Molecular modeling of interstellar ices

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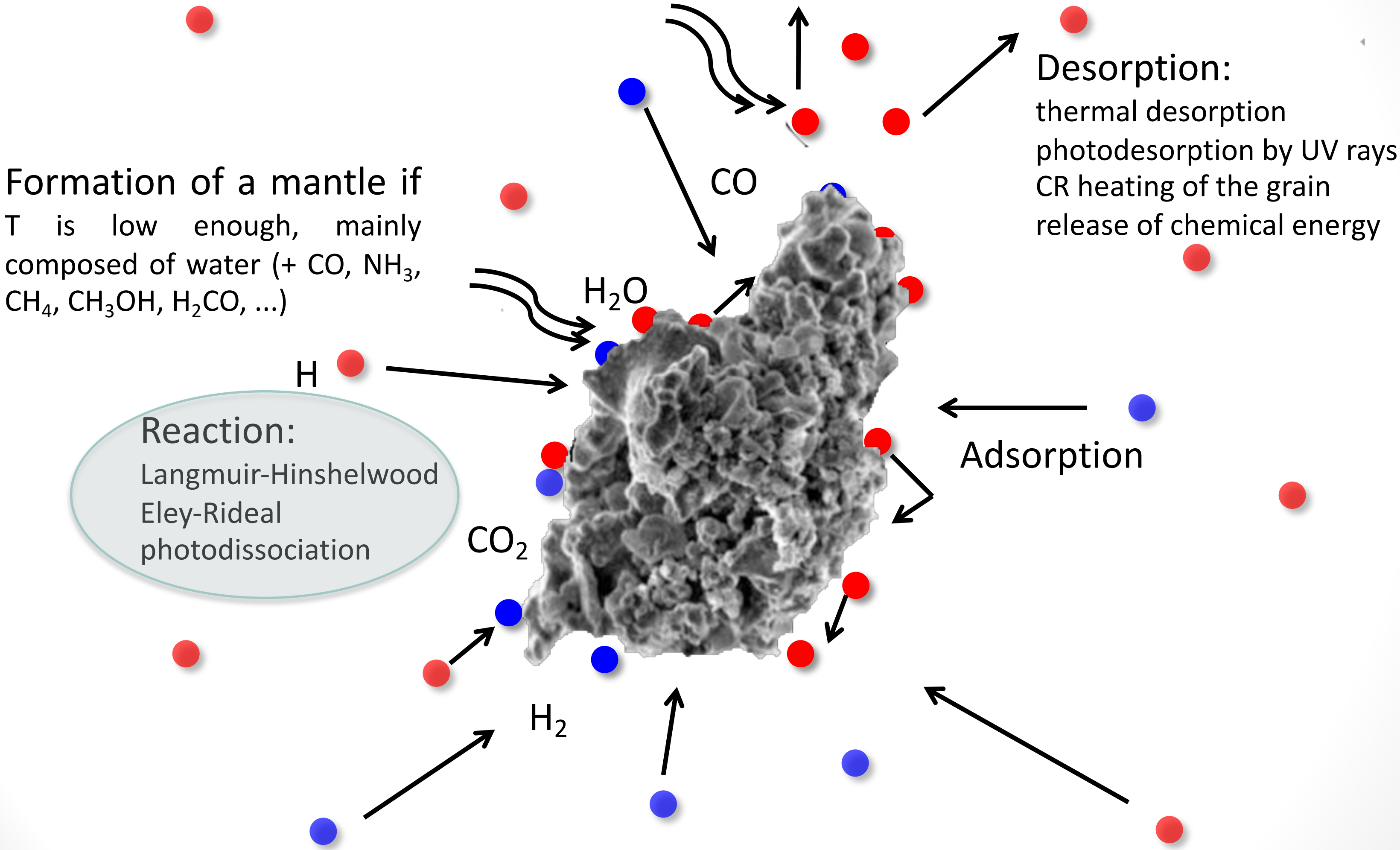
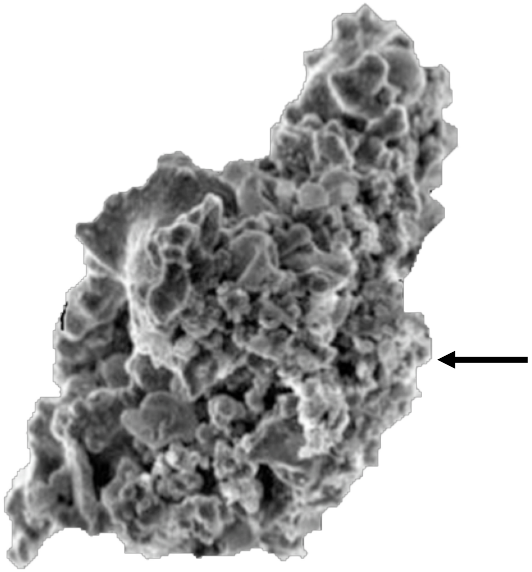
Heterogeneous processes at the surface of interstellar grains



Heterogeneous processes at the surface of interstellar grains

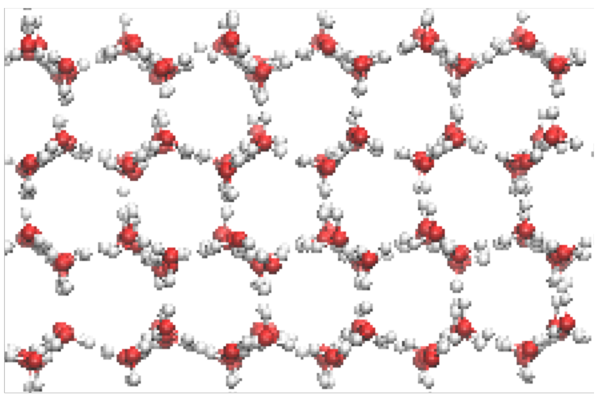


H_2O ices
CO ices
Mixed ices
…

How to model astrophysical ices ?

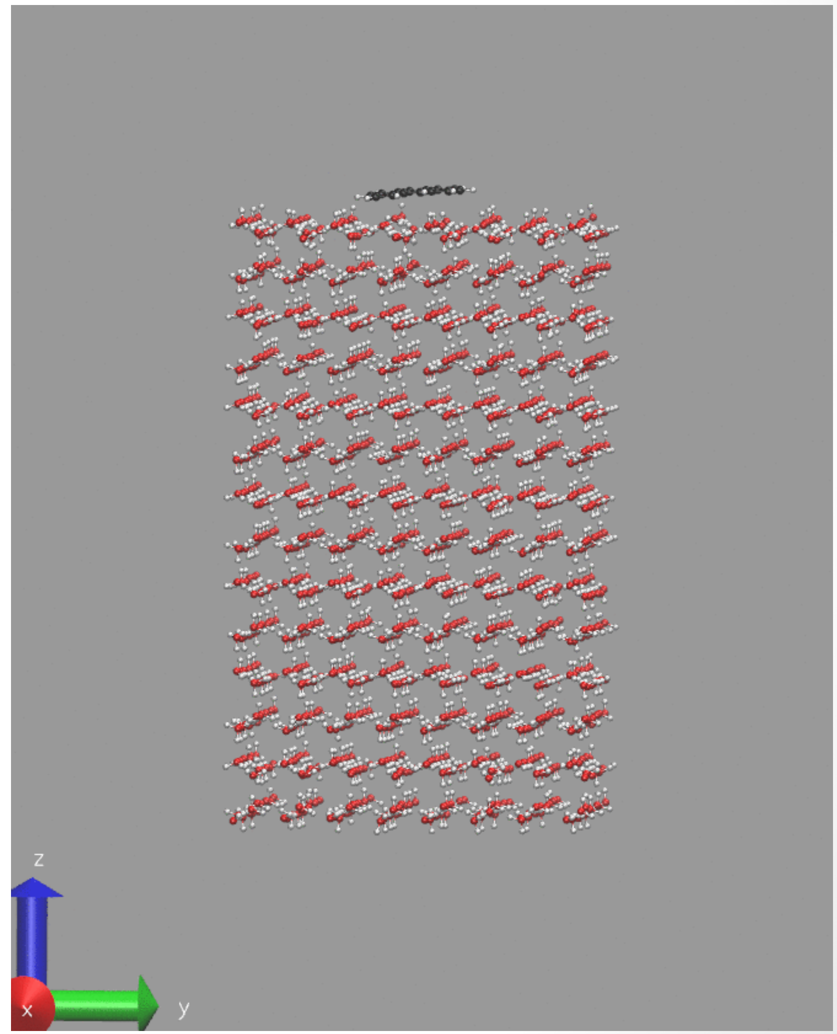
What can we learn from molecular modeling methods

Binding energies, diffusion coefficients, sticking coefficients, thermal effects, activation energies, ionization energies, IR spectrum



Static representation

Dynamical treatment



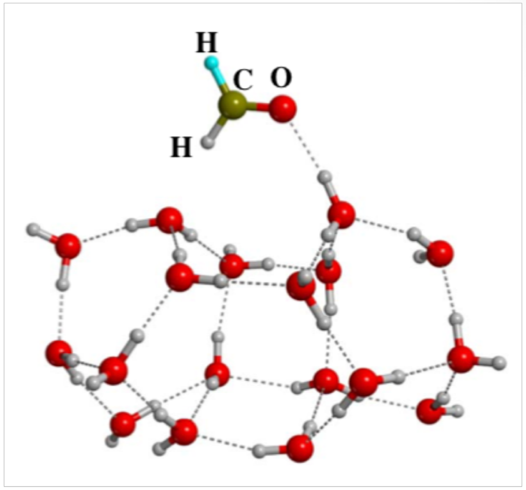
Static description

Cluster model

Small clusters of ices can be modeled with DFT or ab initio methods

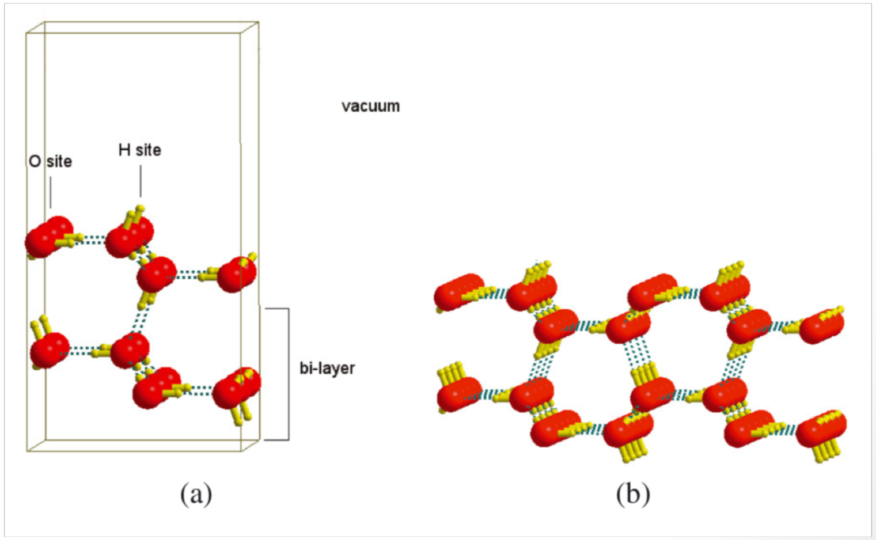
- properties may depend on the chosen density functional.
- realistic or unrealistic ice structures ?

Rimola et al, A&A 572, A70 (2014)



Periodic representation

DFT periodic calculations
Lattelais et al,
A&A 532, A12 (2011)

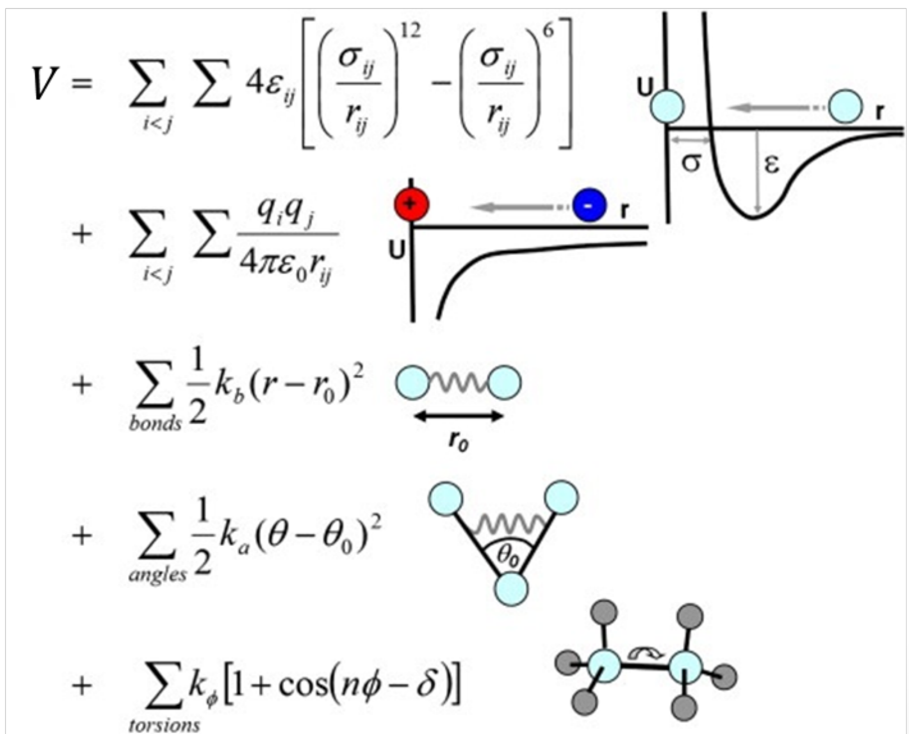


Static description

Periodic representation

Force Field based periodic calculations

- the empirical parameters of the commonly used force fields or user-defined force fields are often determined from a limited number of model systems (problems of ions and radicals).
- the accuracy of MD simulations depends on the quality of the original parametrization and transferability of the parameters to new molecular environments.



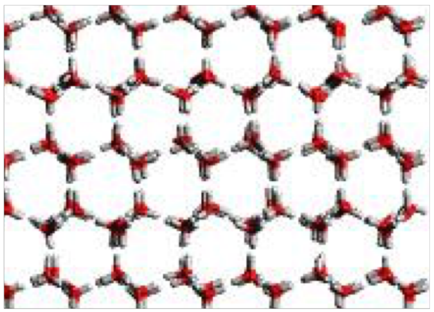
$$V = \sum_{i<j}\sum 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \sum_{i<j}\sum \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + \sum_{bonds}\frac{1}{2}k_b(r-r_0)^2 + \sum_{angles}\frac{1}{2}k_a(\theta-\theta_0)^2 + \sum_{torsions}k_\phi[1+\cos(n\phi-\delta)]$$

Classical MD: Force field (FF) issue

Problem of polarizable water models to reproduce crystalline ice

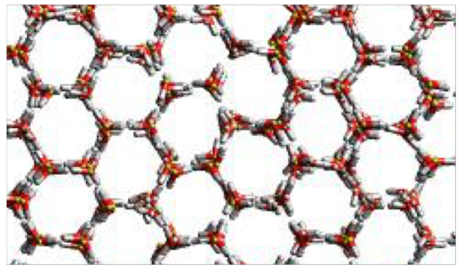
Non polarizable

TIP4P/2005
(T_m = 252 K)



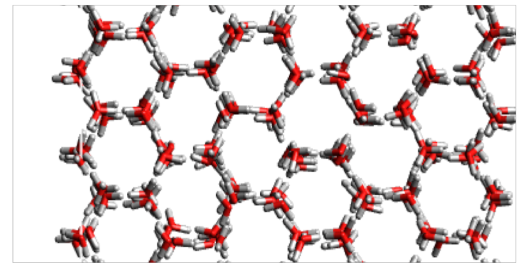
Polarizable

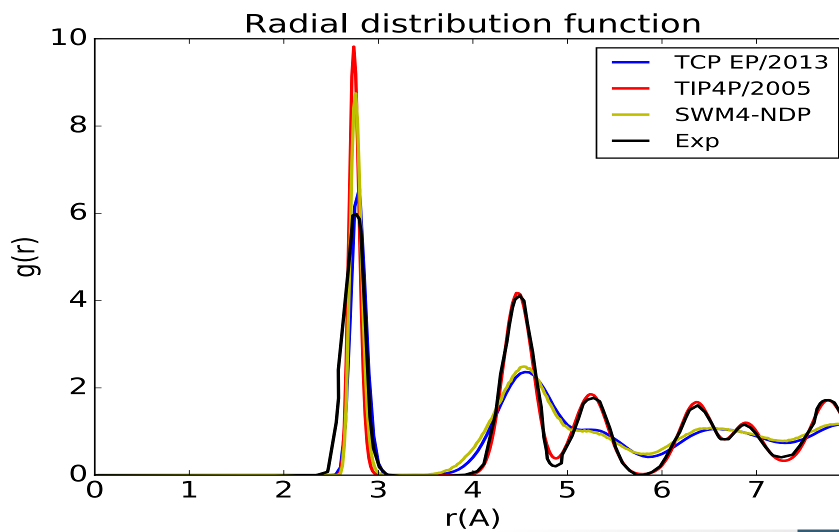
SWM4-NDP
(T_m = 185 K)



TCPE/2013*
(T_m = ?)

POLARIS





Radial distribution function of the O-O pair for crystalline hexagonal ice at T= 77 K

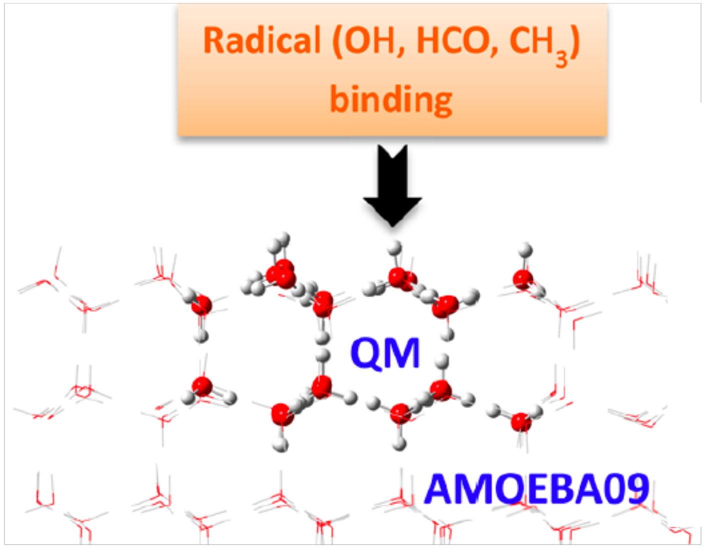
Réal, F.; Vallet, V.; Flament, J.-P.; Masella, M. J. Chem. Phys. **2013, 139 (11), 114502.*

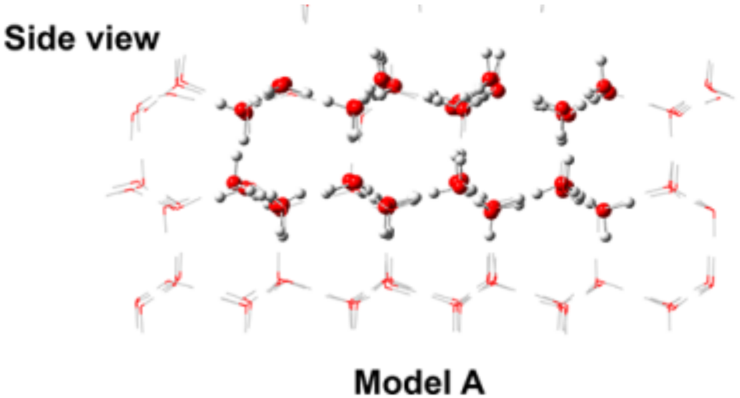
Reproducing the melting temperature of ice remains an important issue when introducing charged species

E. Michoulier's PhD

Static description

QM/MM approach





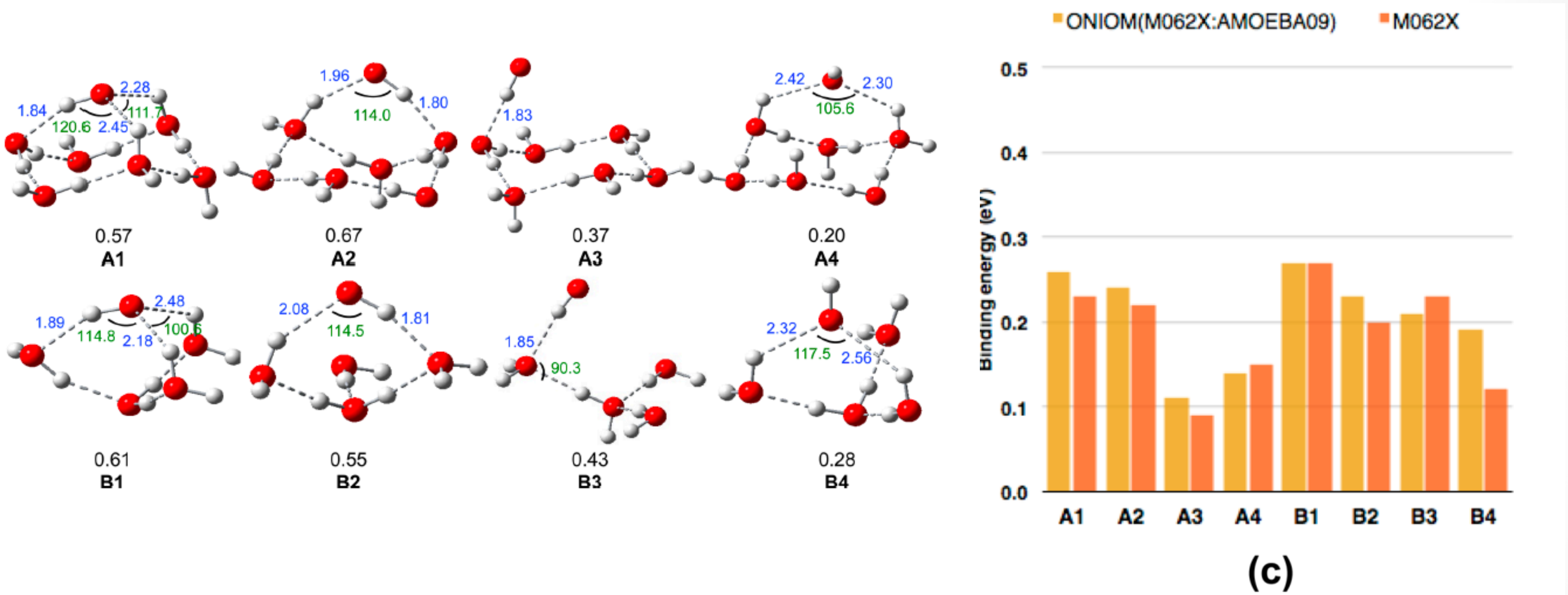
(A) : 162 H2O, QM = 48, MM = 114
ONIOM(M062X/6-31+G(d,p):AMOEBA09)

Size of the QM region can be adjusted , no distortion of the water rearrangement

Sameera et al J. Phys. Chem. C 2017, 121, 15223−15232

Static description

QM/MM approach



Size of the QM region can be adjusted, no distortion of the water rearrangement
Binding energies distribution can be calculated
Sameera et al J. Phys. Chem. C 2017, 121, 15223−15232

→ Test of the method on amorphous ices adapting the QM region for each case (D. Duflot, M. Monnerville, J.C. Loison, V. Wakelam – PCMI action)

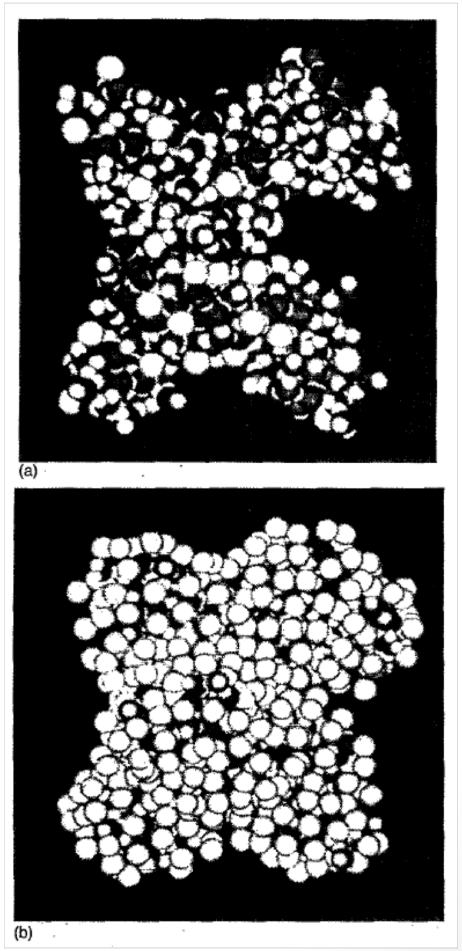
Dynamical description

Semi empirical, FF based MD remains very efficient compared to DFT-based MD methods, (CPMD) that more accurate, but significantly more demanding (limitations in terms of system size and time scales).

Amorphous ice modeling

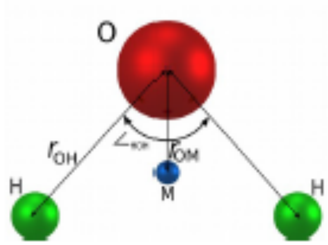
Pioneering work of V. Buch et al. *(J. Chem. Phys. 98, 4195 (1993))*

Cluster of 450 H_2O molecules formed by MD calculations mimicking the experimental formation process of **amorphous ice**, i.e., slow condensation of water vapor at T=10 K.

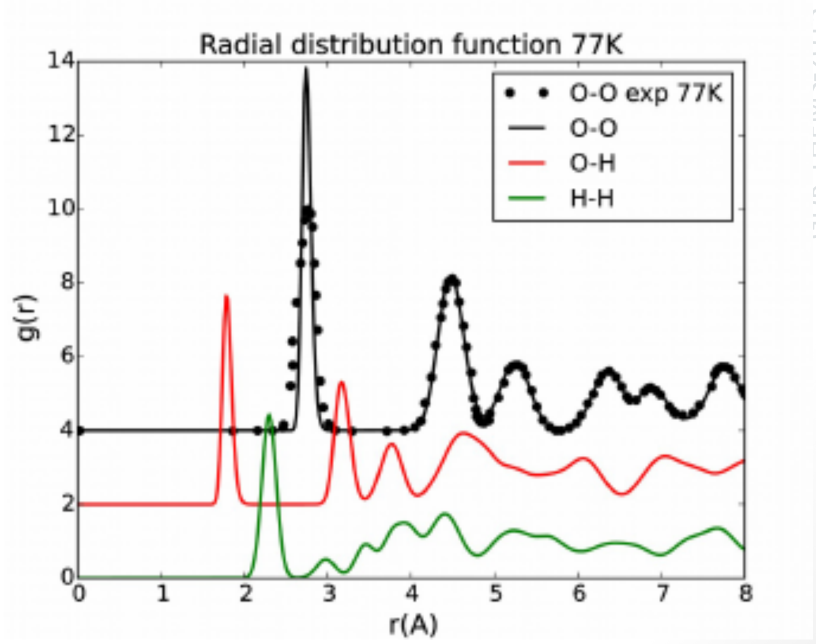


Simulation of different ice phases

Potential TiP4P/2005
Non polarizable point charge model



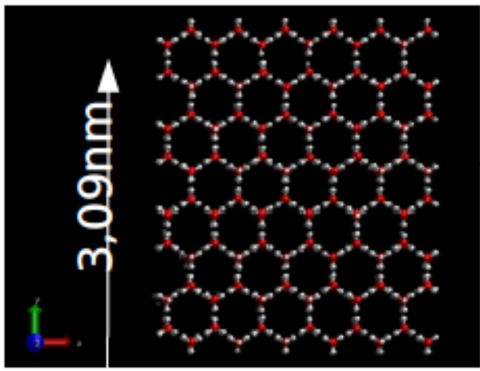
Box with 1344 H2O molecules
Dimension (nm) 2.65 3.06 5.24
With periodic boundaries



A. H. Narten et al Journal of Chemical Physics , 64(3) :1106 1121, 1976

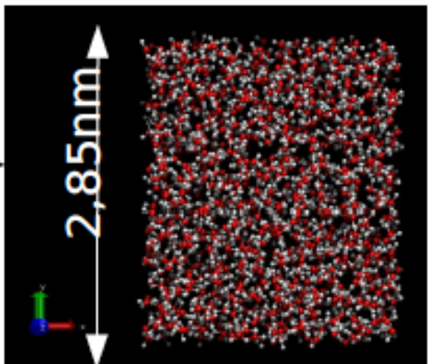
Simulation of different ice phases

Hexagonal Ice



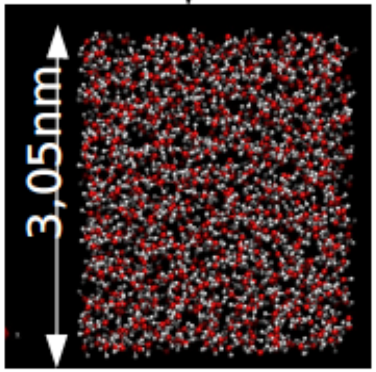
Applied pressure of 15kbar →

HDA (**H**igh **D**ensity **A**morphous) ice



Annealing → release constraint

LDA (**L**ow **D**ensity **A**morphous) ice



At 77K	Ih	HDA	LDA
Density num (g/ml)	944	1161	955
Density exp (*) (g/ml)	933	1170	940
delta(x)/x (%)	1,17	0,76	1,59

(*) C. J. Tainter, L. Shi, and J. L. Skinner The Journal of Chemical Physics 140, 134503 (2014)

PAHs on amorphous ices

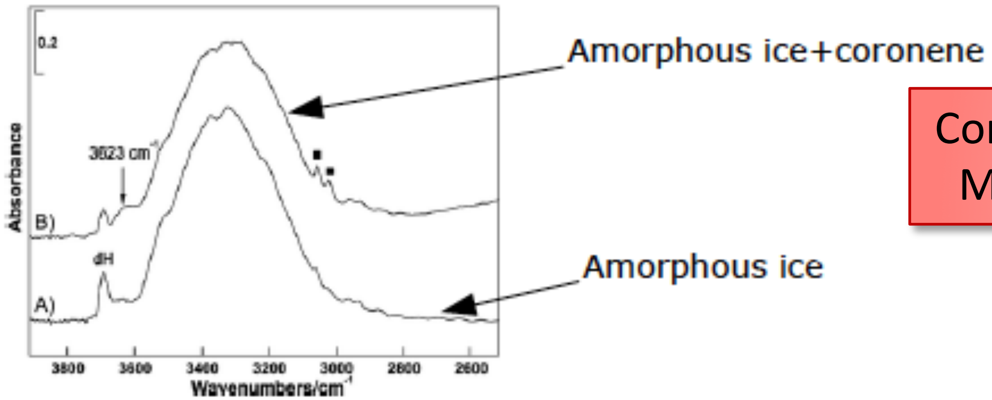
PhLAM : Semi empirical FF and classical MD

- Modelling of crystalline and amorphous ice surfaces
- FF parametrization and characterization of the adsorption of PAH on ices

A. Simon

LCPQ : Density Functional Tight Binding (DFTB)

Calculation of the IR spectra and ionization potential for selected configurations of the PAH adsorbed on ice



Comparison with experiments from J. Mascetti , J. Noble (ISM, Bordeaux)

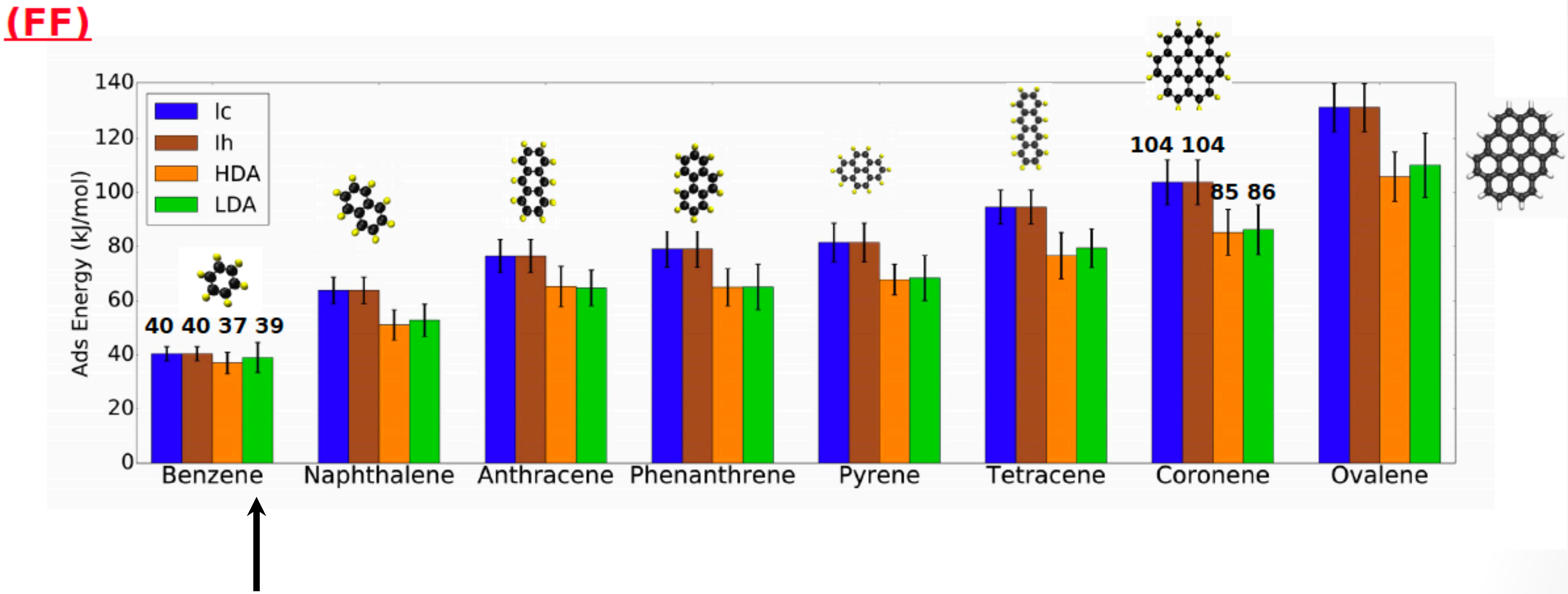
Z. Guennoun, C. Aupetit, J. Mascetti, PCCP 2011, 13, 7340-7347.

The dangling OH of amorphous water ice is used as a probe for adsorption of coronene

E. Michoulier's thesis

PAHs on amorphous ices

Binding energy distributions

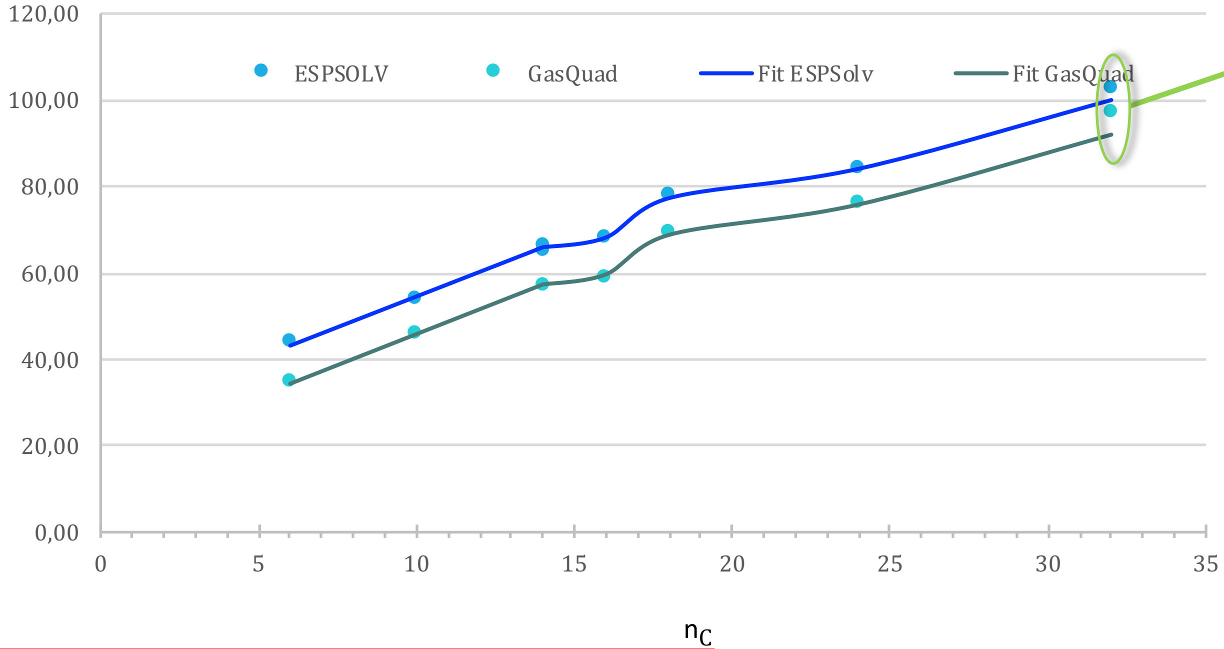


Our value 39.0 kJ/mol
TPD value:
41 ± 0.5 kJ/mol [1]
39 kJ/mol [2]
40.6 kJ/mol [3]

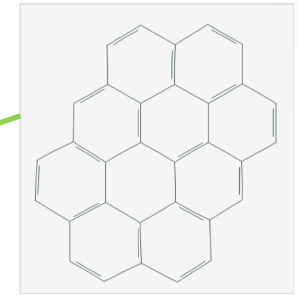
[1] J. D. Thrower et al., J. Chem. Phys., 131(24), 244711 (2009)
[2] R. Souda, J. Phys. Chem. B, 108(1), 283–288 (2004)
[3] Stubbing et al., in preparation

PAHs on amorphous ices

Prediction of the binding energy for larger PAHs on LDA



$C_{32}H_{14}$



Prediction of the adsorption energy for bigger PAHs:

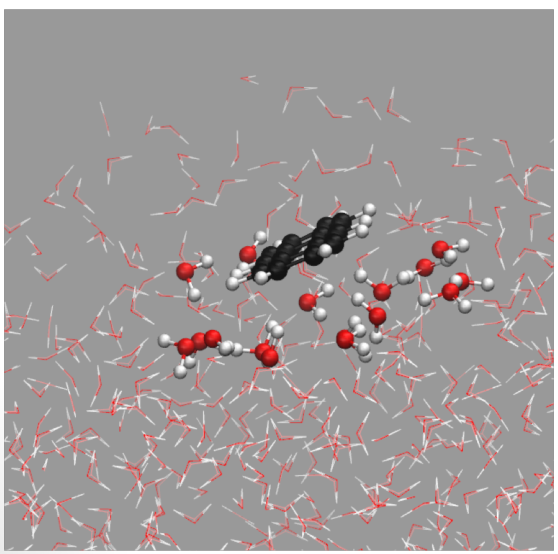
$$E_{ads} = a + b \cdot n_{Carbon} + c \cdot n_{Hydrogen}$$

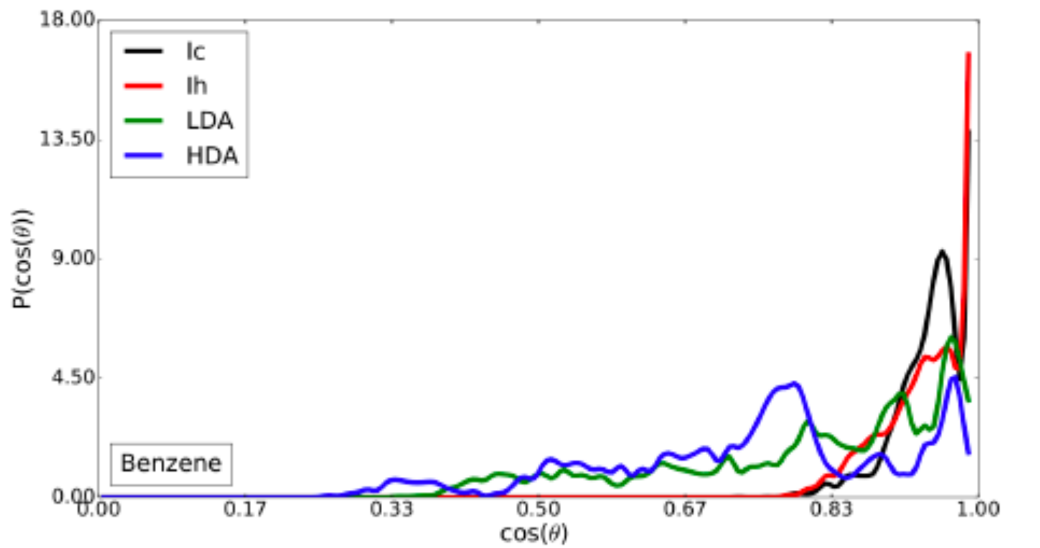
Interesting for astrophysicists to refine the models (KIDA database, ...)

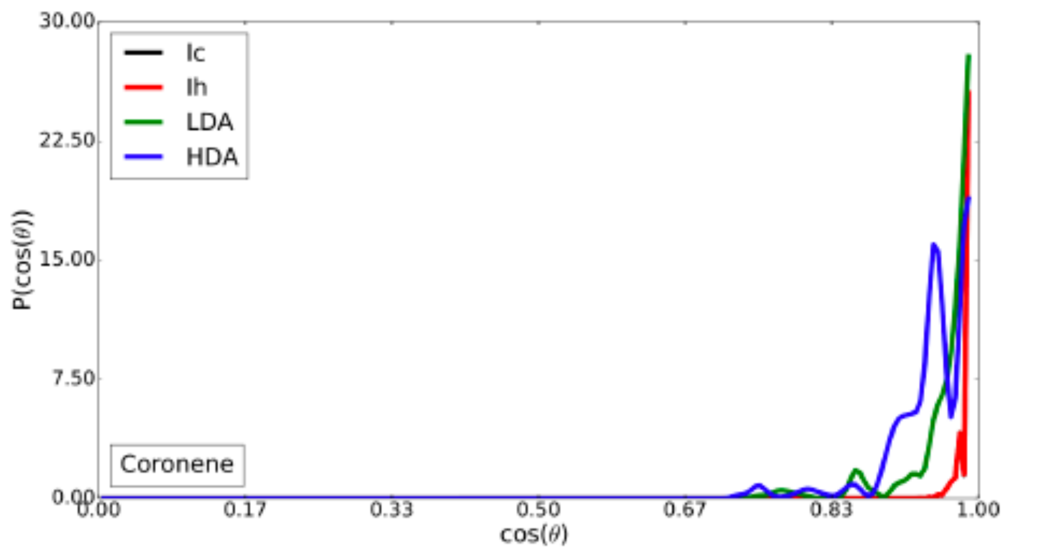
KIDA KINETIC DATABASE FOR ASTROCHEMISTRY

PAHs on amorphous ices

Orientation and type of binding of the molecule can be characterized over the sampled configurations

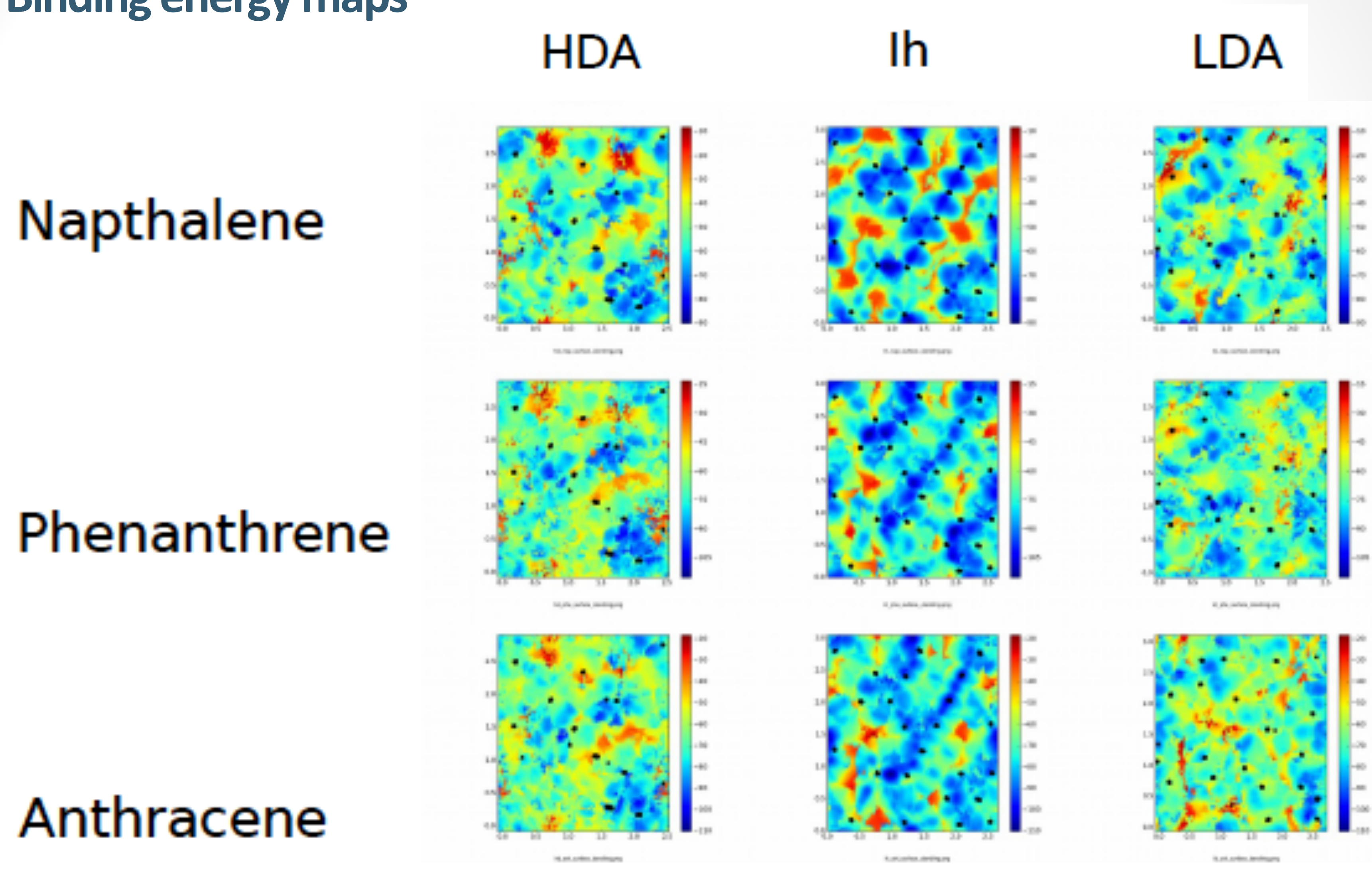






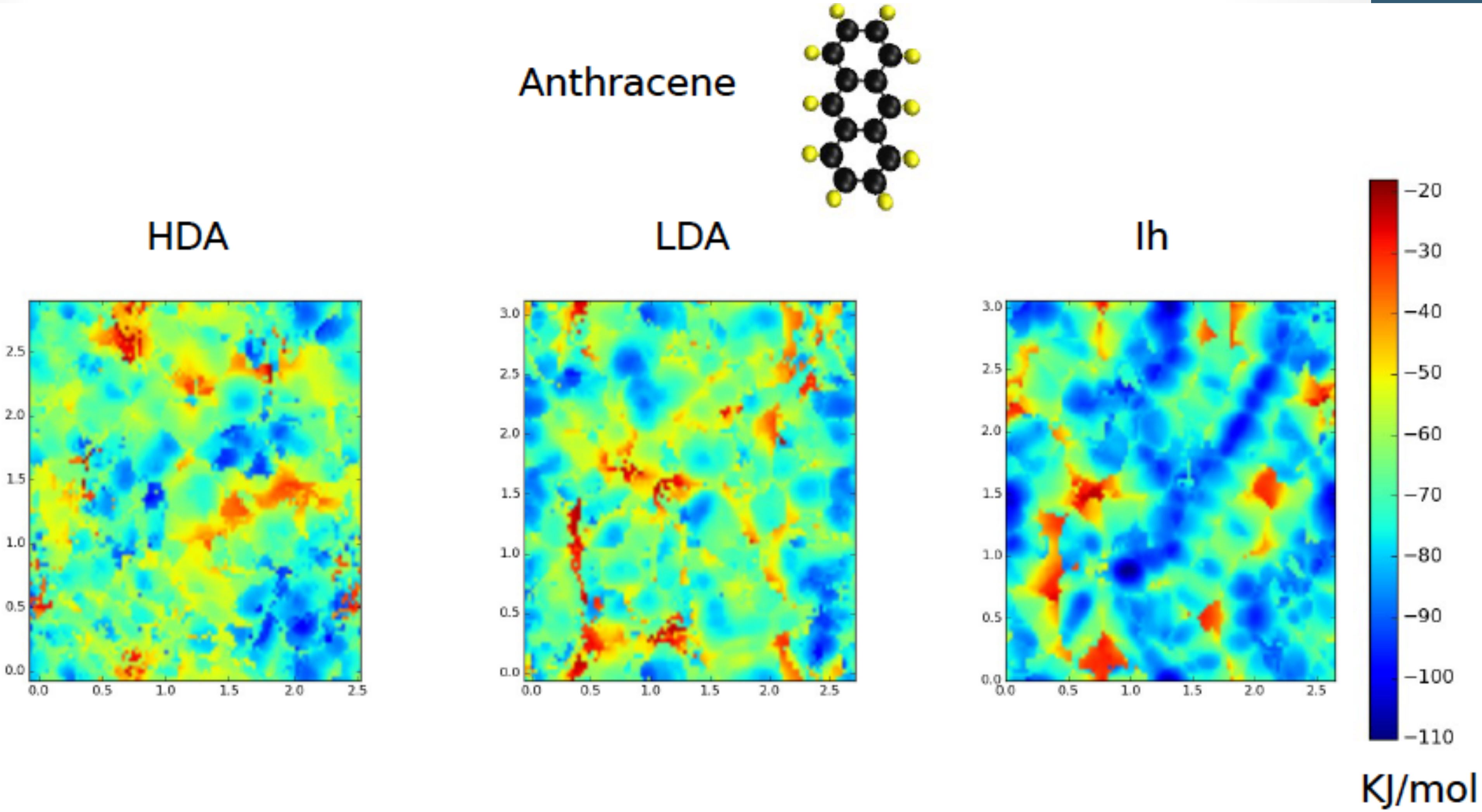
PAHs on amorphous ices

Binding energy maps



PAHs on amorphous ices

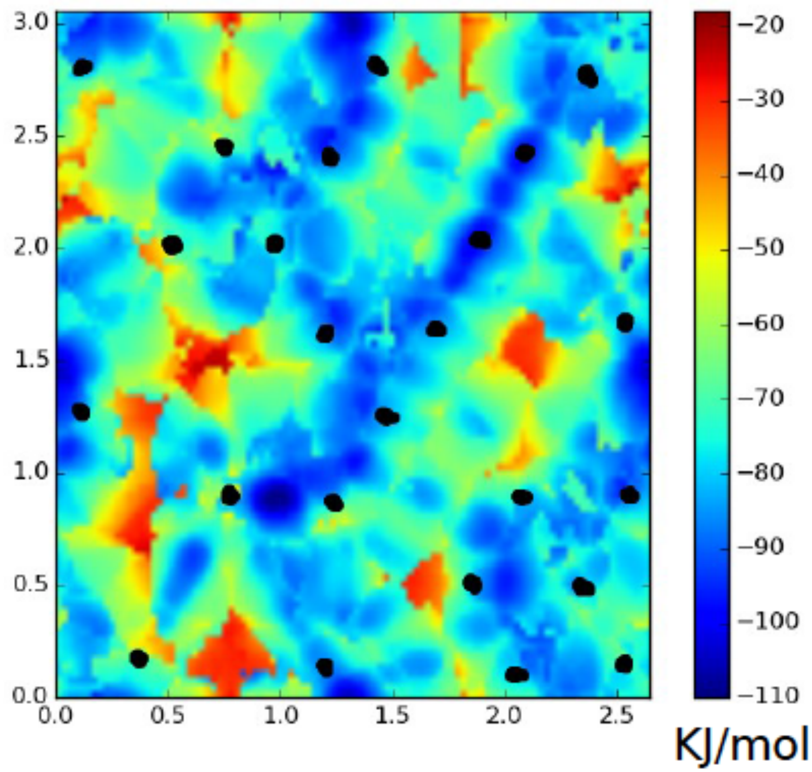
Binding energy maps

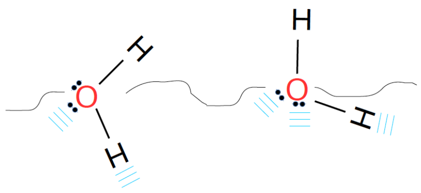


PAHs on amorphous ices

Correlation with the dangling hydrogens

Anthracene on ice Ih
black dots represent the dH





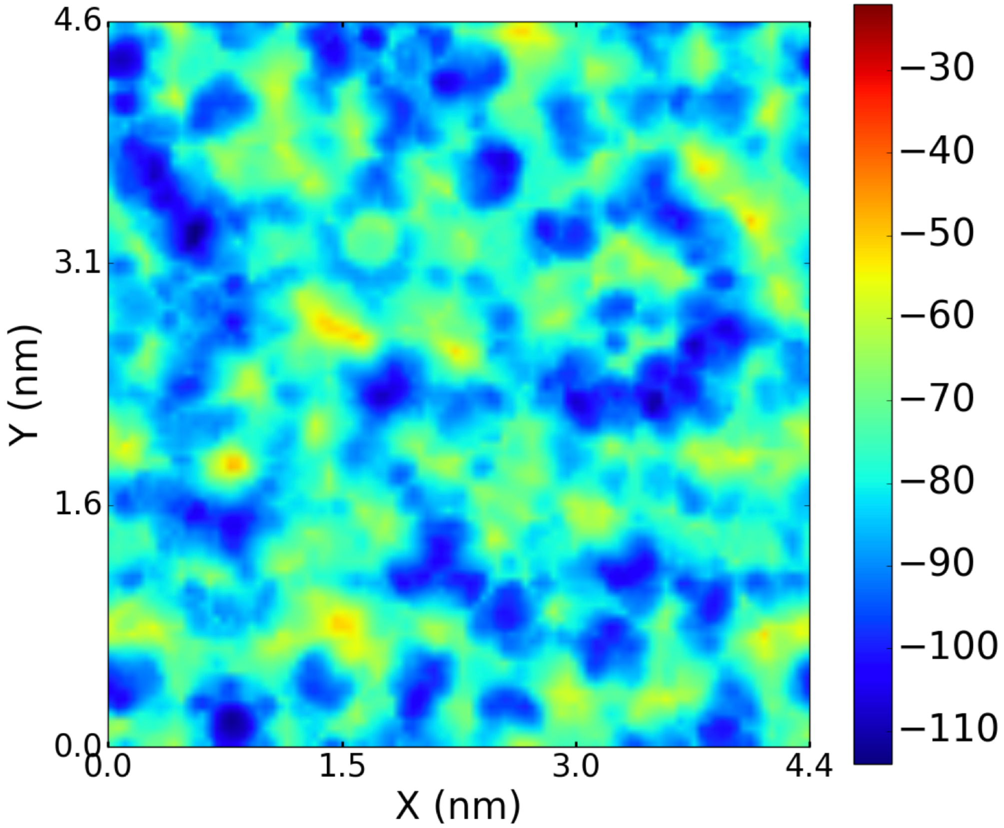
Number of dangling H-bonds per nm^2

LDA	HDA	Ih
1,4	1,1	2,9

E. Michoulier et al, Phys. Chem. Chem. Phys, 2018, 20, 8753-8764.

PAHs on amorphous ices

Coronene on ice Ih

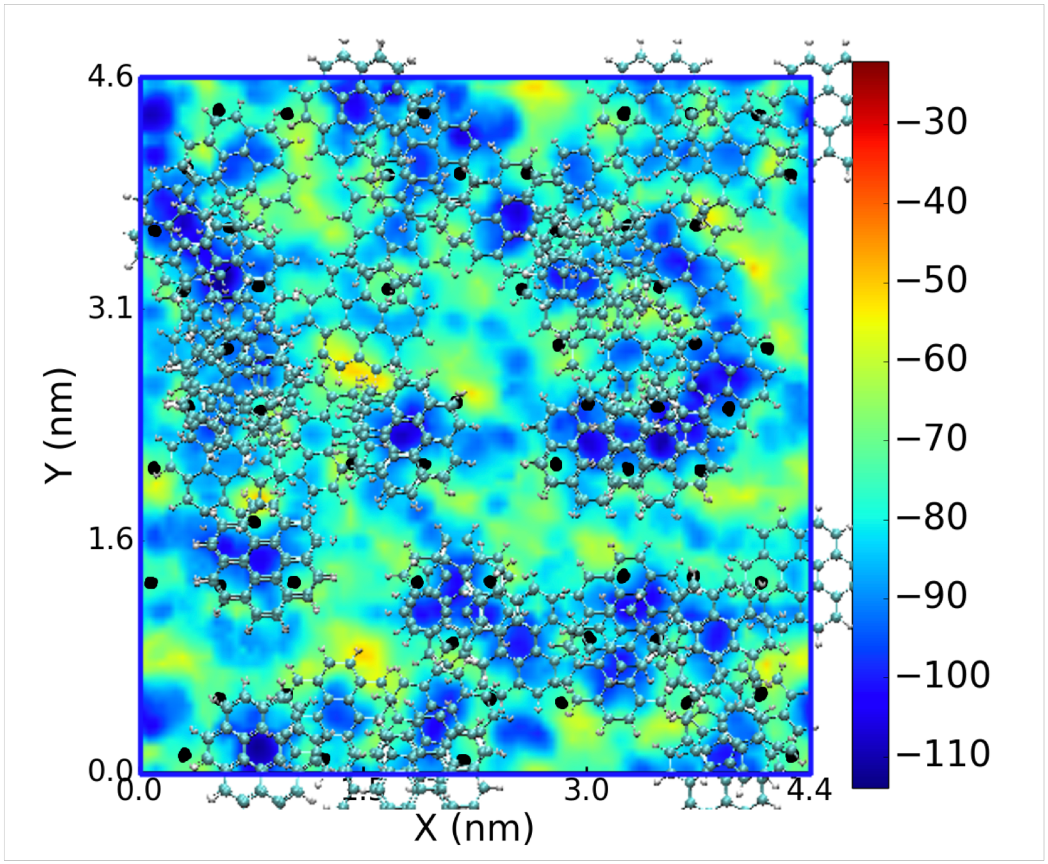


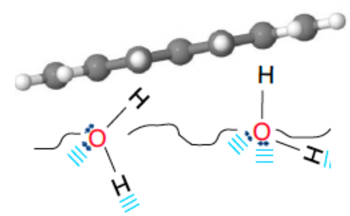
E. Michoulier et al, Phys. Chem. Chem. Phys, 2018, 20, 8753-8764.

PAHs on amorphous ices

Coronene on ice Ih

Positions of the dangling hydrogens (black dots)





Correlation between adsorption sites and dangling H-bonds

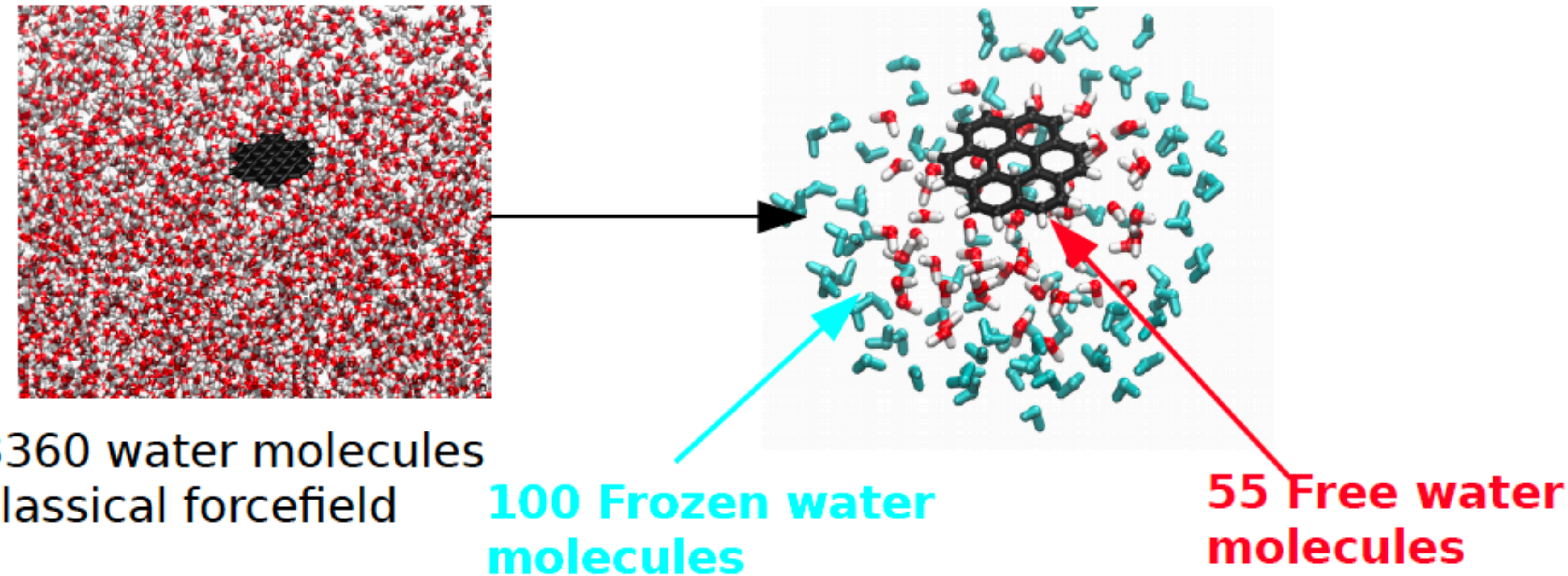
E. Michoulier et al, Phys. Chem. Chem. Phys, 2018, 20, 8753-8764.

PAHs on amorphous ices

Identification of configurations

Selection of configurations

Reduction for the DFTB treatment



Ionization potential

E. Michoulier et al, PCCP 2018, 20, 11941-11953

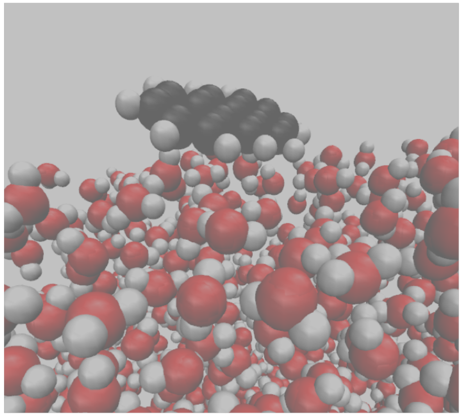
Harmonic spectra

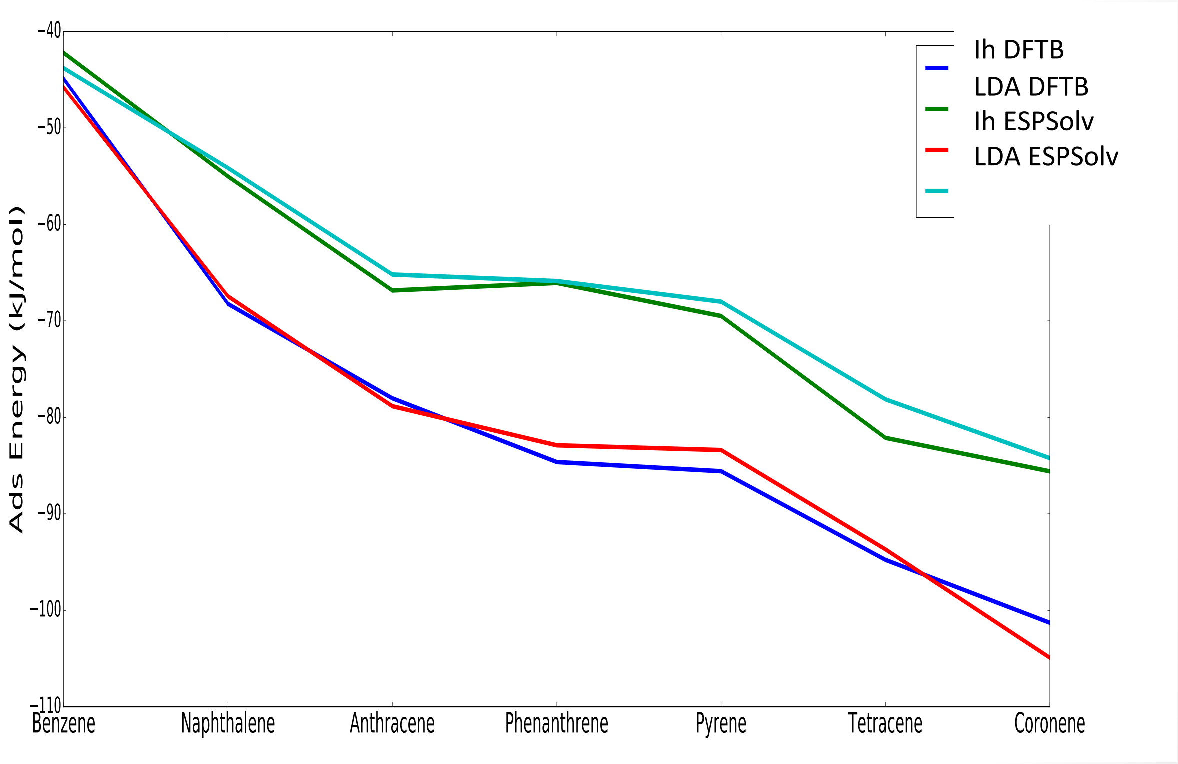
E. Michoulier et al, soumis

PAHs on amorphous ices

Benchmark of the approach

Good agreement between DFTB and FF adsorption energies





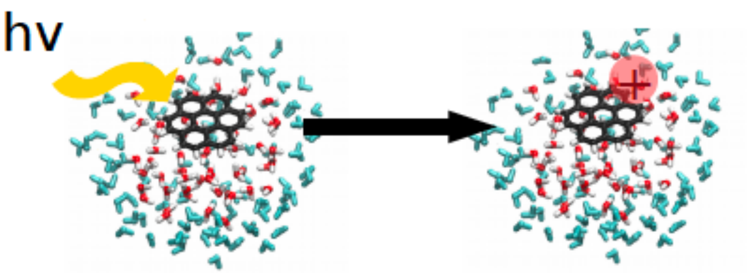
PAHs on amorphous ices

Effect of ice environment on the ionization potential (IP)

Previous studies suppose that the PAH's IP is lowered (by 2 eV) due the presence of water and that it could explain the reactivity of PAH
But the models used are not explicit (dielectric continuum representing the ice).

[1] M. S. Guidipati and L. J. Allamandola, Astrophys. J, 615:L177–L180 (2004)
[2] D. E. Woon, J. Y. Park, Astrophys. J, 607:342–345 (2004)

Determination of the Vertical Ionization Potential (VIP)

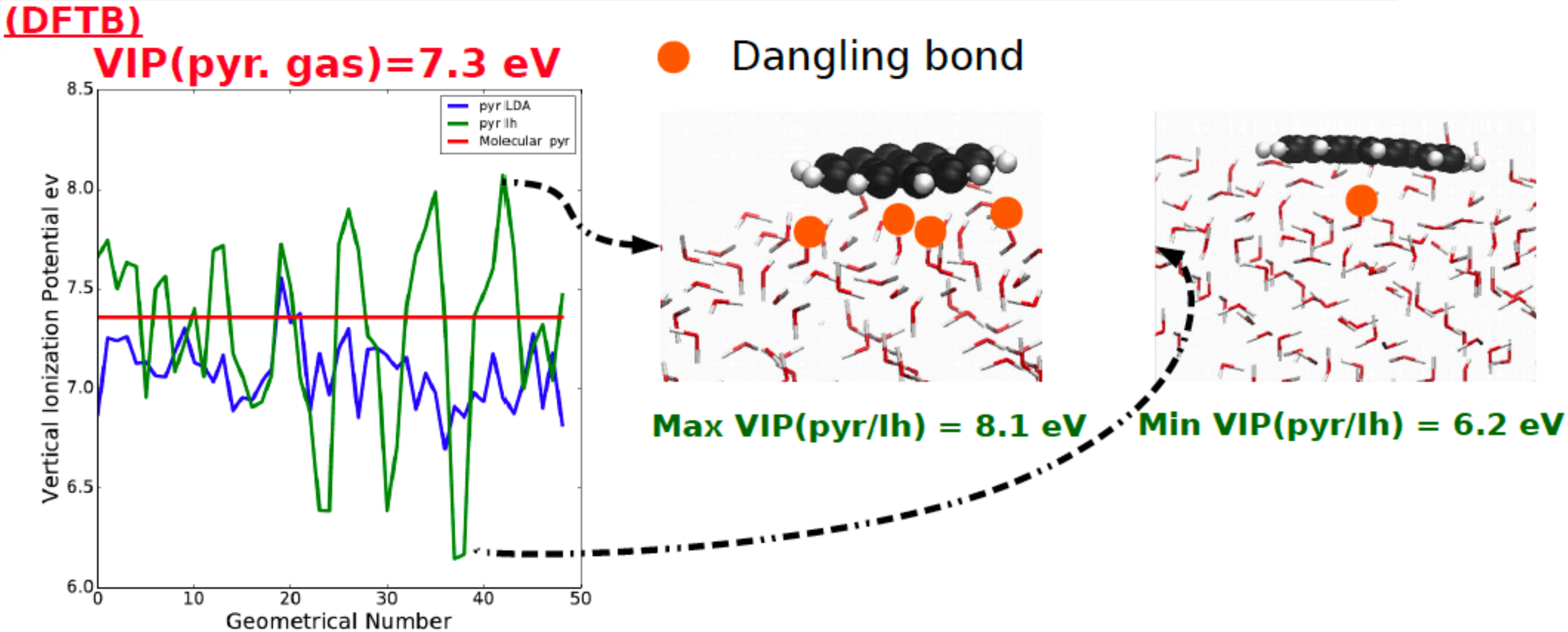


$$VIP = E(q=1) - E(q=0)$$

Benchmark:Excellent agreement between :
- Experimental and SCC-DFTB VIPs of PAHs in gas phase
-MP2 and C-DFTB PAHs/$(H_2O)_n$ system

PAHs on amorphous ices

Effect of ice environment on the ionization potential (IP)



At most, the VIP of pyr/Ih is lowered by 1.1 eV

At most, the VIP of pyr/LDA is lowered by 0.5 eV

VIP **depends** on the **explicit** description of water molecules

Ices do not lower the PAH's IP by 2eV!

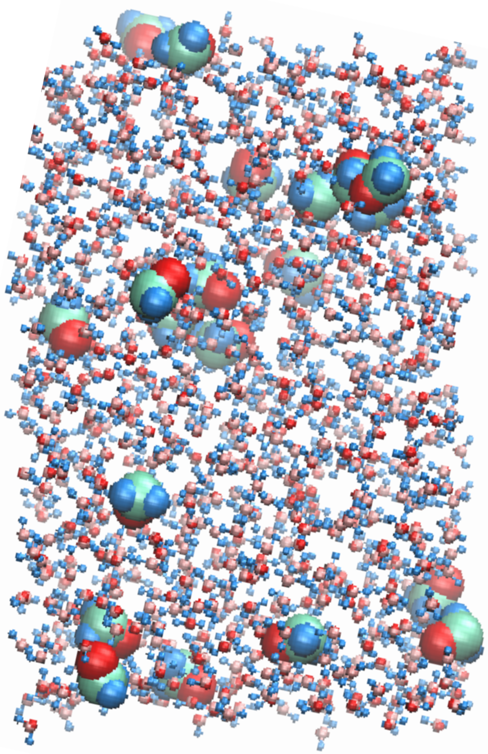
E. Michoulier et al, Phys. Chem. Chem. Phys, 2018, 20, pp.11941-11953.

Conclusion

Molecular description of ices by classical MD provides a representative sampling of the configurations for large ice samples
For reactivity, ionization, IR spectra, needs to be coupled with QM methods (DFTB, QM/MM)

Still some challenges remain

Describing pores remain difficult
(coarse grain approaches or MC)
Problems of charged species
Diffusion remains difficult to access
Problems in describing quantum effects
(tunneling…)
Mixed ices



H_2CO doped ice – M. Hechmi et al, in prep.

Coworkers

E. Michoulier, D. Duflot, M. Monnerville – PhLAM (Lille)`

A. Simon, M. Rapacioli, F. Spiegleman - LCPQ (Toulouse)

J. Mascetti, J. Noble – ISM (Bordeaux)

Support from PCMI, GDR EMIE

PhLAM

Université de Lille

cnrs

ANR