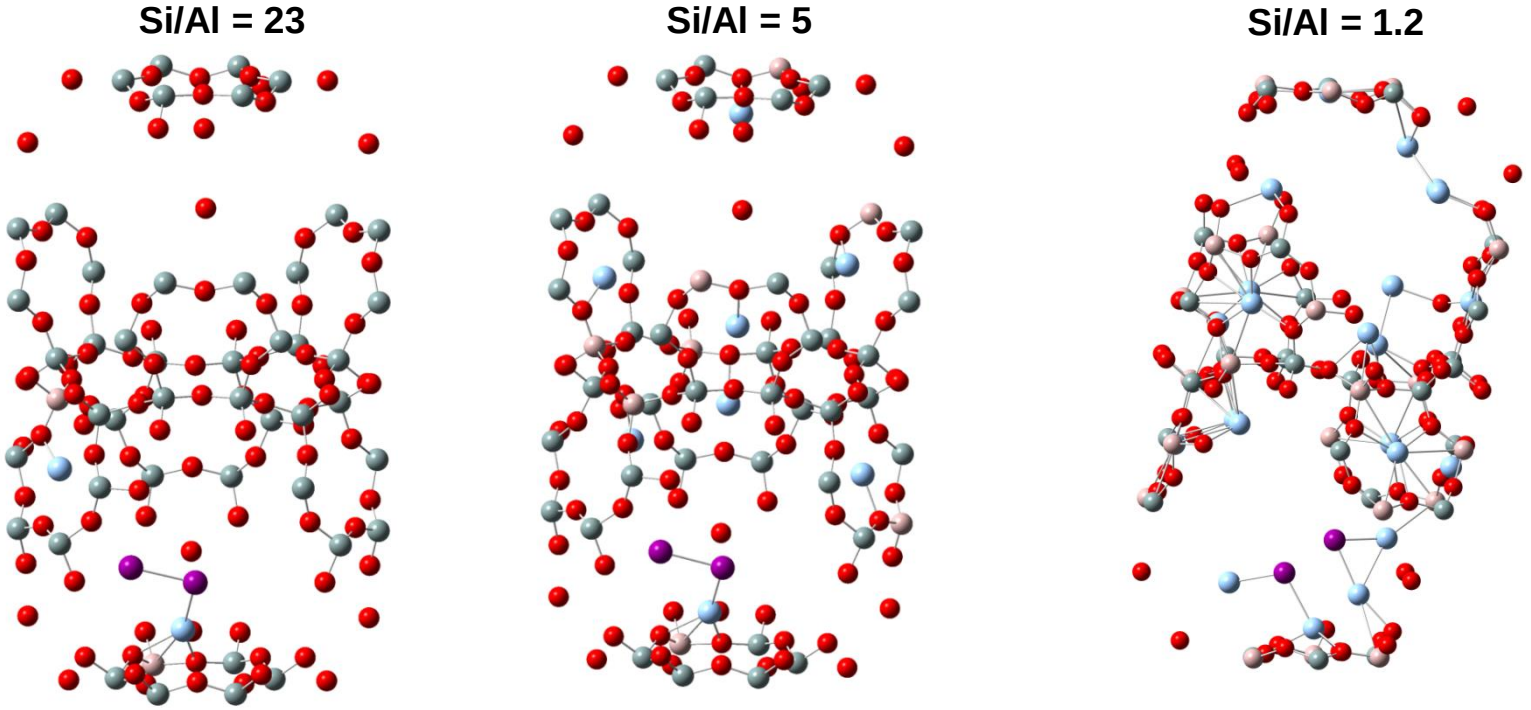
Effect of the Si/Al ratio in Ag-MOR : Summary



Decreasing the Si/Al ratio (i.e. increasing the silver content) improve the adsorption selectivity of iodine compounds

S. Chibani, M. Chebbi, S. Lebègue, L. Cantrel, M. Badawi, *Impact of the Si/Al ratio on the selective capture of iodine compounds in silver-mordenite: a periodic DFT study*, Phys. Chem. Chem. Phys. 18 (2016) 25574

Effect of Si/Al ratio in Ag-FAU

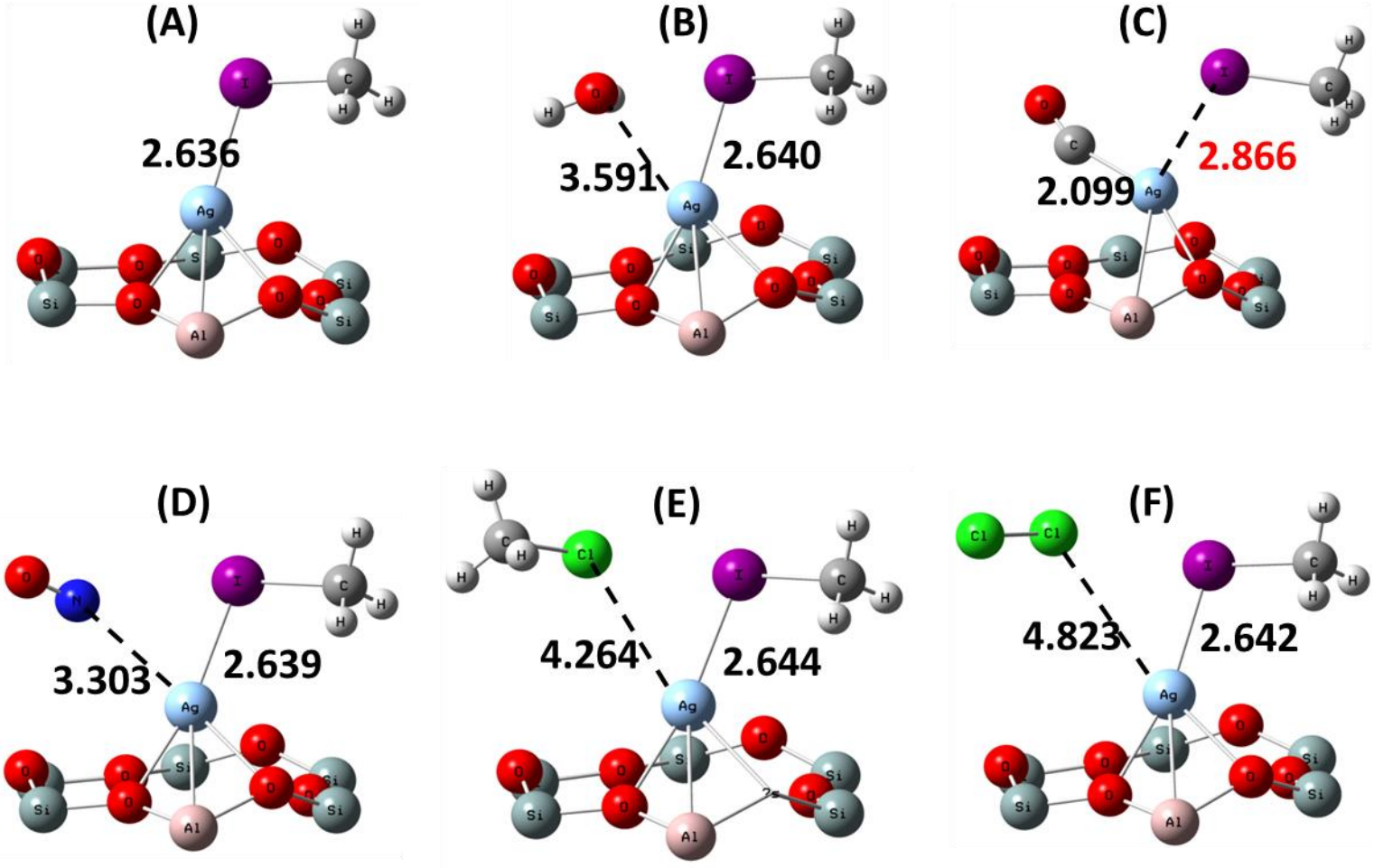


Molecule / ratio	47	23	5	1.2
CO	-114	/	/	-160 (bidentate)
CH_3I	-118	/	/	-148 (bidentate)
I_2	-108	-107	-103	**-257 (dissociated)**

Decreasing the Si/Al ratio (i.e. increasing the silver content) improve the adsorption selectivity of iodine compounds

S. Chibani, M. Chebbi, S. Lebègue, L. Cantrel, M. Badawi, *Impact of the Si/Al ratio on the selective capture of iodine compounds in silver-mordenite: a periodic DFT study*, Phys. Chem. Chem. Phys. 18 (2016) 25574

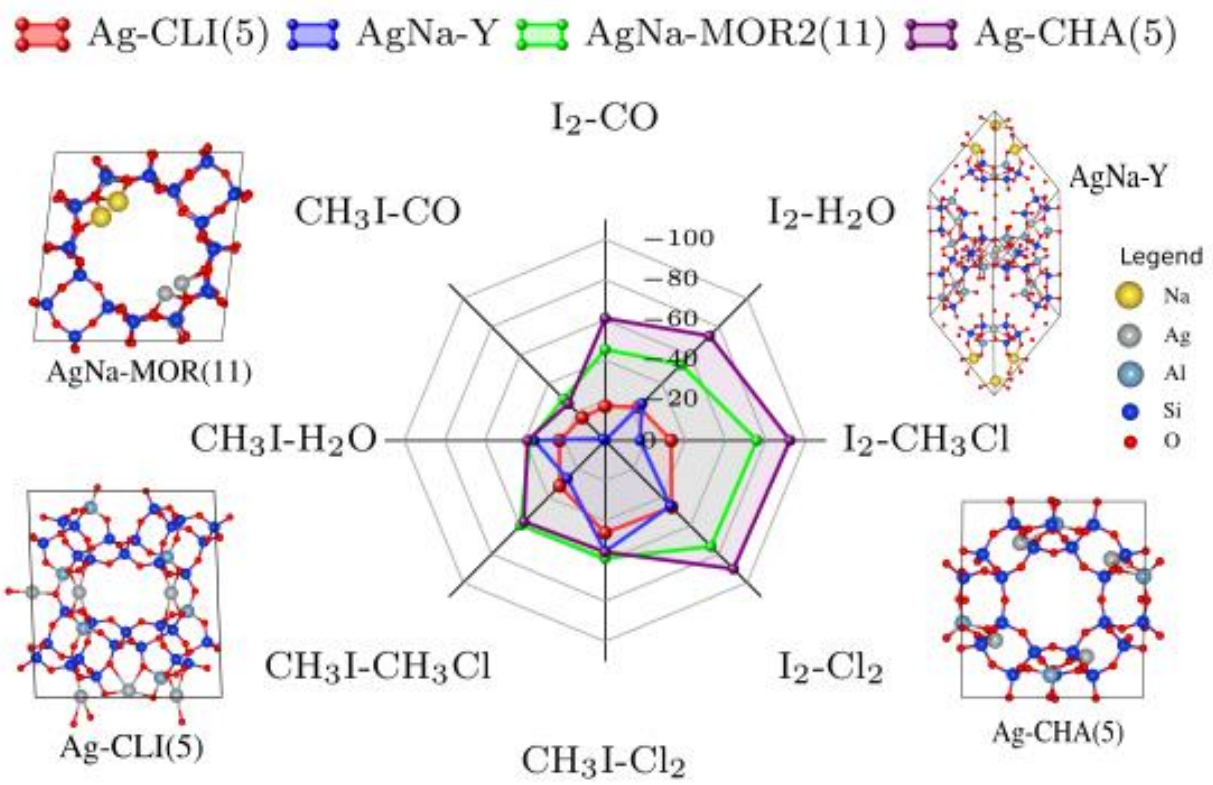
Coadsorption: Ag-FAU



- Only presence of CO increases the Ag-I bond

M. Chebbi, S. Chibani, J.-F. Paul, L. Cantrel, M. Badawi, Evaluation of volatile iodine trapping in presence of contaminants: a periodic DFT study on cation exchanged-faujasite, Micro. Meso. Mater. 239 (2017) 111

Screening of several structures of silver zeolites



Radar plot to identify the best formulations

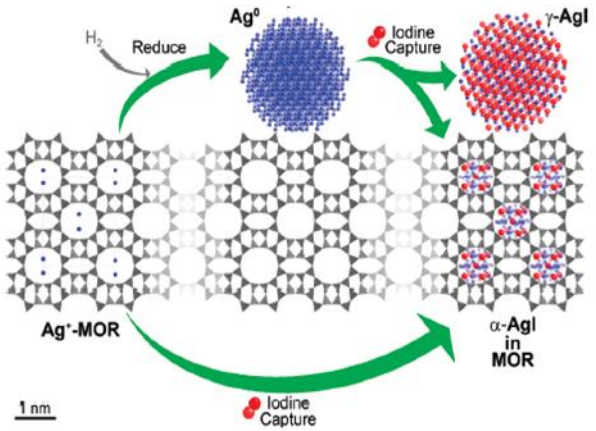
T. Ayadi et al, Molecular Systems Design and Engineering, just accepted

Trapping mechanism more complex

What do we know from experiment?

- proportionality between Ag^+ content and sorption capacity
- up to two CH_3I per a silver site [1]

- **formation of $(AgI)_n$ clusters of size ~7 Å [2] containing about 4 AgI units [3]**



- formation of products such as CH_4, C_2H_4, C_3H_6, C_3H_8, C_2H_6O, or CH_3OH [3]

- analogy with well-known zeolite chemistry suggests reaction route involving alkoxy species [3]:

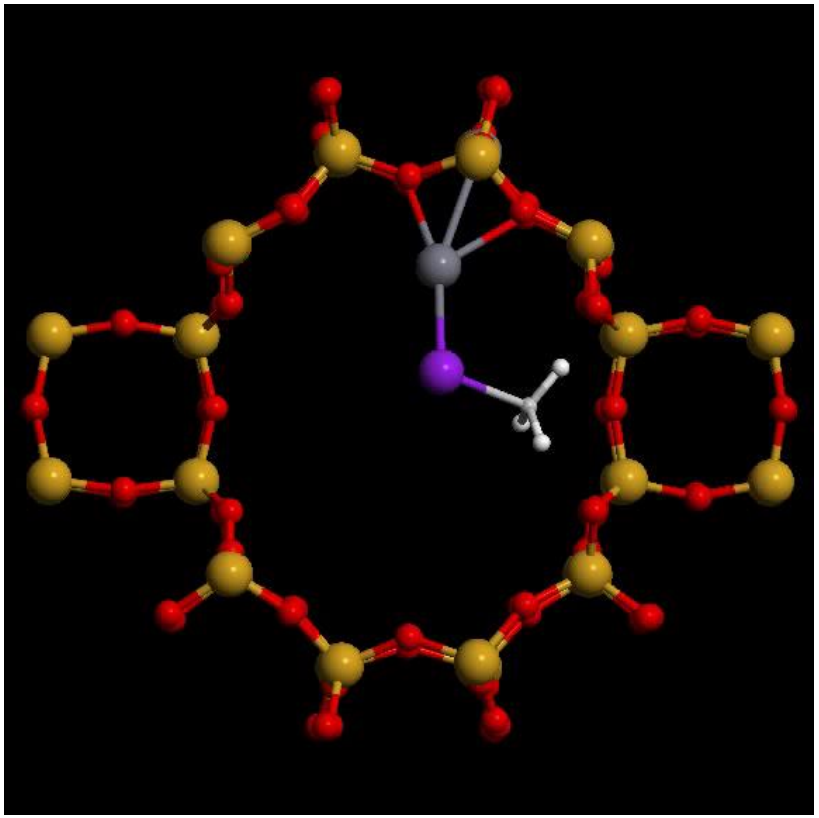
$$CH_3I + Ag\text{-}Zeo \longrightarrow CH_3\text{-}Zeo + AgI$$

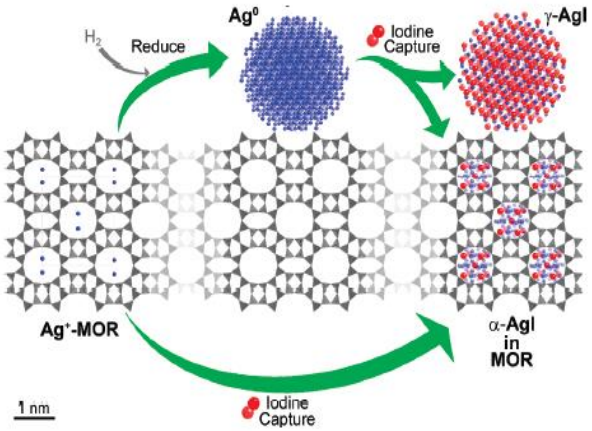
Molecular Adsorption → Dissociation of CH_3I → ?? → AgI phase

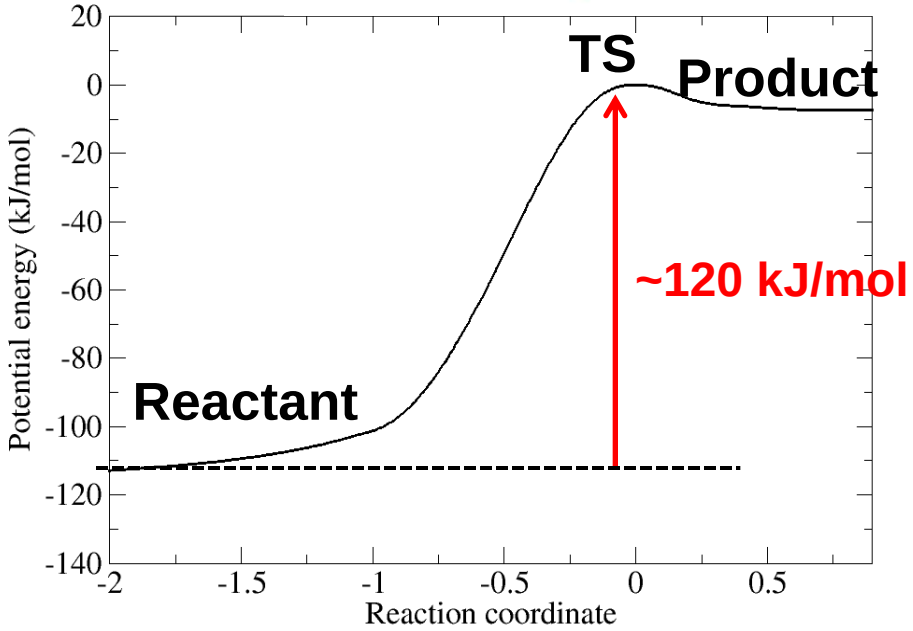
[1] A. Belapurkar et a., Surf. Technol. 21 (1984) 263.
[2] K.W. Chapman et al., J. Am. Chem. Soc. 132 (2010) 8897.
[3] M. Chebbi et al., J. Phys. Chem. C 120 (2016) 18694–18706.

Dissociation of CH_3I to form AgI phase

- Iodine compounds are chemisorbed as a first step
- **Towards a durable, irreversible trapping : formation of AgI phase*** K. W. Chapman, P. J. Chupas, T. M. Nenoff, J. Am. Chem. Soc. 132 (2010) 8897-8899
- Si/Al = 47, Static Transition State Theory







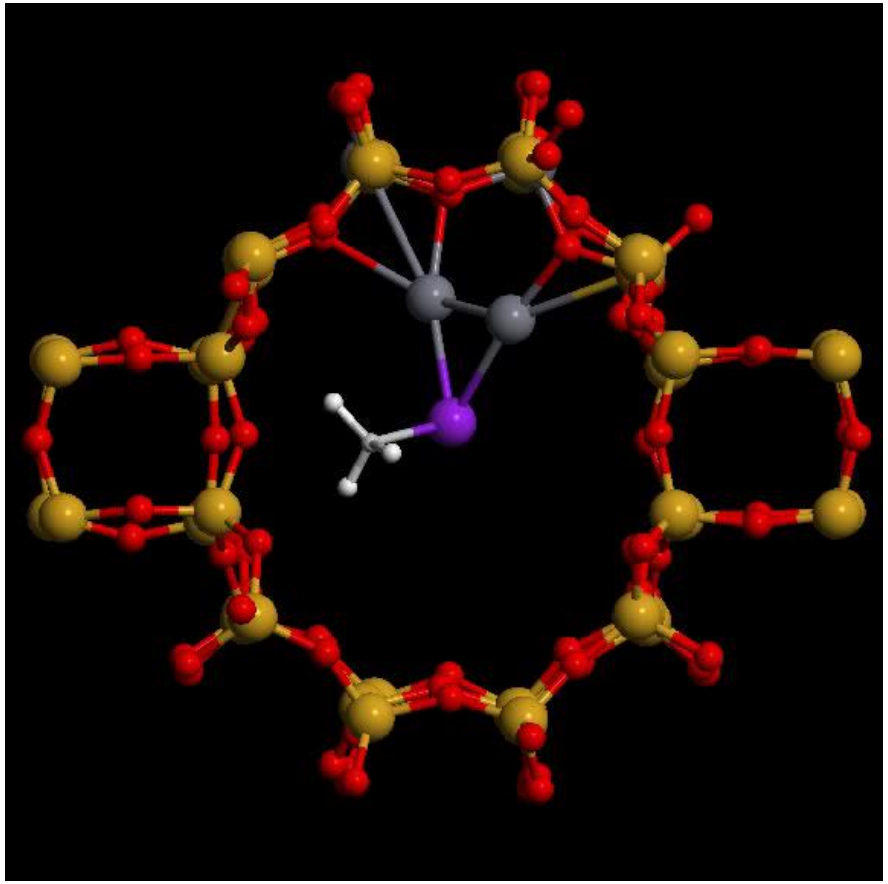
- ICH_3 dissociation ⟹ formation of O-CH_3 and AgI

Ab initio Molecular dynamics

- Ab initio Molecular dynamics
- NVT ensemble (T= 373 K)
- Nose-Hoover thermostat
- Integration step: Δt = 1 fs
- **For free energy calculations:**
- **Slow-growth method***

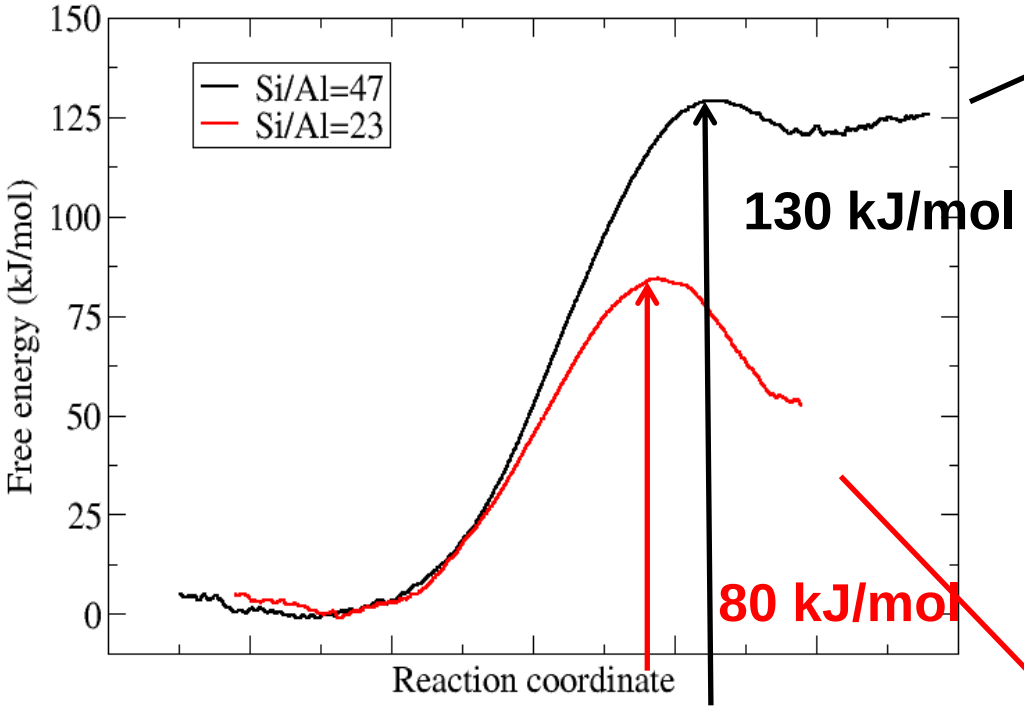
**J. Phys. Chem. B*, 1997, 101 (40), pp 7877–7880

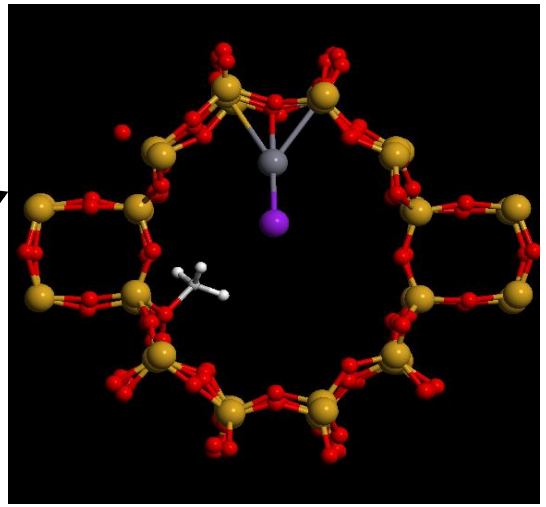
- Si/Al = 23, MD simulations, T= 373 K

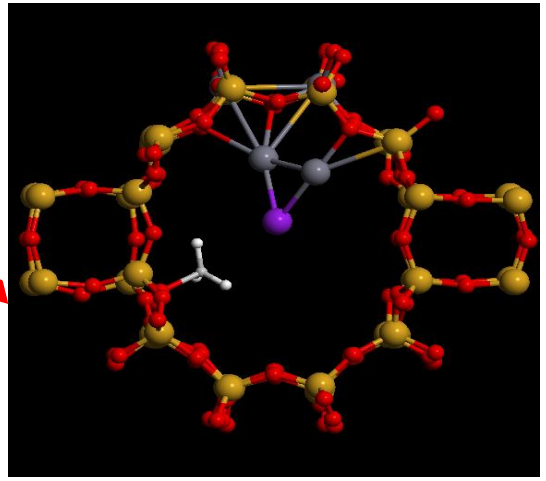


Si : yellow
O : red
Ag : grey
I : purple
H : white

Effect of Si/Al ratio

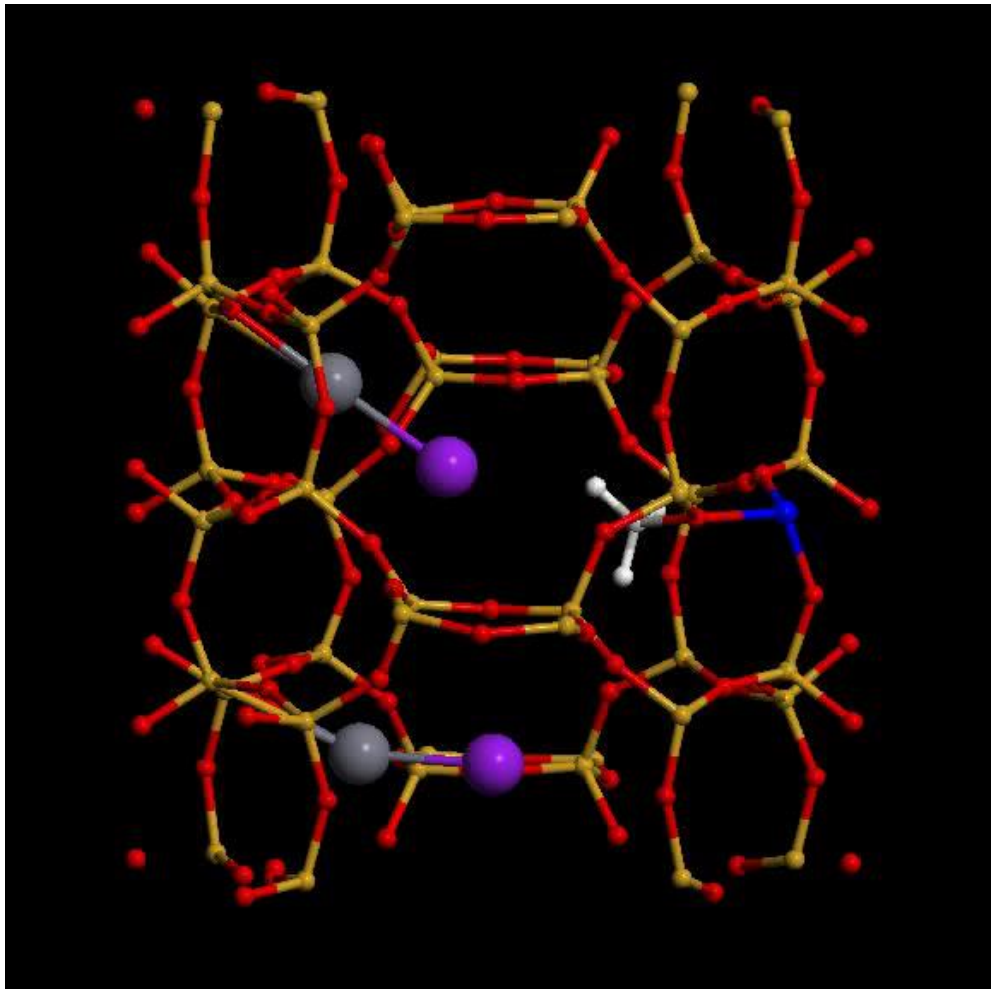






Formation of AgI phase : Mechanism

- charge-neutral AgI units are free to move in the MC and form clusters spontaneously



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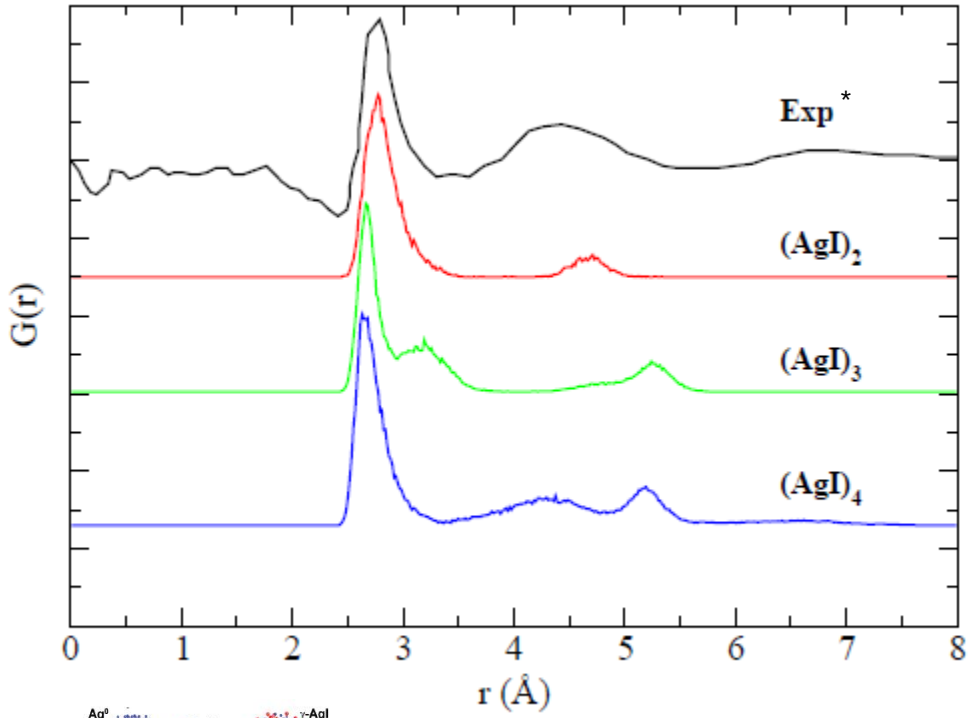
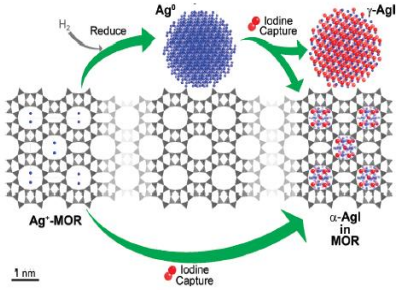
I : purple
H : white

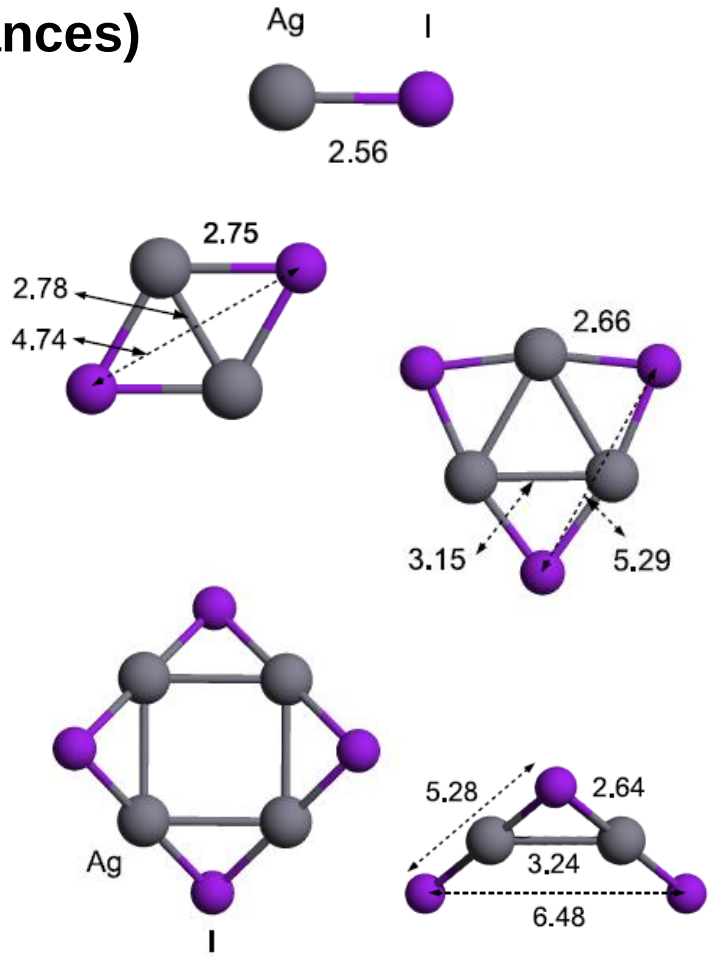
T. Bučko, S. Chibani, J.-F. Paul, L. Cantrel, M. Badawi, *Dissociative iodomethane adsorption on Ag-MOR and formation of AgI clusters: an ab-initio molecular dynamics study*, Phys. Chem. Chem. Phys. 19 (2017) 27530--27543

Formation of AgI phase (Pair Distribution Function)

PDF (average Ag-Ag, Ag-I or I-I distances)







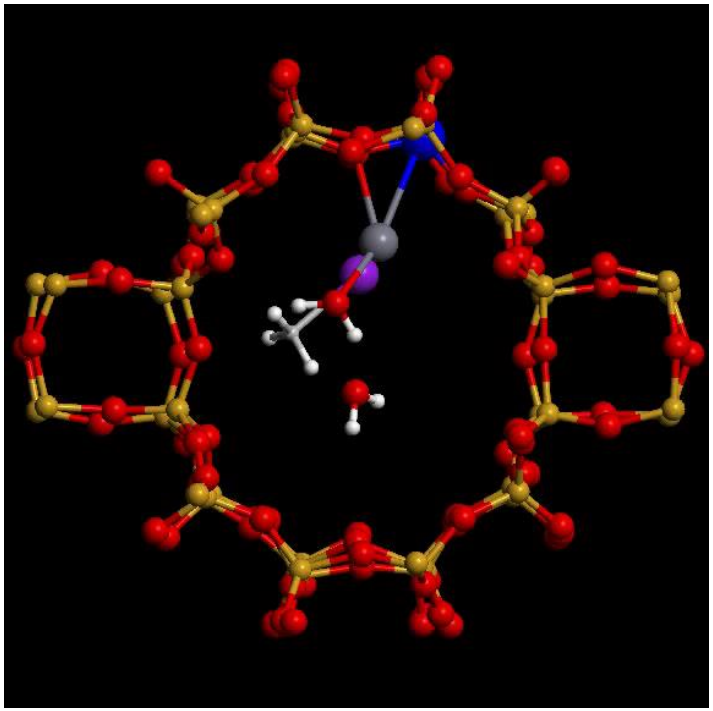
* K. W. Chapman, P. J. Chupas, T. M. Nenoff, J. Am. Chem. Soc. 132 (2010) 8897-8899

T. Bučko, S. Chibani, J.-F. Paul, L. Cantrel, M. Badawi, *Dissociative iodomethane adsorption on Ag-MOR and formation of AgI clusters: an ab-initio molecular dynamics study*, Phys. Chem. Chem. Phys. 19 (2017) 27530--27543

Perspectives for iodine trapping

- adsorbent for the use in technological applications must be efficient in the presence of water, CO, Cl_2 and CH_3Cl

- competition for adsorption sites? decrease of free-energy barrier via increased mobility upon co-adsorption?



✓ Effect of water on the dissociation of iodine compounds
✓ Formation of iodide precipitate phases **(AgI vs AgCl)**

Outline

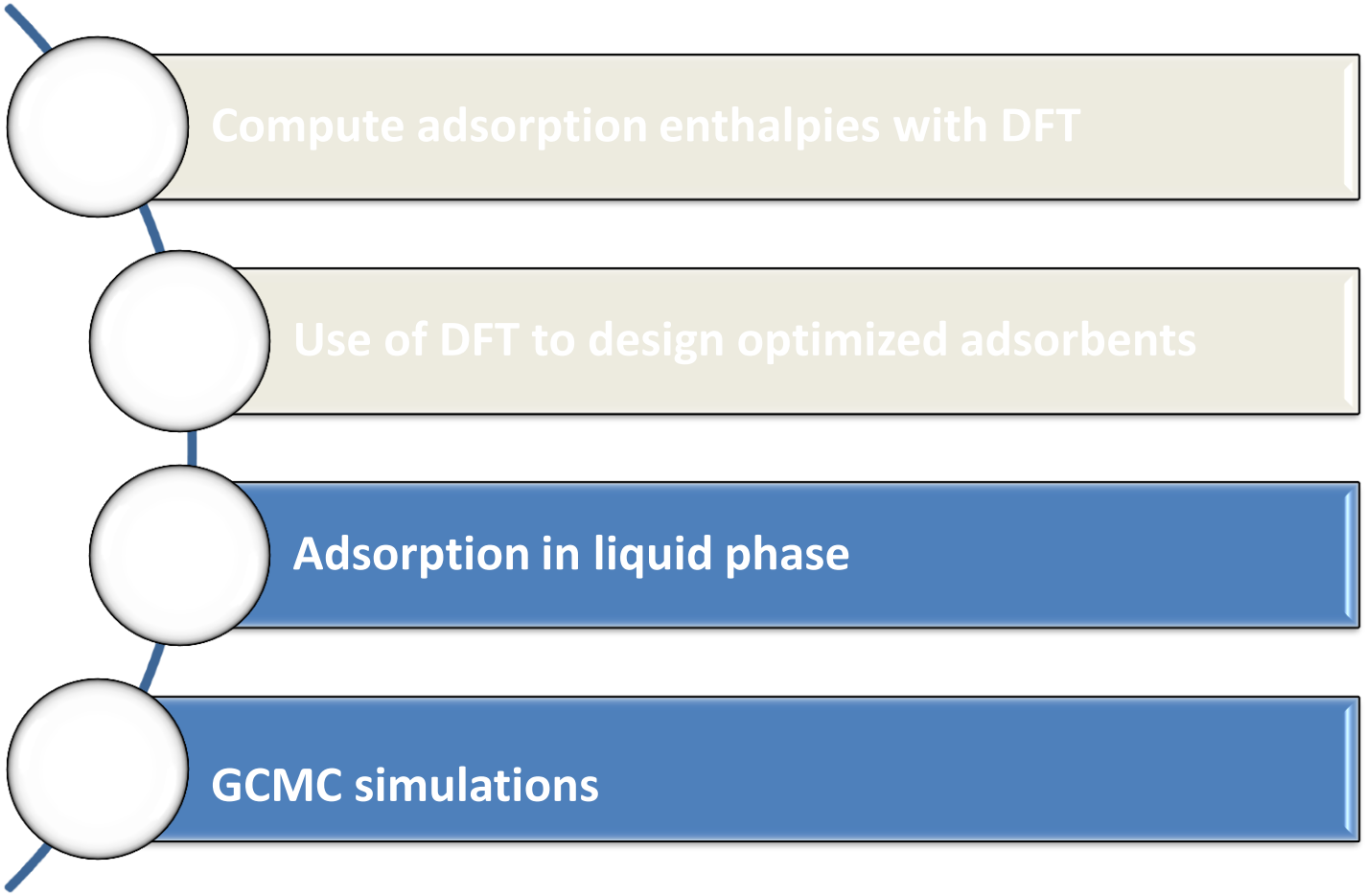
Adsorption performances

- ✓ **Ag^+ is the most selective monovalent cation**
- ✓ CO can inhibit adsorption of iodine compounds over Ag-FAU and Ag-MOR under severe nuclear accident conditions
- ✓ Decrease the Si/Al ratio (i.e. increase the silver content) improves significantly the adsorption selectivity of iodine species

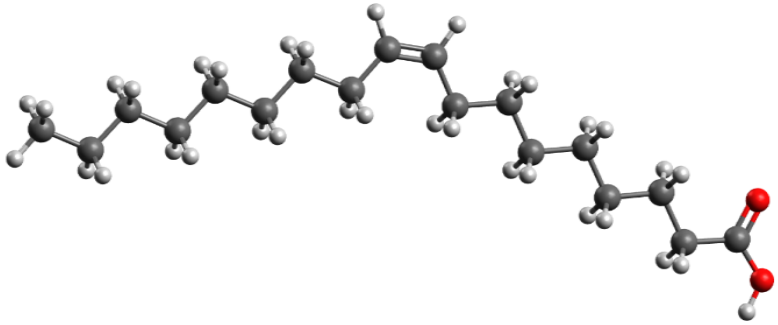
Mechanistic study

- ✓ Dissociation of iodine compounds to form AgI phase : durable trapping
- ✓ Effect of Si/Al ratio : increase silver content favor C-I bond cleavage
- ✓ Outline: Effect of water on the dissociation of iodine compounds
- ✓ Outline 2 : Formation of iodide precipitate phases **(AgI vs AgCl)**

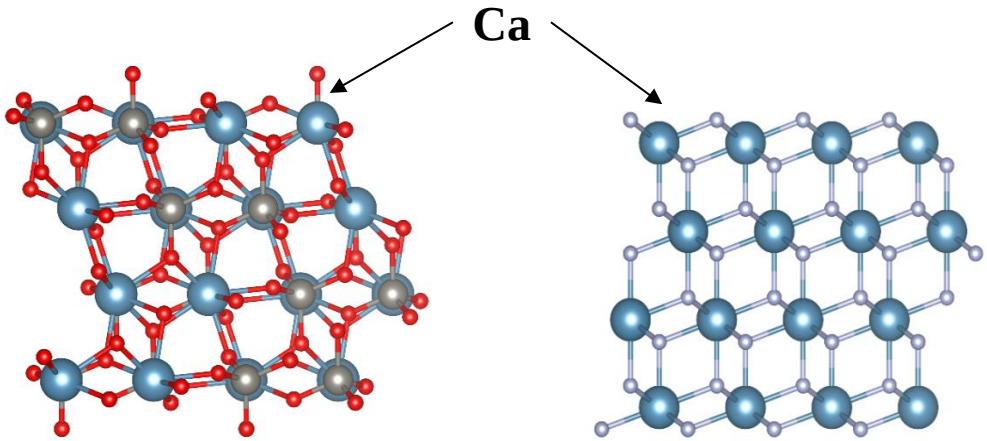
- **Here, we have to design one material to separate two or more gaseous species**
- **Why not considering a more complex issue? Design one chemical reagent to separate many minerals? => Minerals Enginnering, and in liquid phase!**


Compute adsorption enthalpies with DFT
Use of DFT to design optimized adsorbents
Adsorption in liquid phase
GCMC simulations

Part 3
Adsorption in liquid phase



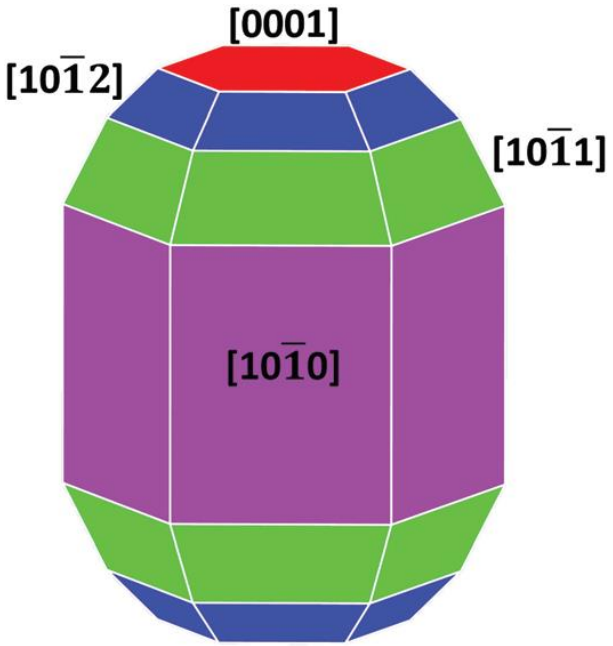
Undestanding the adsorption mechanisms of collectors and depressants onto minerals is a key step to design new efficient flotation reagents

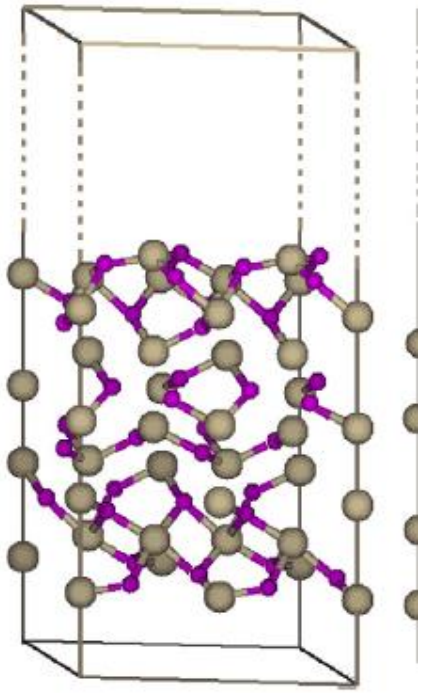


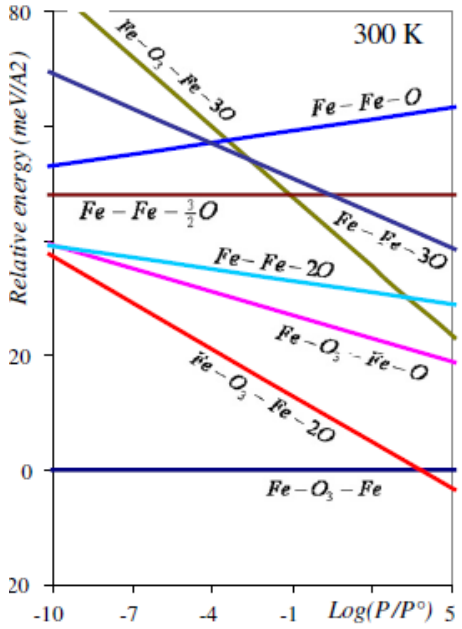
Scheelite

Fluorite

Modeling of crystals in water







- Several surfaces exposed
- Surface state under operating conditions : water, pH
- Adsorption of reagents in water ….

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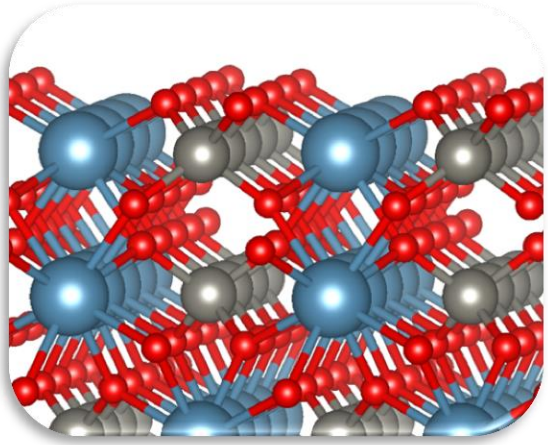
Methodology

Exposed surfaces



(001)

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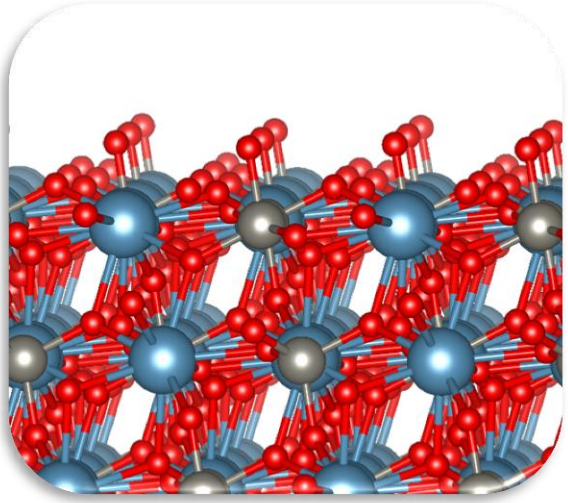

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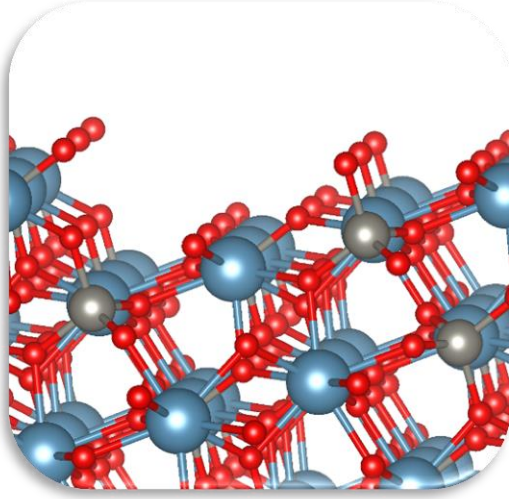

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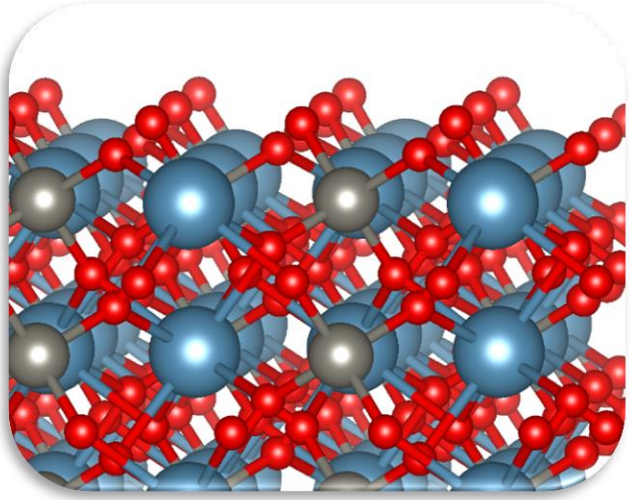

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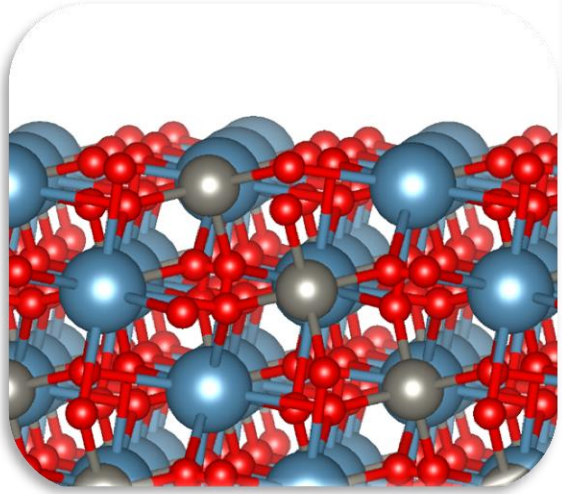


(110)

Methodology

Hydration

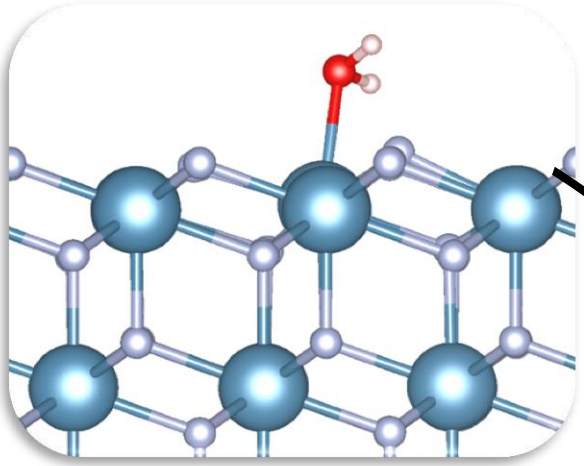
- Adsorption of molecular water?
- Adsorption of dissociated water, leading to a hydroxylation of surface cations?
- Substitution of a surface anion by a hydroxyl group (HO^-)?
- Influence of the surface on several water layers at the interface?

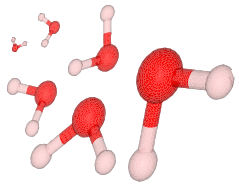
Adsorption of reagents

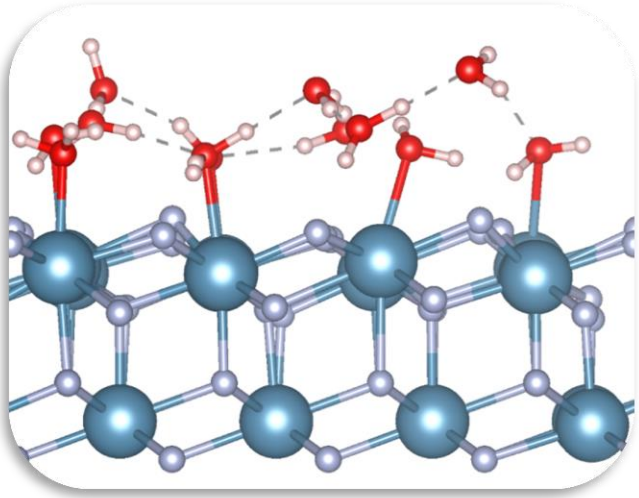
- Adsorption of one collector molecule on the hydrated surface
- Adsorption of several collectors until 100% surface coverage
- Tune chemical functions of the collector
- Mixture of different collectors : synergetic effect?

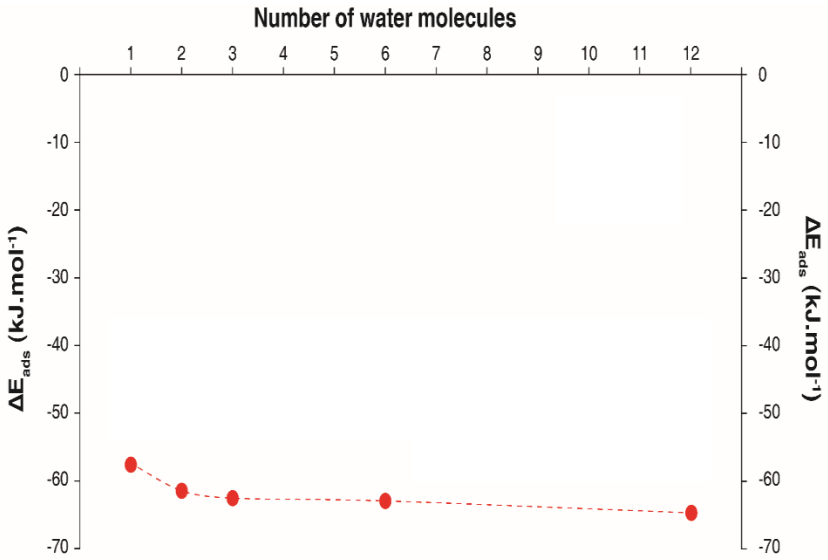
Results - Hydration

Hydration of fluorite (111)









Molecular water

ΔE_{ads} = **-55.9 kJ.mol^{-1}**

Dissociated water

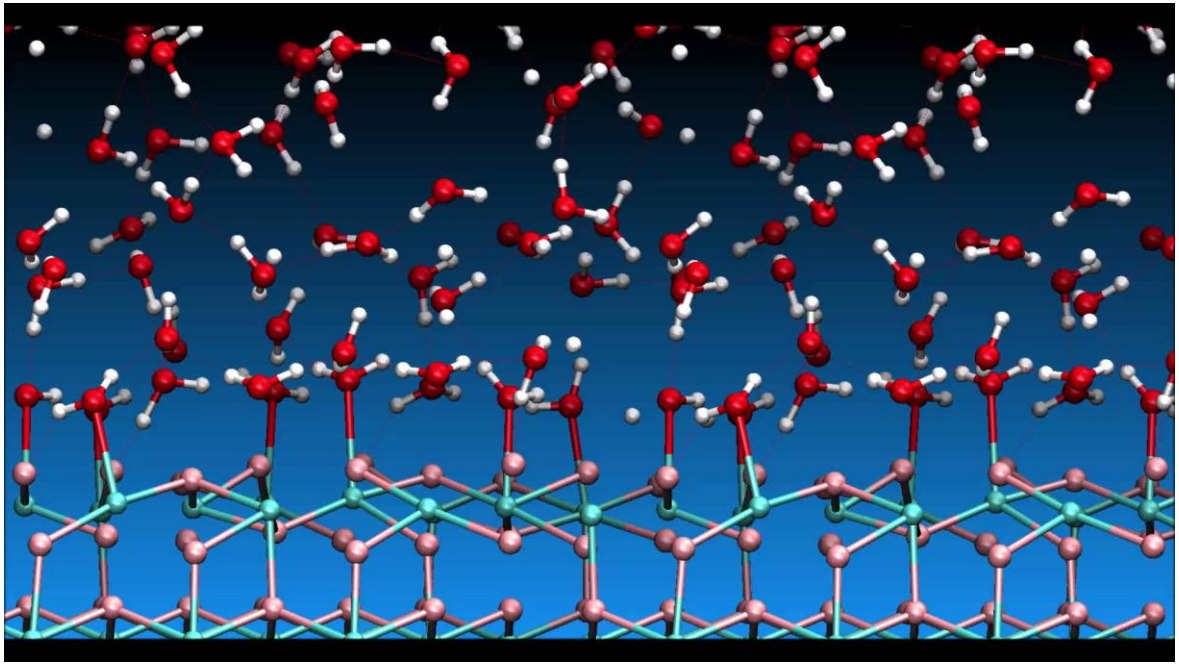
ΔE_{ads} = **+247.8 kJ.mol^{-1}**

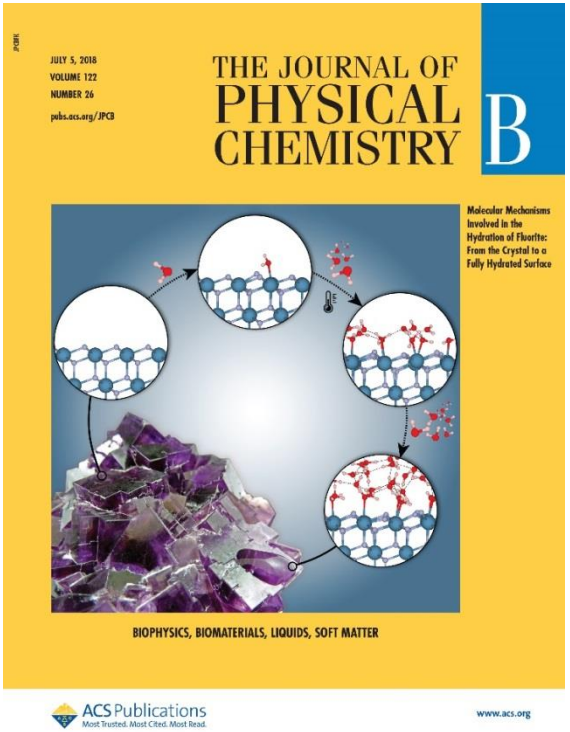
- **Dissociated water highly disfavoured**
- **Half of surface Ca atoms occupied by adsorbed H_2O molecules**
- **Temperature?**

Foucaud et al., J. Phys. Chem B, 2018, 122 (26), pp 6829–6836

Results - Hydration

Hydration of fluorite (111)



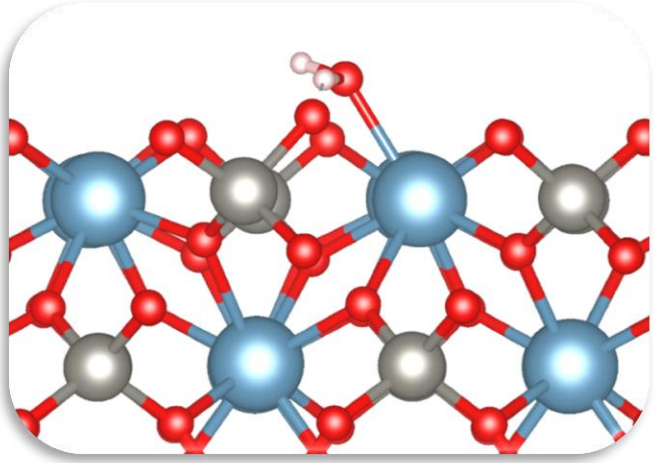


T = 300 K, ρ = 1 g.cm^{-3}, t = 60 ps

Foucaud et al. J. Phys. Chem. B, 2018, 122 (26), pp 6829–6836 (10.1021/acs.jpcb.8b02717)

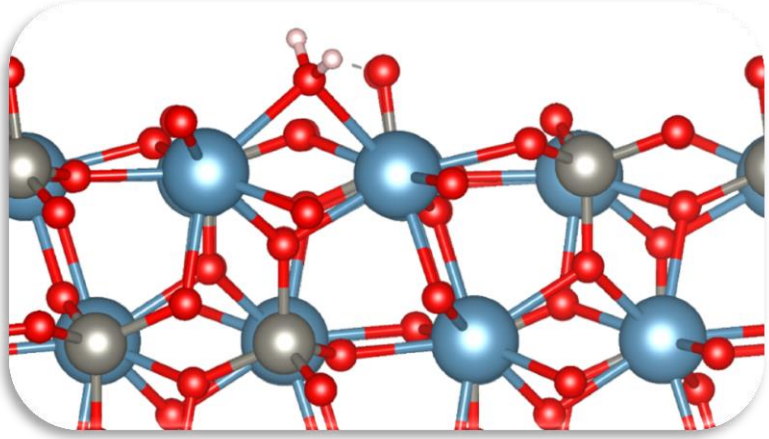
Results - Hydration

Hydration of scheelite

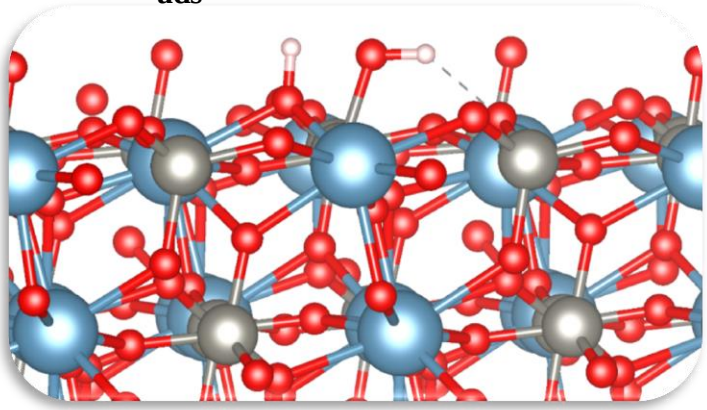


(001) surface
Molecular water
ΔE_{ads} = -87.8 kJ.mol^{-1}

Dissociated water
ΔE_{ads} = +11.4 kJ.mol^{-1}



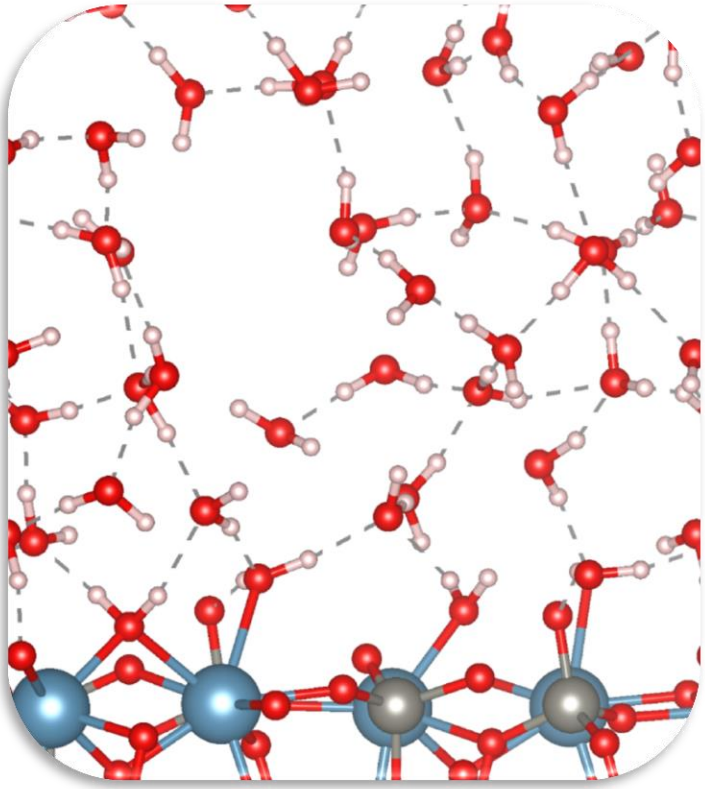
(112) surface
Molecular water
ΔE_{ads} = -131.9 kJ.mol^{-1}



(112) surface
Dissociated water
ΔE_{ads} = -91.0 kJ.mol^{-1}

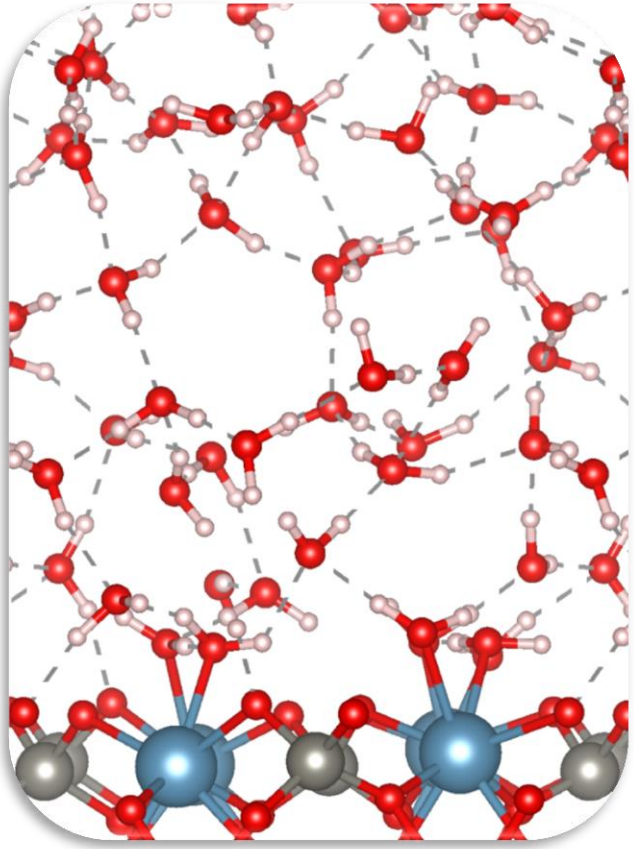
Results - Hydration

Hydration of scheelite



Surface (112)
1 adsorbed molecular water per surface calcium atom

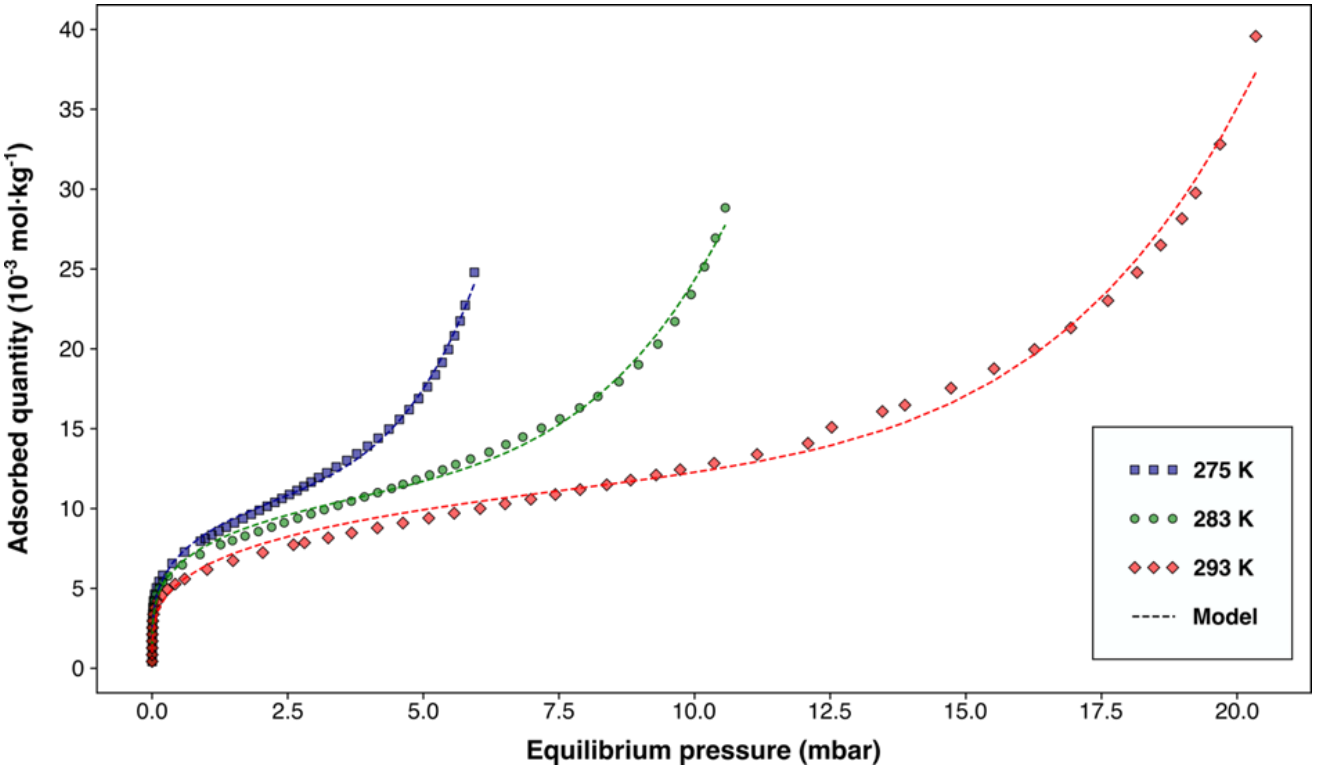
T = 300 K
t = 50 ps
$\rho = 1\ g.cm^{-3}$



Surface (001)
3 adsorbed molecular water per 2 surface calcium atoms

Results - Hydration

Hydration of scheelite : experimental results

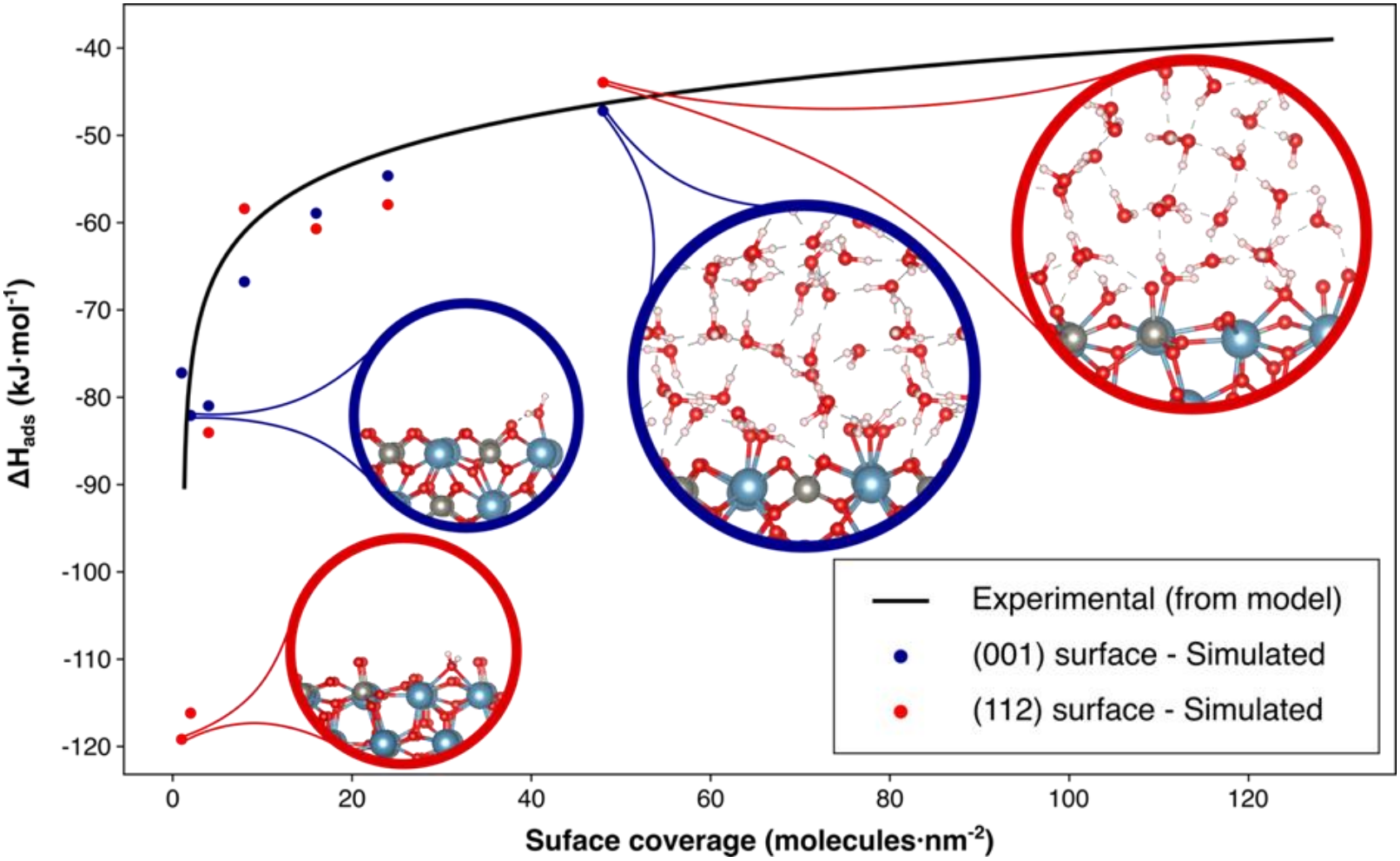


Adsorption isotherms of gas water on scheelite at 275, 283, and 293 K (dots) and their fits with the Dual-Site Freundlich-Langmuir model (Eq. 4, dashed lines).

Y. Foucaud, R.L.S. Canevesi, A. Celzard, V. Fierro, M. Badawi, **Applied Surface Science** 562 (2021) 150137 (IF 2020 = 6,7).
https://doi.org/10.1016/j.apsusc.2021.150137

Results - Hydration

Hydration of scheelite



Y. Foucaud, R.L.S. Canevesi, A. Celzard, V. Fierro, M. Badawi, **Applied Surface Science** 562 (2021) 150137 (IF 2020 = 6,7).
https://doi.org/10.1016/j.apsusc.2021.150137

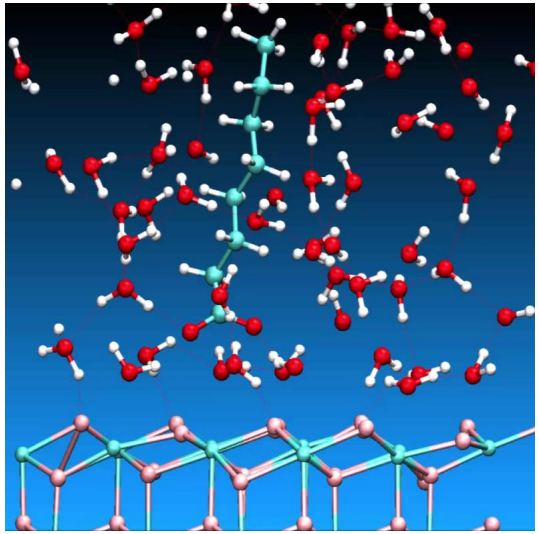
Investigation of the adsorption of collectors

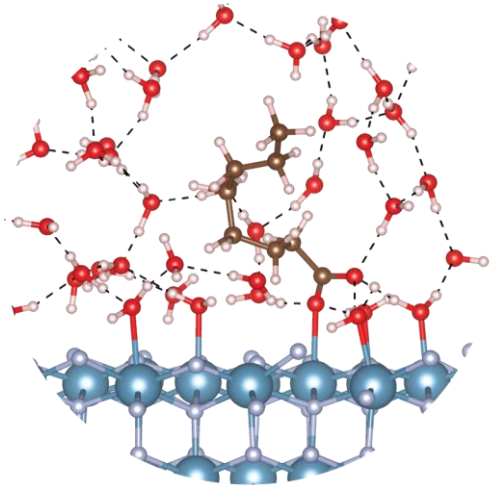
Procedure

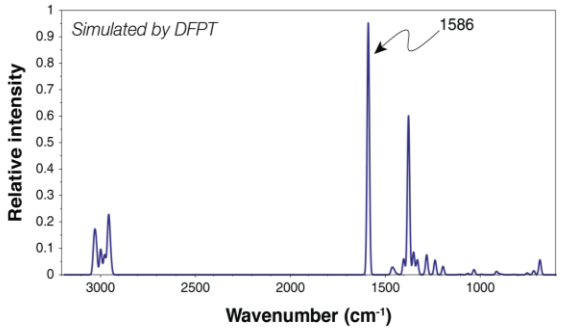
1 – AIMD : finding the most realistic configuration under real conditions (H_2O and 300 K)

2 – DFPT : Infrared spectra simulation

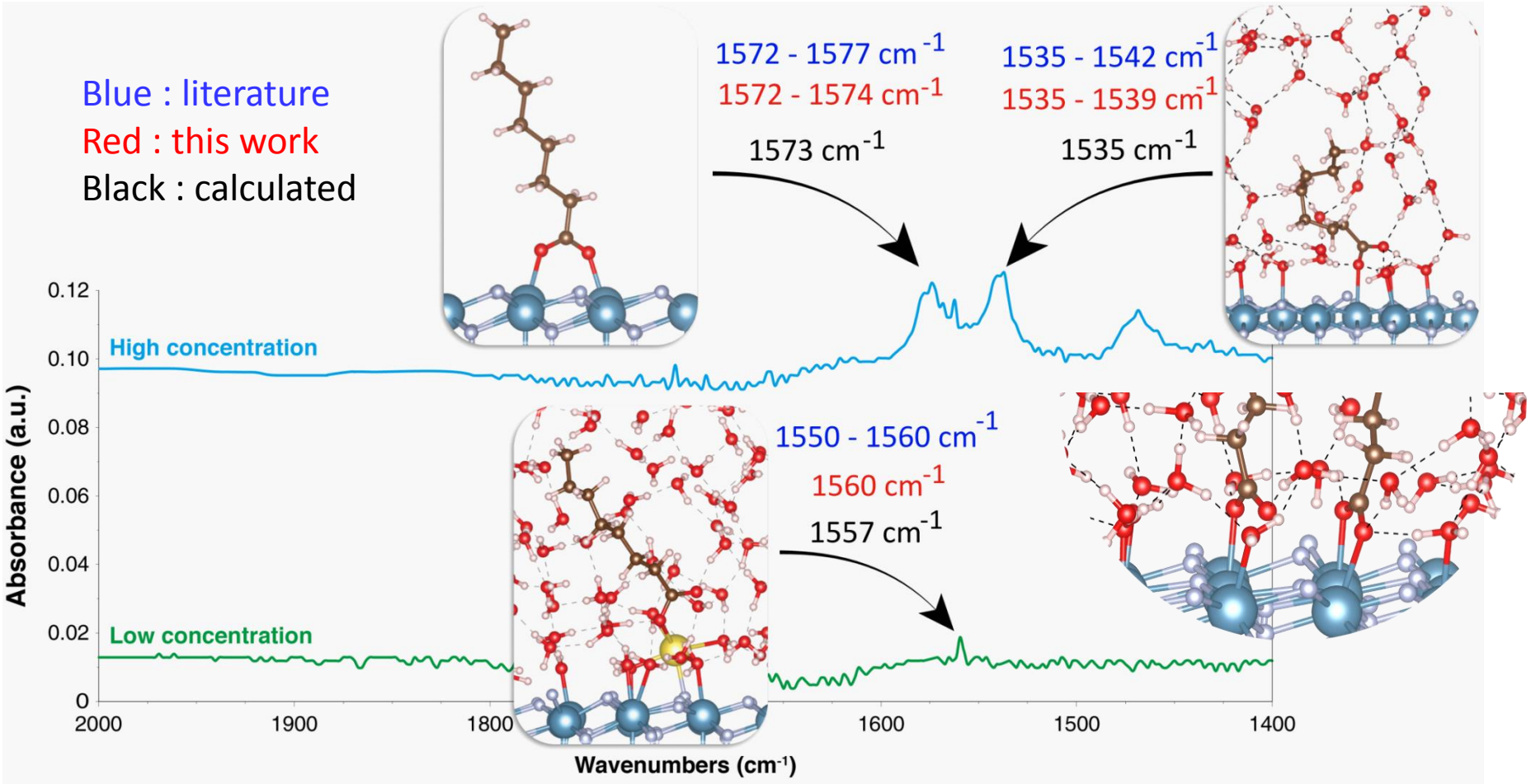
3 – Comparison with FTIR/DRIFT results







Results on collectors



Conclusion on collectors

- **The role of the counter cation that initiates the formation of the adsorption layer** seems to be important
- This study offers new perspectives to understand the flotation mechanisms and enhance them
- Modelling of the **adsorbed monolayers**

Journal of Colloid and Interface Science 583 (2021) 692–703

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Adsorption mechanisms of fatty acids on fluorite unraveled by infrared spectroscopy and first-principles calculations

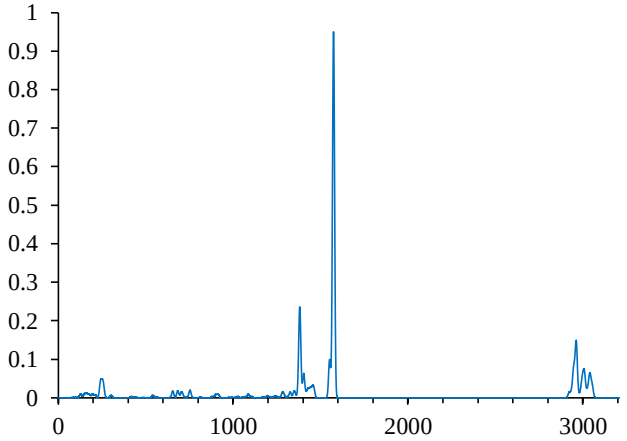
Yann Foucaud [a,*], Juliette Lainé [b], Lev O. Filippov [a,c], Odile Barrès [a], Won June Kim [d], Inna V. Filippova [a], Mariachiara Pastore [b,*], Sébastien Lebègue [b,*], Michael Badawi [b,*]

[a] Université de Lorraine and CNRS, GeoRessources, F54000 Nancy, France
[b] Université de Lorraine and CNRS, LPCT, F54000 Nancy, France
[c] National University of Science and Technology MISIS, 119049 Moscow, Russia
[d] Changwon National University, Department of Biology and Chemistry, South Korea

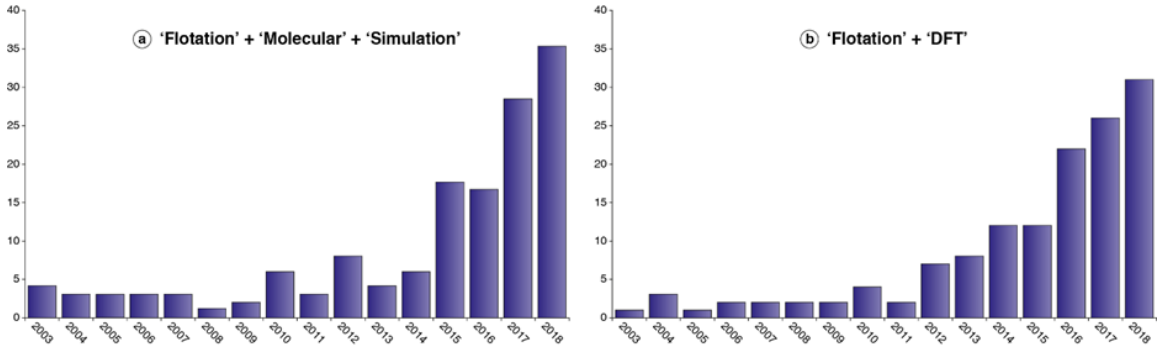
Conclusions

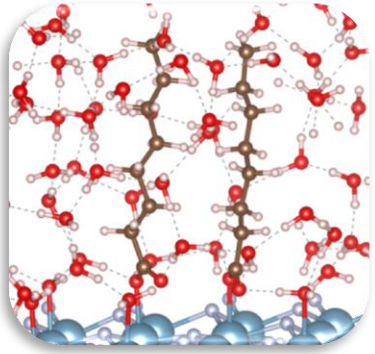
What does molecular modelling bring?

- Geometry of adsorbed molecules
- Adsorption energy (for each type of molecule)
- n°-adsorption energy
- FTIR/Raman simulated spectra
- XPS calculated density of states



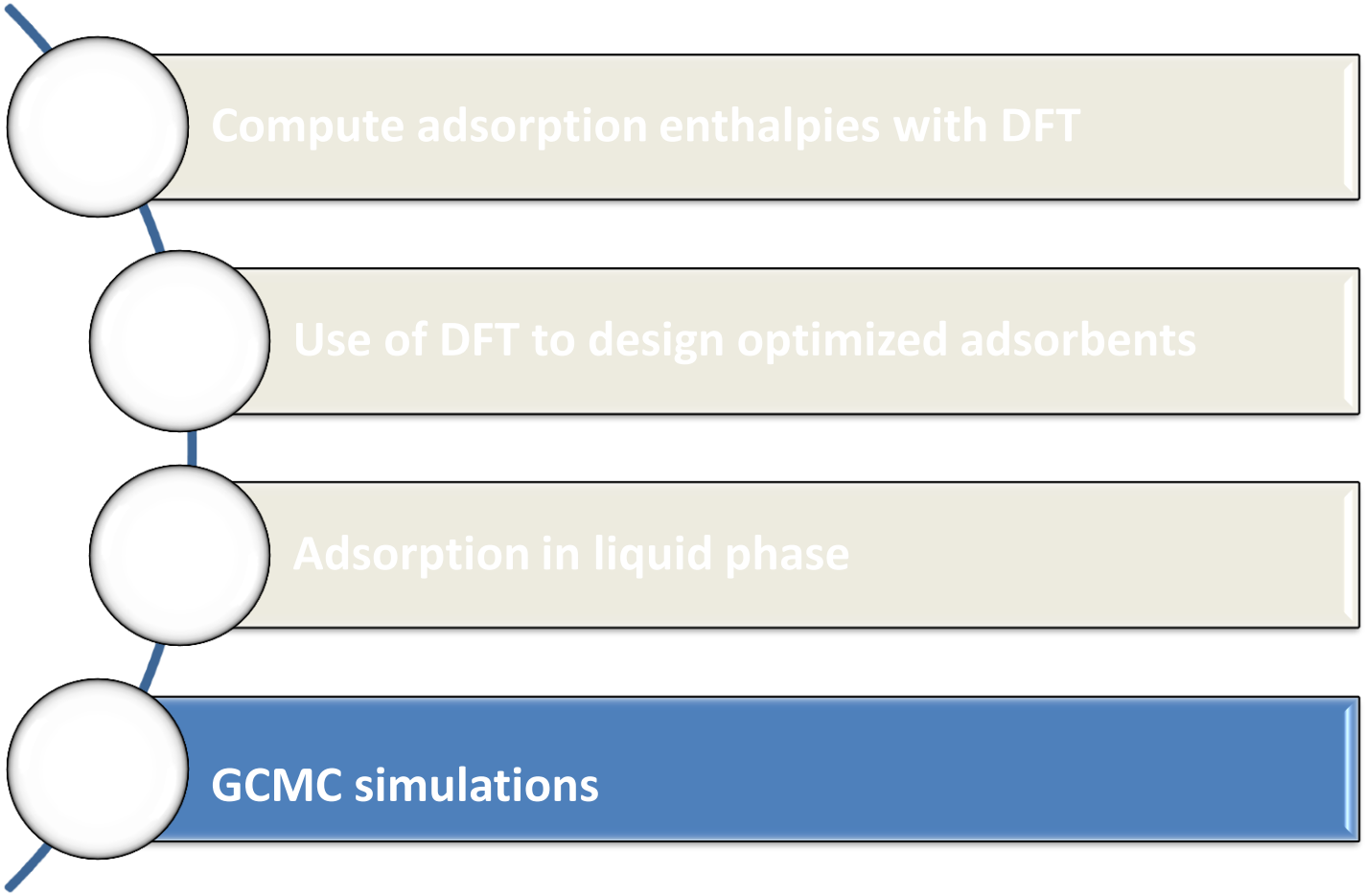
Minerals engineering and molecular modelling, an emerging topic





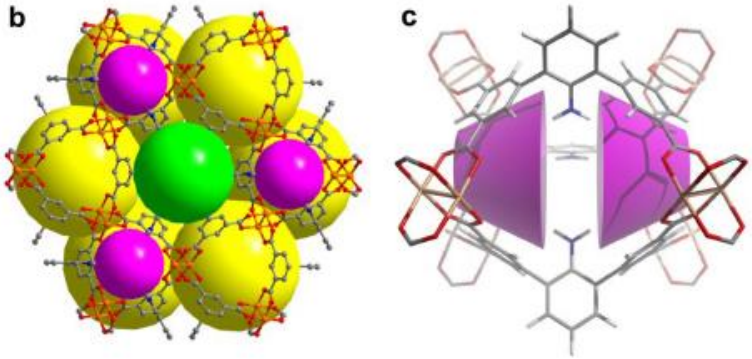
- Associate the high precision of DFT with the high time/system size of CMD
- Surface topography ? Mineral dissolution ?
- Modulate the reagents combinations, types, and concentration

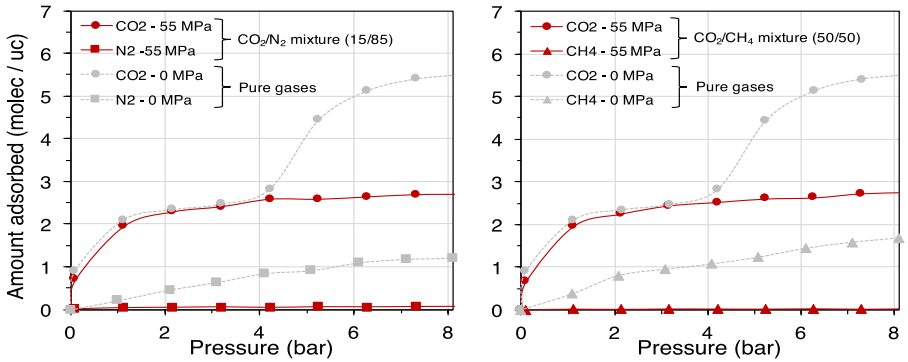
Y. Foucaud, M. Badawi, L.O. Filippov, I.V. Filippova, S. Lebègue, *A review of atomistic simulation methods for surface physical-chemistry phenomena applied to froth flotation*, Minerals Engineering 143 (2019) 106020


Compute adsorption enthalpies with DFT
Use of DFT to design optimized adsorbents
Adsorption in liquid phase
GCMC simulations

ICG Montpellier | Institut Charles Gerhardt DA MP

Part 4
Grand Canonical Monte Carlo Simulations of Metal Organic Frameworks





Thanks to Prof. Guillaume Maurin
For providing the following supports

Monte Carlo simulations
Input

Microscopic description of the Porous solids & Guest molecules

✓ Porous solids

- Crystallographic data / Computational assisted structure determination
- Partial charges (quantum calculations)
- Specific flexible forcefield or generic UFF/Dreiding

✓ Guests

- CO_2 & N_2 : rigid LJ 3 points charge model (EPM2 & TraPPE)
- H_2 & *n*-alkane : rigid 1 LJ neutral United Atom model
- Aromatics (benzene + xylenes) : TraPPE Explicit model

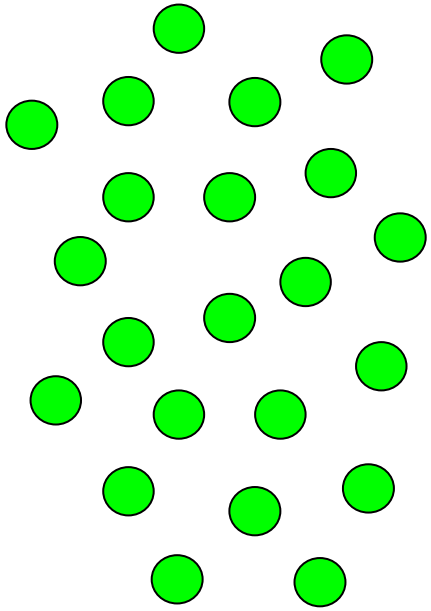
Description of the Porous solids/Guest interactions

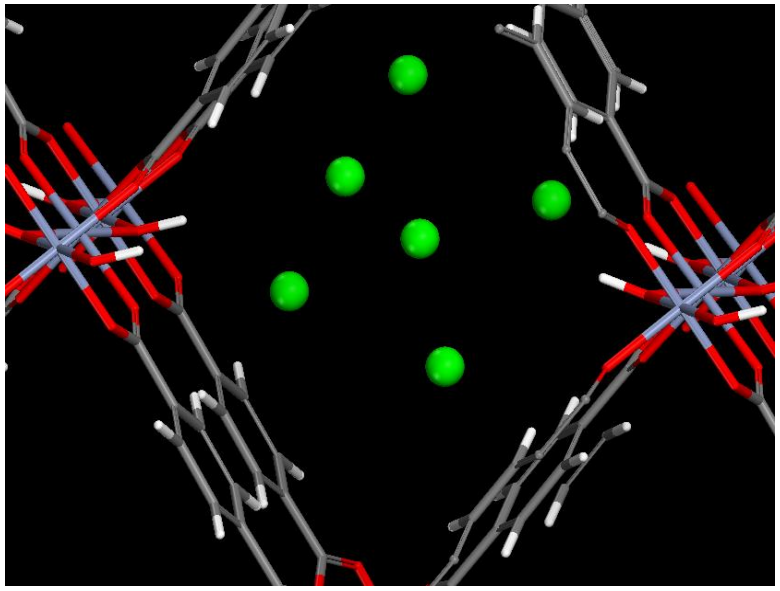
$$U(r_{ij}) = \frac{q_i q_j}{r_{ij}} + 4\varepsilon_{ij}\left(\left[\frac{\sigma_{ij}}{r_{ij}}\right]^{12} - \left[\frac{\sigma_{ij}}{r_{ij}}\right]^{6}\right)$$

Grand Canonical Monte Carlo strategy

(μVT) Ensemble : fluctuation of the number of molecules

μ (gas in the reservoir) = μ (adsorbed gas)





✓ $\mu = \mu^{\circ} + RT \ln f/f^{\circ}$ ⇨ (μVT) ⇔ (fVT) or (pVT) for ideal gas

For a given T & p, knowledge of the equilibrium concentration of the gas inside the porous solids

Grand Canonical Monte Carlo strategy

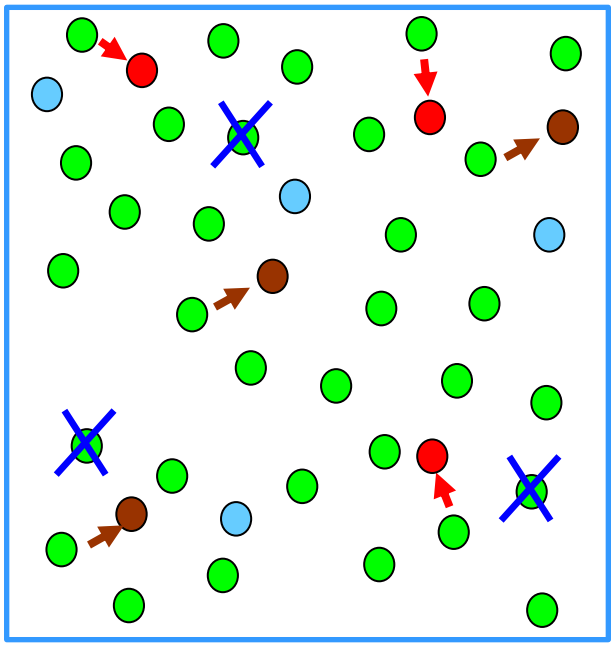
Possible Monte Carlo moves

Displacements (translations & rotations)

Creations

Destructions

Identity change (A→B)



Generation of millions of MC configurations accepted/rejected with appropriate criteria (Metropolis algorithm)

Probability of Acceptance for a MC move: $P = \min\{1, \exp(-\beta\Delta U)\}$

Probability of Acceptance for a MC creation: $P = \min\left\{1, \frac{\beta f V}{N+1}\exp(-\beta\Delta U)\right\}$

Probability of Acceptance for a MC deletion $P = \min\left\{1, \frac{N}{\beta f V}\exp(-\beta\Delta U)\right\}$

Grand Canonical Monte Carlo strategy

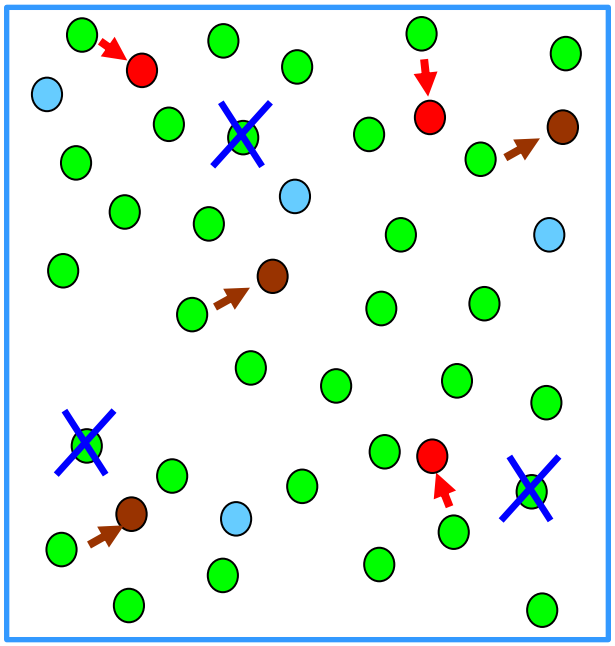
Possible Monte Carlo moves

Displacements (translations & rotations)

Creations

Destructions

Identity change (A→B)



Generation of millions of MC configurations accepted/rejected with appropriate criteria (Metropolis algorithm)

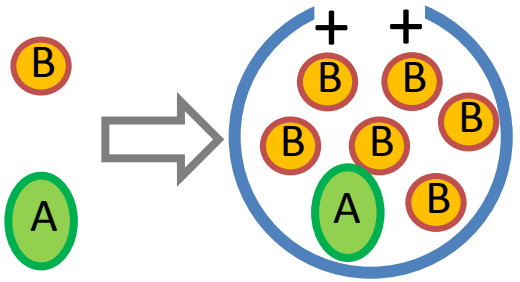
Output

- ✓ Adsorption isotherms for single component and mixture
- ✓ Adsorption enthalpy: $D_{ads}h = RT - \frac{\langle U.N\rangle - \langle U\rangle\langle N\rangle}{\langle N^2\rangle - \langle\langle N\rangle\rangle^2}$
- ✓ Selectivity: $S(A/B) = \frac{x_A}{x_B}\frac{y_B}{y_A}$ x: adsorbed phase, y: gas phase
- ✓ Microscopic co-adsorption mechanism

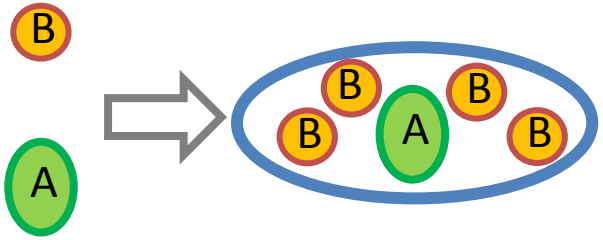
Strategies for the selective adsorption in porous materials

✓ « **Thermodynamics** » : enhancement of the affinity of the porous materials for the molecule we wish to adsorb

→ Incorporation of specific adsorption sites

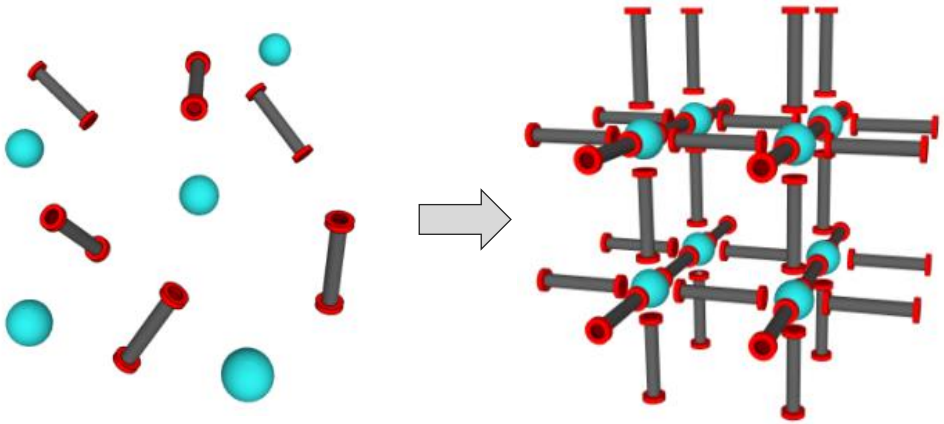


→ High degree of confinement

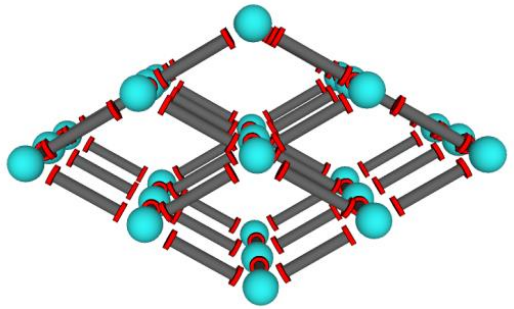


Model Porous Materials

Hybrid porous solids : Metal Organic Frameworks (MOFs)

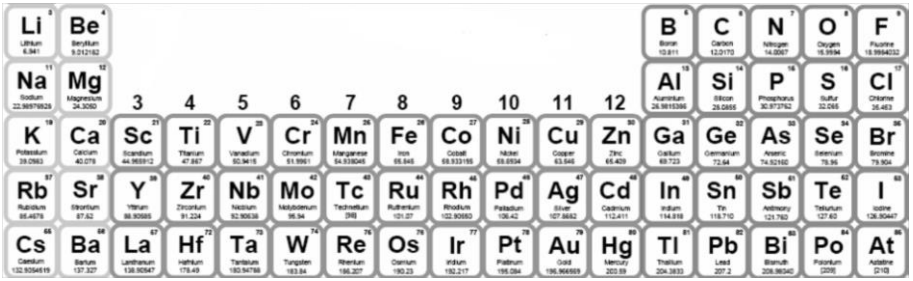


or

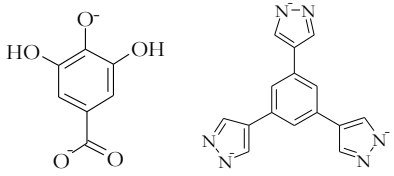


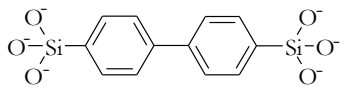
or …

Metal ions



Linkers





or …

Versatile chemistry & topology/connectivity: More than 30,000 MOF structures in CSD

Motivation

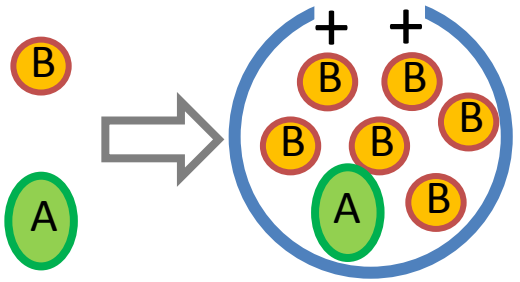
Strategies for the selective adsorption in porous materials

✓ « **Thermodynamics** » : enhancement of the affinity of the porous materials for the molecule we wish to adsorb

→ Incorporation of specific adsorption sites

(i) Case 1 : Ligand functionalization

(ii) Case 2 : Coordinatively unsatured sites



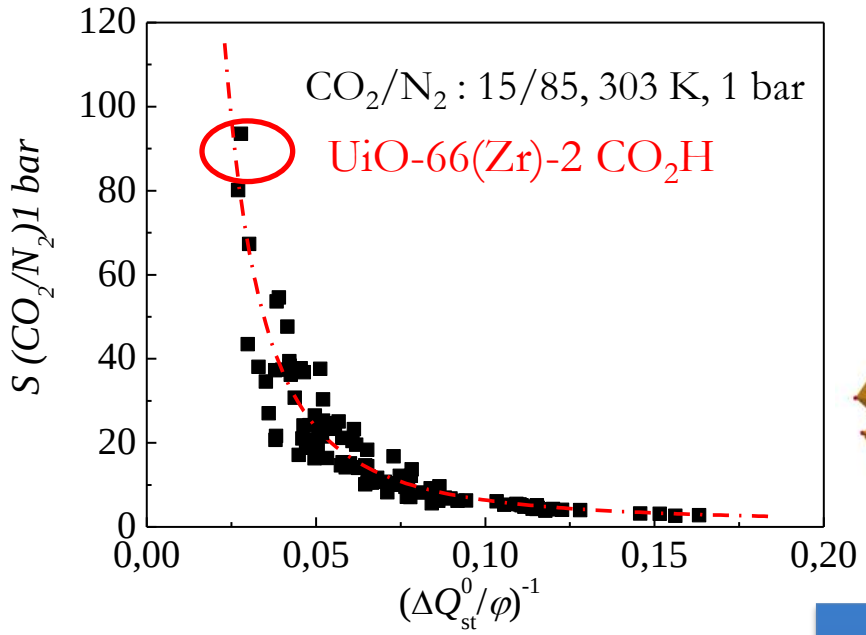
→ *The Chemistry of MOFs* Wiley Edition, 2016,
G. Maurin « Role of molecular simulations in the field of MOFs »

→ K. Adil, M. Eddaoudi, G. Maurin et al, Separation using (Ultra)microporous MOFs, Chem. Soc. Rev. 2017

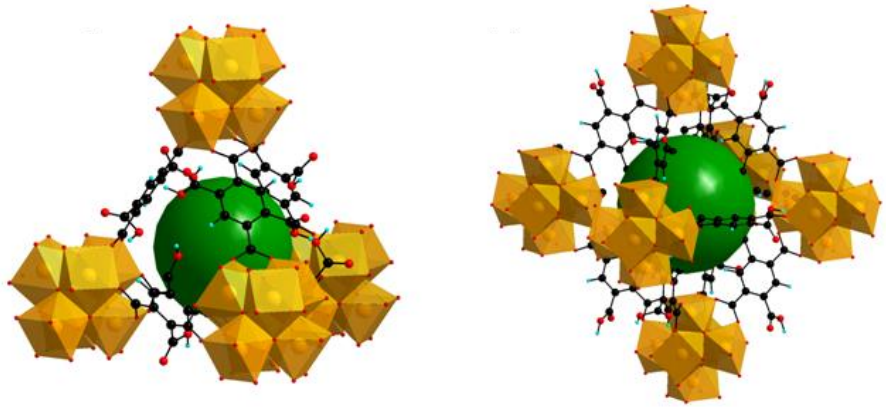
Thermodynamics separation - Case 1

Screening of hundreds of MOFs (topology, porosity, chemistry..)

Grand Canonical Monte Carlo simulations



Identification of the best MOF



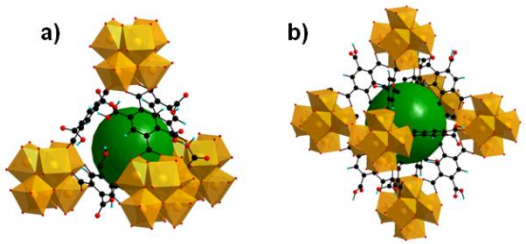
UiO-66(Zr)-2 CO_2H
$S(CO_2/N_2)$= 85

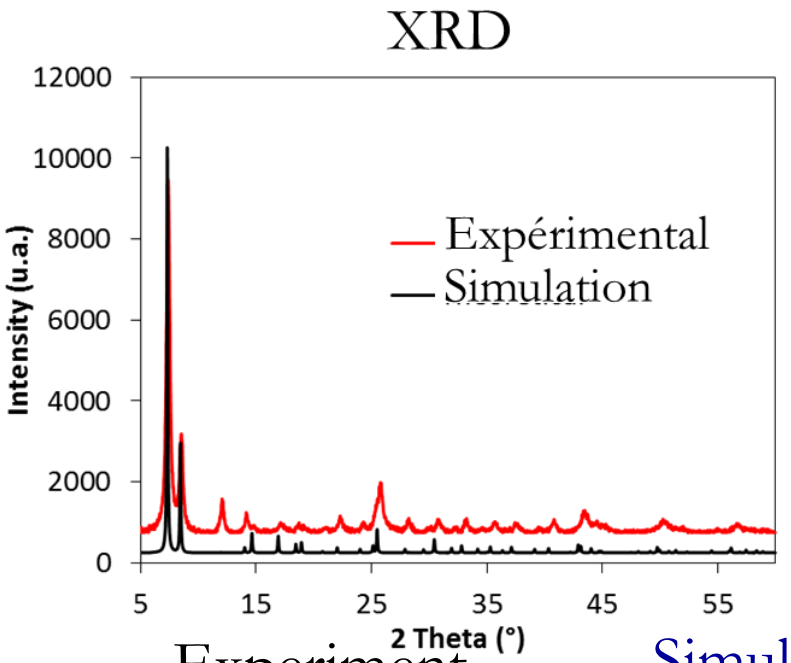
✓ ***Synthesis*** of the predicted material & Validation of the crystal structure

Q. Yang et al, Angew. Chem. Int. Ed., 2013, 52, 10316

Validation of the new UiO-66(Zr)-2 CO_2H phase

XRD-Simulations-NMR: SMARTER Strategy





Experiment Simulation

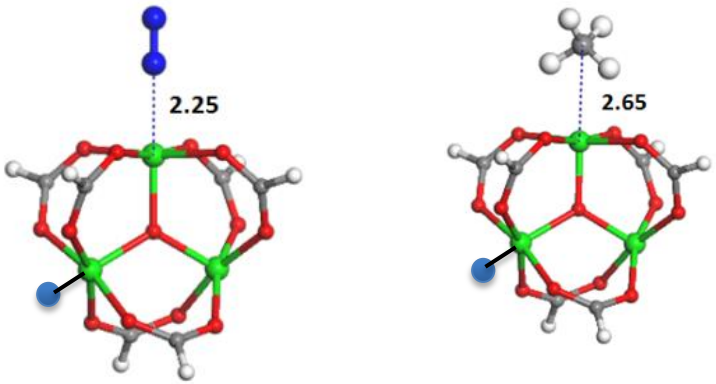
Materials / Cubic symmetry	Lattice sizes (Å)	a_{BET} (m^2/g)	V_{pore} (cm^3/g)	Lattice sizes (Å)	V_{pore} (cm^3/g)	a_{acc} (m^2/g)
UiO-66(Zr)-$(COOH)_2$	20.736(5)	415	0.21	20.9674	0.26	428

→ Unit cell dimensions & space group → adsorption characterization : a_{BET}/a_{acc} & V_{pore}

MOFs for CH_4 purification

Cluster-based DFT calculations*

→ Understanding of the host/guest interactions in play



✓ Binding Energy -48.7 kJ/mol - 35.7 kJ/mol

✓ End-on coordination geometry for N_2 towards Cr(III) CUS sites: consistent with IR observations

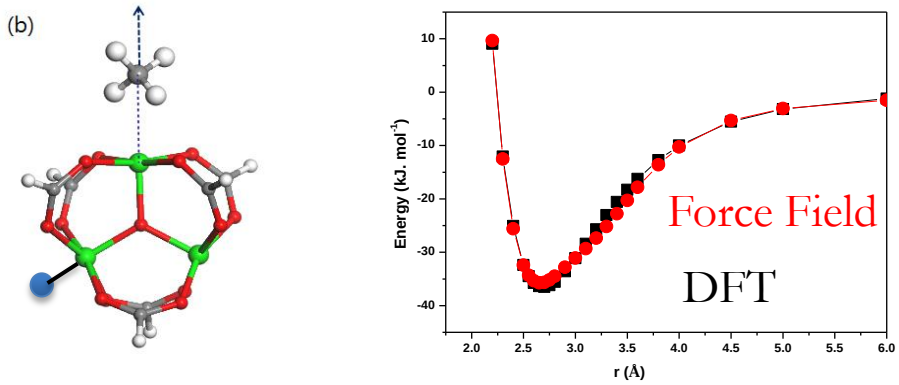
✓ Back bonding interactions for N_2: HOMO d Cr(III) shows a bonding state to the originally unoccupied π* (N_2)

* PBE Functional, DNP basis set, TS Dispersion correction

Thermodynamics separation - Case 2

Cluster-based DFT calculations

→ Deriving accurate Force Field parameters for the guest/Cr CUS interactions



✓ DFT potential energy surface constructed by moving progressively the guest away from the Cr sites

✓ Force Field fitting using Buckingham potential and electrostatic term

ESP partial charges for MOF

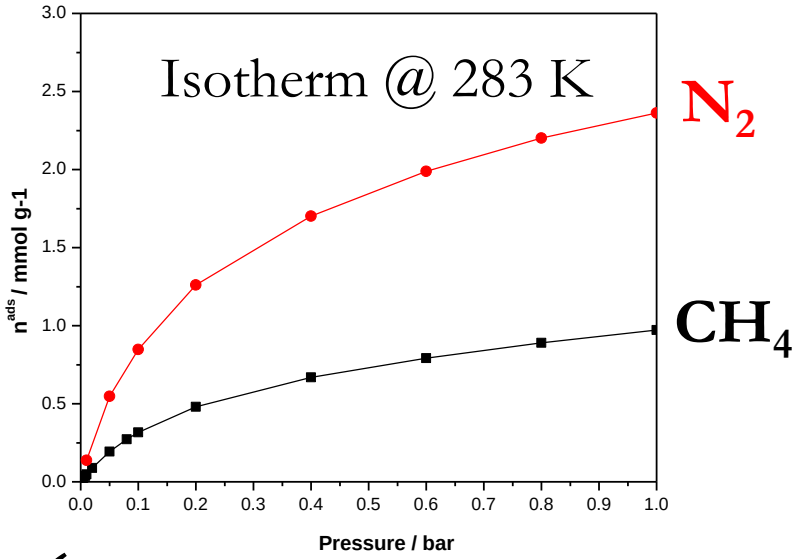
CH_4 & N_2 TraPPE models

$$U_{ij} = \underbrace{\sum_{\substack{i,j \\ i<j}} \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}}}_{\text{Electrostatic term}} + \underbrace{\left[A_{ij} e^{-B_{ij} r_{ij}} - S_g \frac{C_{ij}}{r_{ij}^6}\right]}_{\text{Buckingham term}}$$

Thermodynamics separation – Case 2

Grand Canonical Monte Carlo simulations

→ Adsorption of single components



✓ Higher affinity for N_2 vs CH_4

(ΔH_{ads} (N_2) ≈ -37 kJ mol^{-1} > ΔH_{ads} (CH_4) ≈ -26 kJ mol^{-1} 283 K

✓ Confirmation of the large N_2 uptake at 283 K: 2.4 mmol/g >> ETS-4 (0.5 mmol/g)

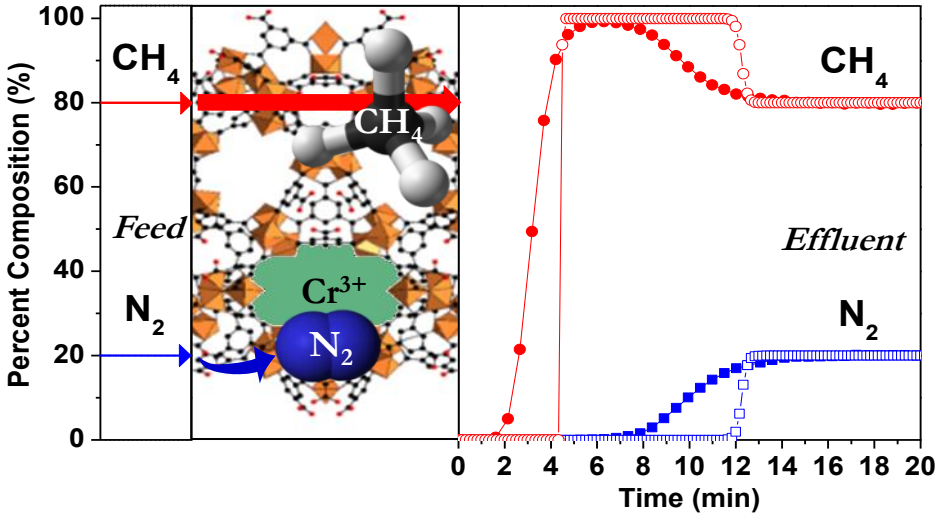
Thermodynamics separation – Case 2

Grand Canonical Monte Carlo simulations

→ Adsorption of the binary mixture

✓ Simulated selectivity: S(N_2/CH_4) ≈4 (20/80; 283 K,1 bar):
Confirmation by breakthrough experiments: S (N_2/CH_4) = 4.6

KRICT
Korea Research Institute of Chemical Technology

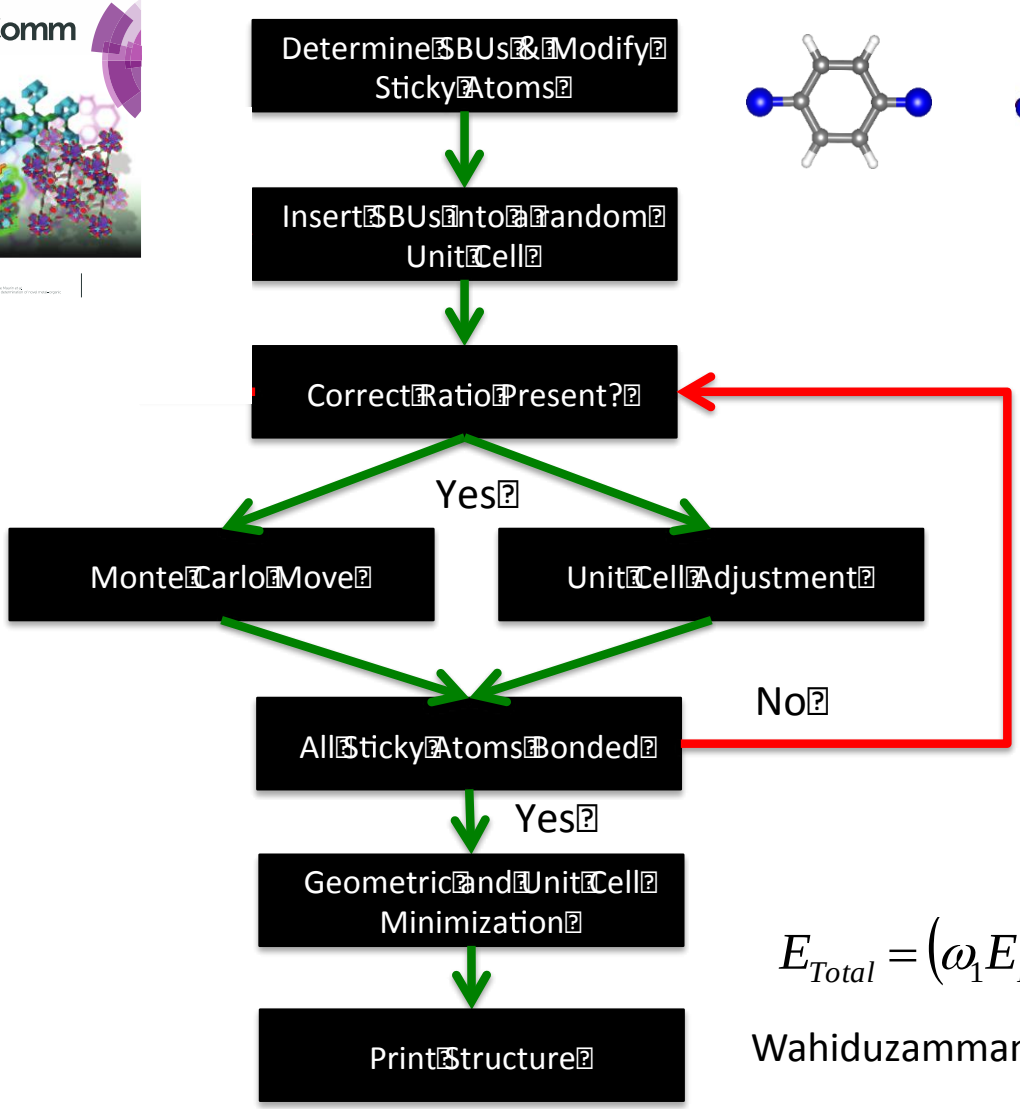


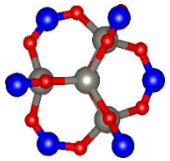
The first adsorbent able to thermodynamically capture N_2 over CH_4!

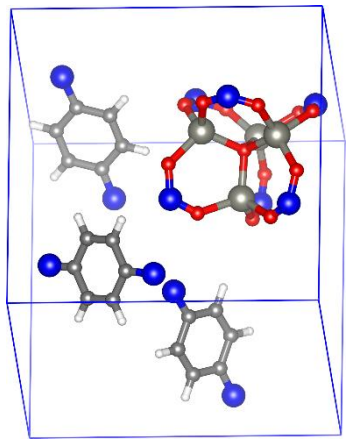
Yoon, Pillai, Maurin, Chang et al, ***Nature Materials DOI: 10.1038/NMAT4825***

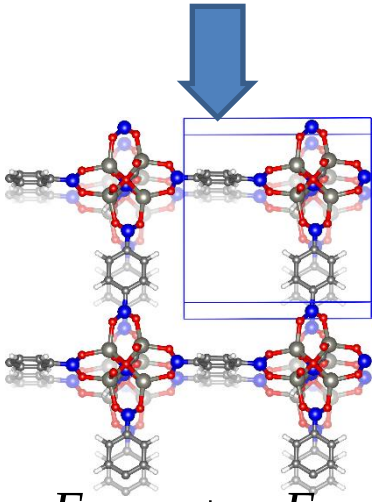
Accelerating MOF discovery by Monte Carlo

Automated Assembly of Building Units







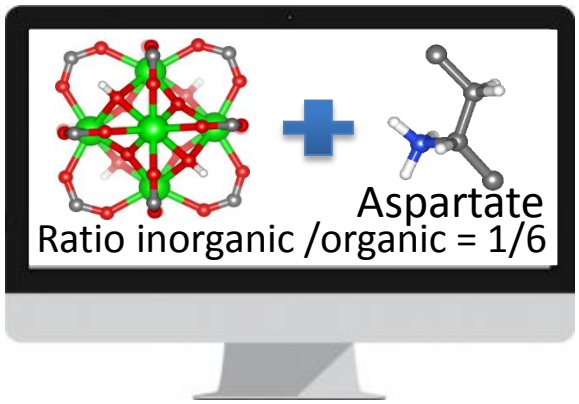


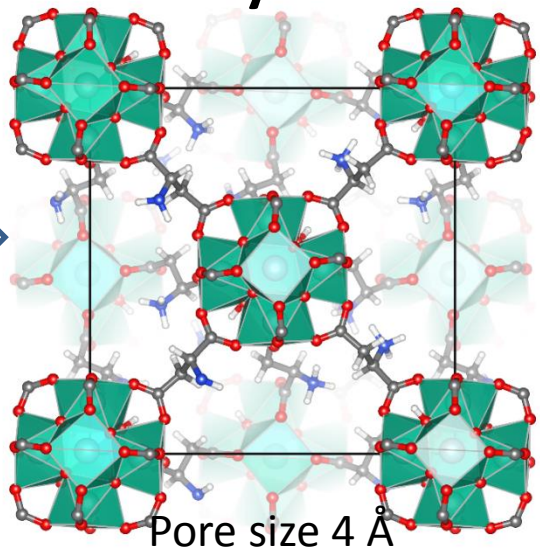
$$E_{Total} = \left(\omega_1 E_{LJ} + \omega_2 E_{Bonding} + \omega_3 E_{Bending} + \omega_4 E_{Torsion}\right)$$

Wahiduzamman *et al*, Chem. Commun. 54,10812, 2018

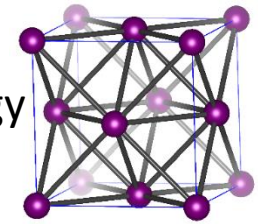
Accelerating MOF discovery

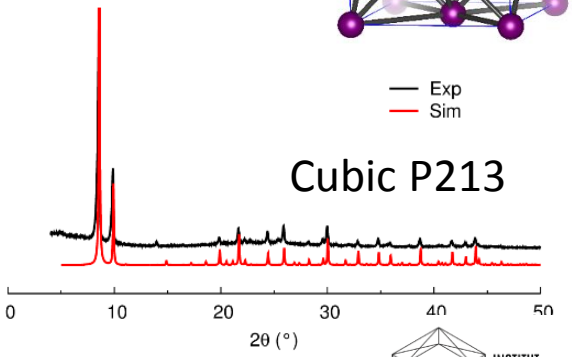
Automated Assembly of Building Units





FCU topology





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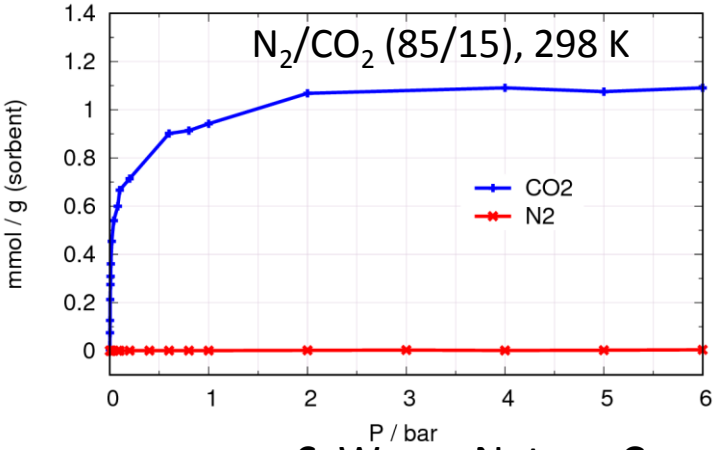
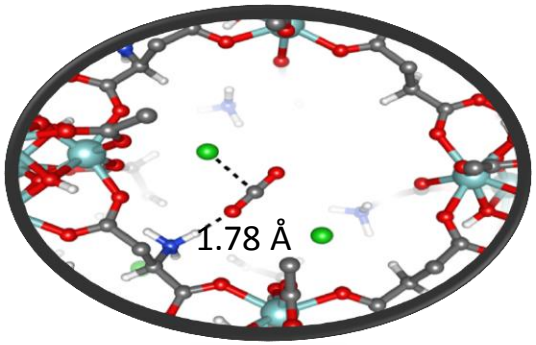
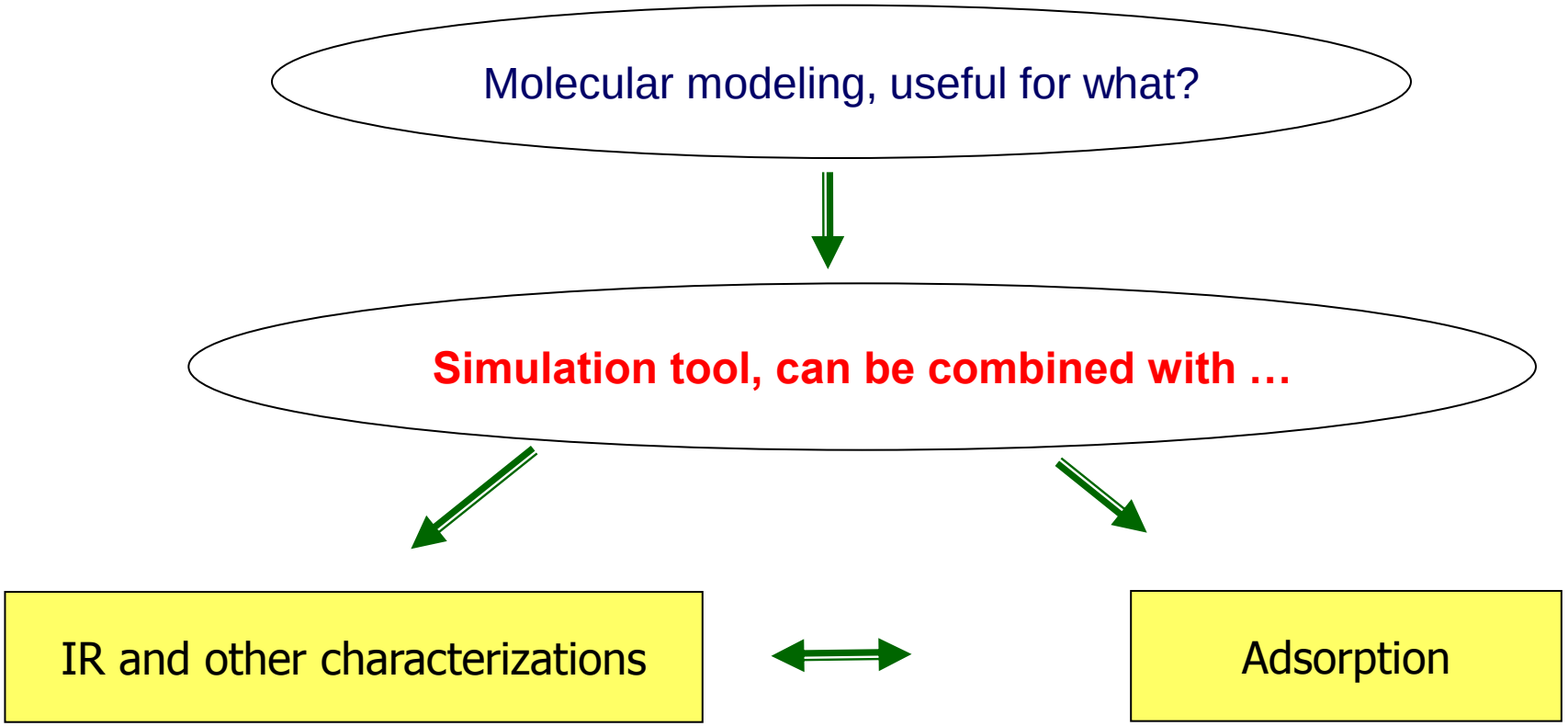
CO_2 capture by Molecular Sieving





S. Wang, Nature Commun. 9, 4937, 2018

General conclusion



Theory can help to design efficient and selective sorbent materials

Perspectives for other selective trapping applications

- In silico screening of sorbent formulations can be extended
  - to divalent cations, other structures, in the case of zeolites
  - Other class of materials such as silicas or MOFs

  - Other applications currently investigated :
    - separation toluene / phenol for the purification of biofuels
    - Selective capture of NO_x in presence of H_2O and CO_2 :

  - Other applications to be considered in a near future:
    - Separation of hydrocarbons (propylene vs propane)
    - Adsorption of Volatile Organic Compounds

    ….

List of experts in France (non exhaustive)

- Experts in AIMD : FX Coudert, Marie-Pierre Gaigeot (Ile de France), …
- Classical molecular dynamics: Jean-Marc Simon, Marcos Salazar (Dijon)
- Prediction of adsorption capacities, co-adsorption at high coverage: GCMC simulations, Guillaume Maurin (Montpellier)
- Diffusion, transport in nanoporous media: Benoit Coasne (Grenoble)

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Thank you for your attention

CPU resources

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- ExploR, computing center @ Univ Lorraine
- GENCI-CCRT/TGCC grants (2017 to 2019)

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