Contribution of the DFTB scheme to the modeling of water clusters

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Collaborators

MAD group :

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- Céline Toubin (PhLAM, Lille)
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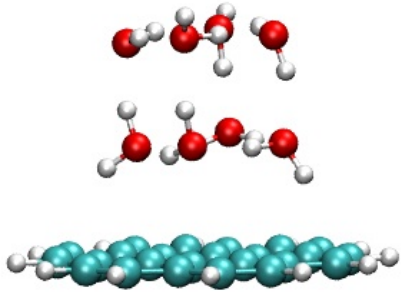
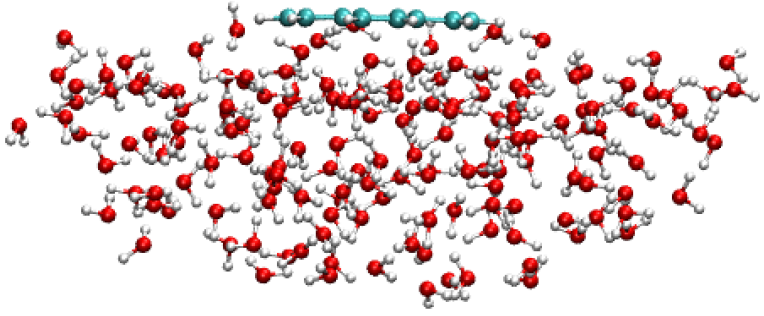
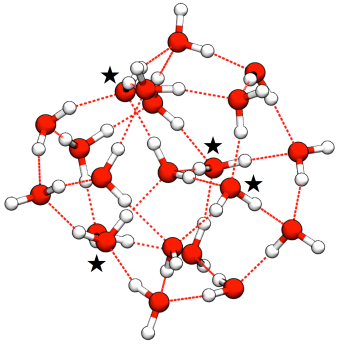
Which systems ?

- Pure water clusters (small : benchmark)
- In interaction with PAHs : clusters/ice

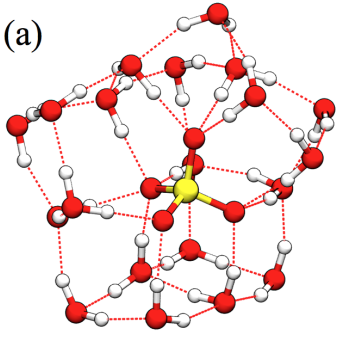




- Solvating impurities : proton, sulfate



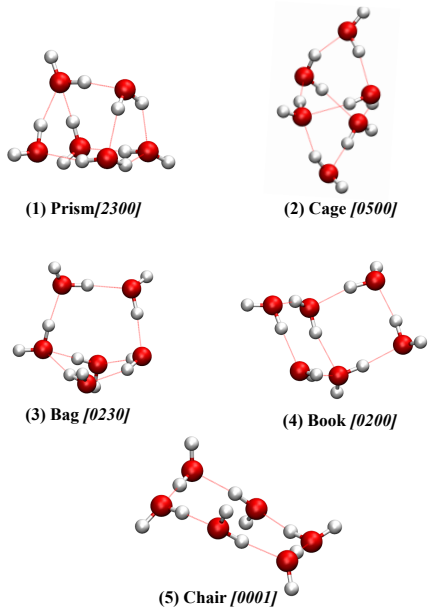
$[(H_2O)_{21}H]^+$

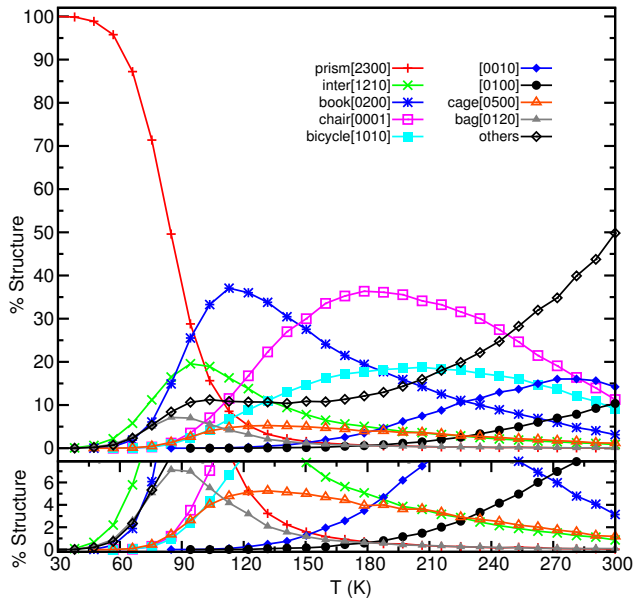


$[(H_2O)_{20}SO_4]^{2-}$

Properties of water clusters

- Complex potential energy surfaces : many isomeric structures



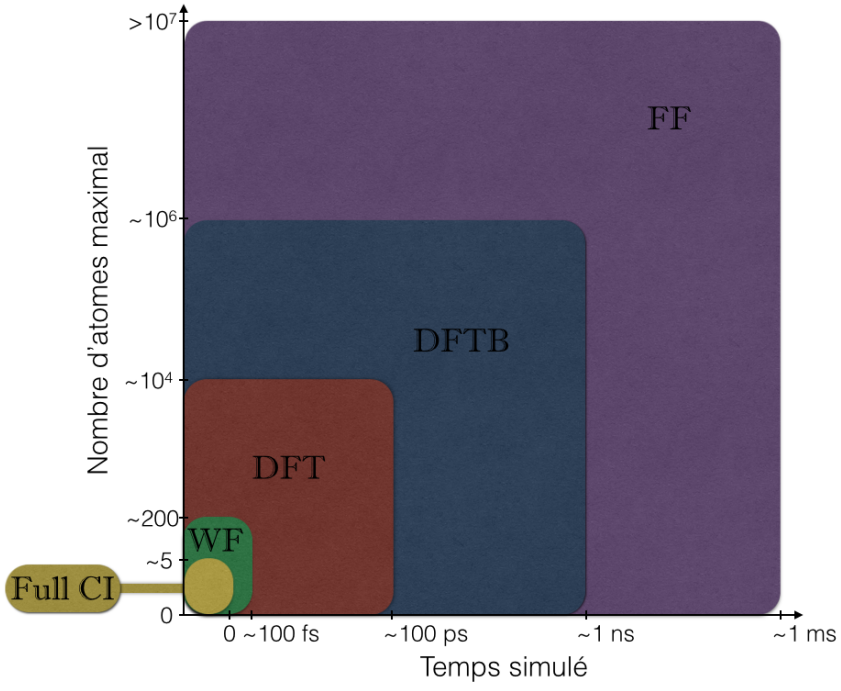


- Intermolecular interactions : hydrogen bonds, a challenge to describe
- Methods : DFTB + molecular dynamics (MD)

Equilibrium properties : structures, energetics, IR spectra, thermodynamics

The SCC-DFTB scheme : an approximate DFT method

- Self-Consistent-Charge Density Functional based Tight Binding (SCC-DFTB) method (*Elstner PRB 2008*) : parameterized functions and integrals, and reduced basis sets.



- Modifications of the SCC-DFTB hamiltonian to describe large molecular clusters ($\sim$ 1000 atoms) *(Rapacioli et al. Phys. Stat. Solid. B 2012)*

The SCC-DFTB scheme : an approximate DFT method

(1) Development of the Kohn-Sham energy up to the 2^{nd} order around ρ_0 :

$$E^{SCC-DFTB} = \sum_{i}^{occ} n_i \langle \psi_i | \hat{h}[\rho_0] | \psi_i \rangle + E^{rep}(\rho_0) + \frac{1}{2} \sum_{\alpha\beta} \gamma_{\alpha\beta}(R_{\alpha\beta}) \delta q_\alpha \delta q_\beta$$

* q : Mulliken charges in the initial SCC-DFTB scheme
* $E^{rep}(\rho_0)$, $\gamma_{\alpha\beta}(R_{\alpha\beta})$, $\langle \phi_\mu | \phi_\nu \rangle$ and $\langle \phi_\mu | \hat{h}[\rho_0] | \phi_\nu \rangle$ (Slater-Koster integrals) : analytically parametrized functions.

(2) Molecular orbitals : minimal (valence) linear combinations of atomic orbitals ϕ_μ :

$$\psi_i = \sum_{\mu} c_{i\mu} \phi_\mu$$

(3) All three-center contributions are neglected in the Kohn-Sham matrix.

Modifications of the SCC-DFTB hamiltonian to describe molecular clusters

- Dispersion Interactions ($(PAH)_2$, *Rapacioli et al. JCP 2009)*

$$V_{disp} = -\sum_{i \neq j} f_{damp.}(R_{ij}) \frac{C_6^{ij}}{R_{ij}^6}$$

- Alternative to Mulliken charges

  - **CM3 charges** (charges Model 3 *Li et al. JPCA 1998, Winget et al. JPCA 2002*)

$$q_k^{CM3} = q_k^{Mull} + \sum_{k' \neq k}^{atomes} D_{Z_k Z_{k'}} B_{kk'} \quad (B_{kk'}\ Mayer's\ bond\ order)$$

  Improvement of :

  - Dipole moments (*Simon et al. PCCP 2012)* $\rightarrow$ IR spectra (*Joalland et al. JPCA 2010)*

  - Long range electrostatic interactions : PAH clusters (*Rapacioli et al. JCP 2009)*, water clusters (*Simon et al. PCCP 2012, JCP 2013, CTC 2014)*

Modifications of the SCC-DFTB hamiltonian to describe molecular clusters

- Dispersion Interactions
- Alternative to Mulliken charges
  - **CM3 charges**

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Improvement of :
- Dipole moments
- Long range electrostatic interactions

Example : Bond dissociation energies (kcal/mol)

	$C_6H_6 - H_2O$	$H_2O - H_2O$
DFTB Mull.	1.4	1.7
DFTB CM3	2.6	3.1
Ref. Th. WF	2.17	3.11
Ref. Exp.	2.4-2.9	3.15-3.16

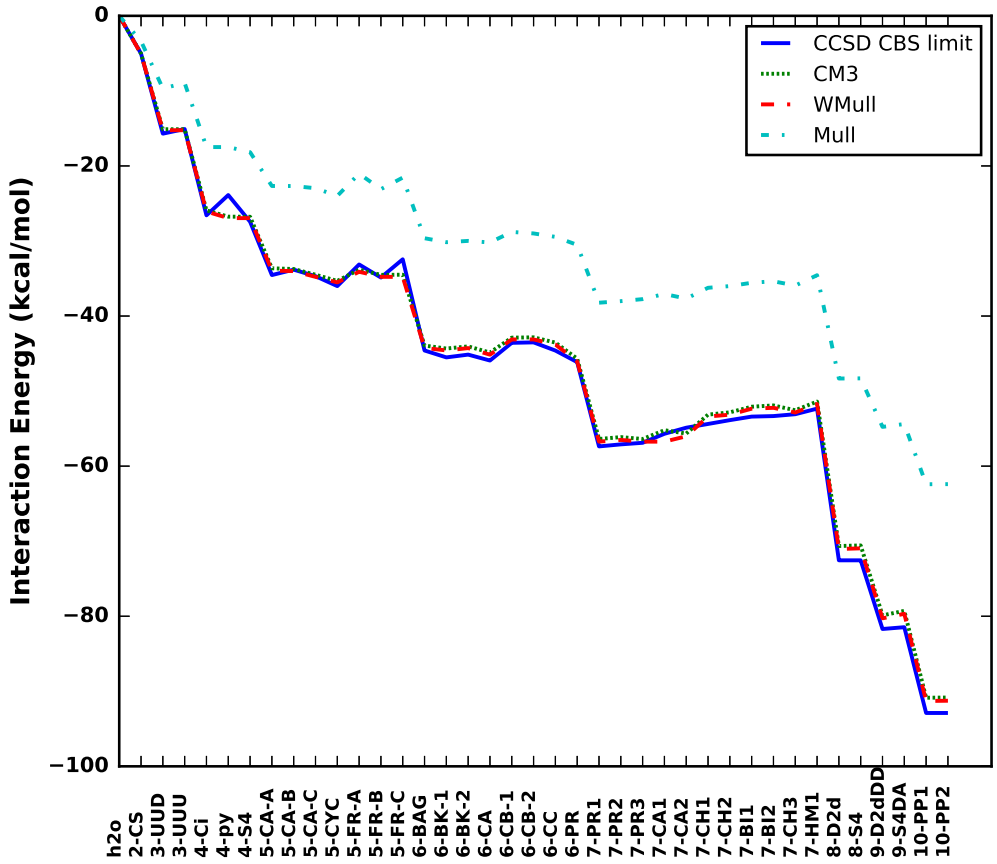
Modifications of the SCC-DFTB hamiltonian to describe molecular clusters

- Dispersion Interactions
- Alternative to Mulliken charges
  - **CM3 charges**
  - **"Weighted" Mulliken Charges** (*Michoulier et al. PCCP 2018, 20, 11941*), a simpler alternative to CM3 charges

$$\phi_\mu(r)\phi_\nu(r) \simeq \frac{1}{2} S_{\mu\nu}((1+t_{\mu\nu})|\phi_\mu(r)|^2 + (1-t_{\mu\nu})|\phi_\nu(r)|^2)$$

Modifications of the SCC-DFTB hamiltonian to describe molecular clusters

- Alternative to Mulliken charges : benchmark

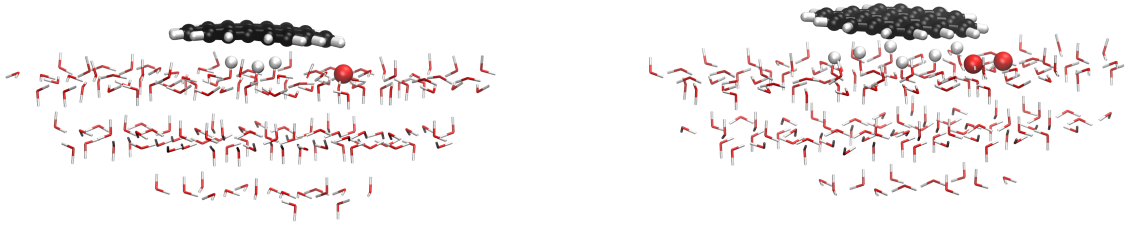


Interaction energies within water clusters : DFTB Mulliken, CM_3 (D_{OH}=0.13), and WMull (t_{OH}=0.39) vs WF calculations.

Static and dynamic approaches

- Static approach : local optimisation of "populations" of isomers of large systems

  Ex. 1 : Diagonalisation of the Hessian matrix : $[\frac{\partial^2 E}{\partial R_{\mu a} \partial R_{\nu b}}]_{eq}$: IR harmonic spectra of several configurations of PAH on ice (cf. talks of C. Toubin & J. Noble)



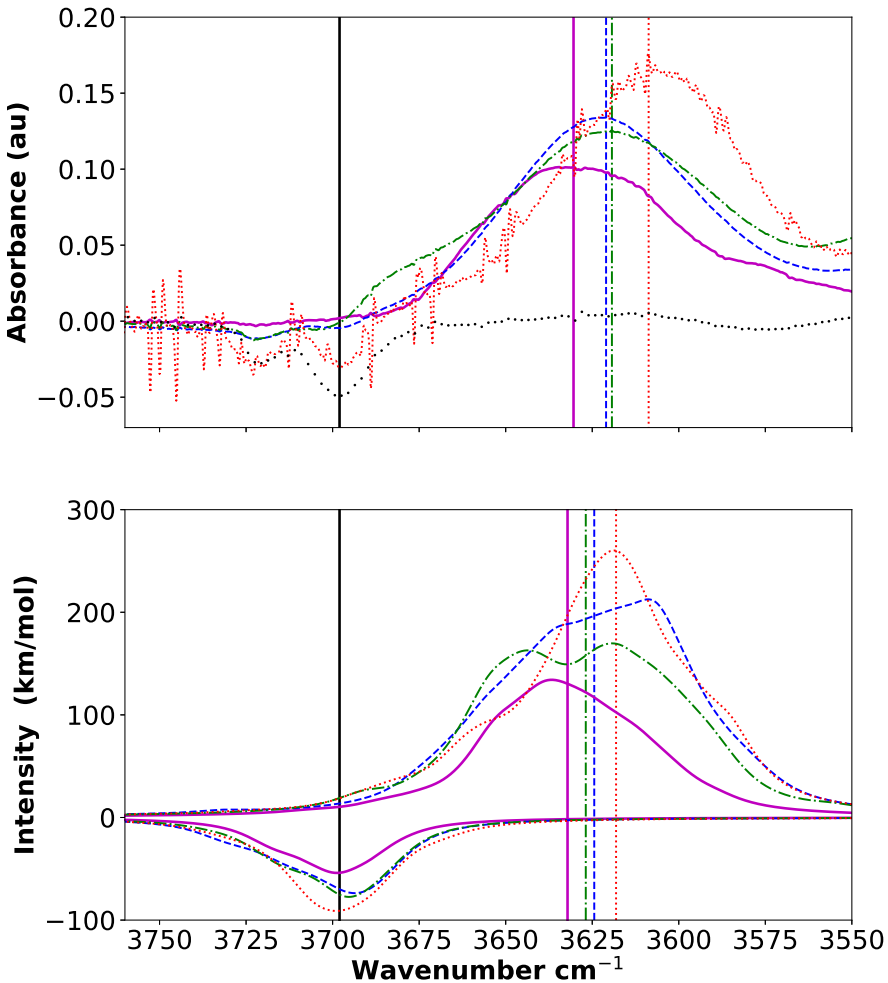
- On-the-fly Born-Oppenheimer MD/DFTB simulations in the ground electronic state : long runs $\rightarrow$ toward convergence

  Ex. 2 : Autocorrelation functions : finite-temperature effects on IR spectra

  Ex. 3 : Replica Exchange Molecular Dynamics (REMD) : heat capacities

Ex. 1 Vibrations : effect of PAH adsorption on dOH mode

Experiments vs calculations (Michoulier et al. JPCC, submitted)



Resonance of dOH mode

(Top : exp., Bottom : theo.)

Pure ASW : black ; + Bz : magenta ; +Anth : blue ; +Pyr : green ; +Cor : red.

Aromatic	δ dOH expt.	δ dOH theo.
Bz	-70	-74
Anth	-78	-79
Pyr	-79	-77
Cor	-84	-85

Good agreement exp./theo. -> cross validation of the approaches

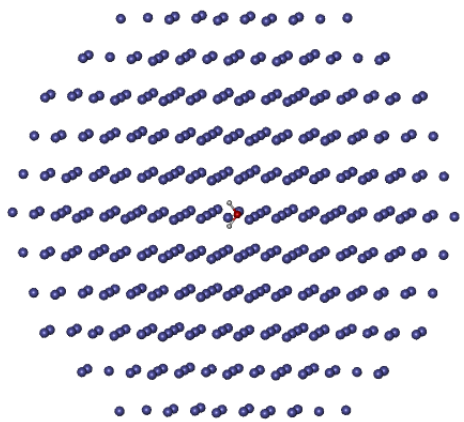
Ex. 2 Finite-temperature IR spectra from BOMD/DFTB

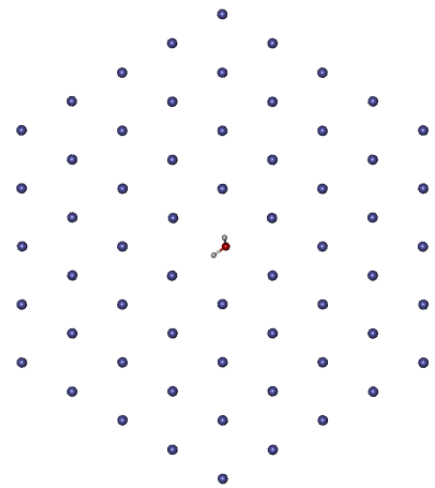
- Local optimization (gradient)
- Born-Oppenheimer MD simulations : (NVT) canonical sampling (a few *ps*) + (NVE) : $\sim$ 10 simulations of 300 ps to reach IR cross-section convergence
- IR cross sections obtained from the Fourier Transform of the dipole autocorrelation function

$$\alpha(\omega) \quad \propto \quad \omega^2 \int_0^{+\infty} \mathrm{d}t \langle \mu(0).\mu(t) \rangle \; e^{i\omega t}$$

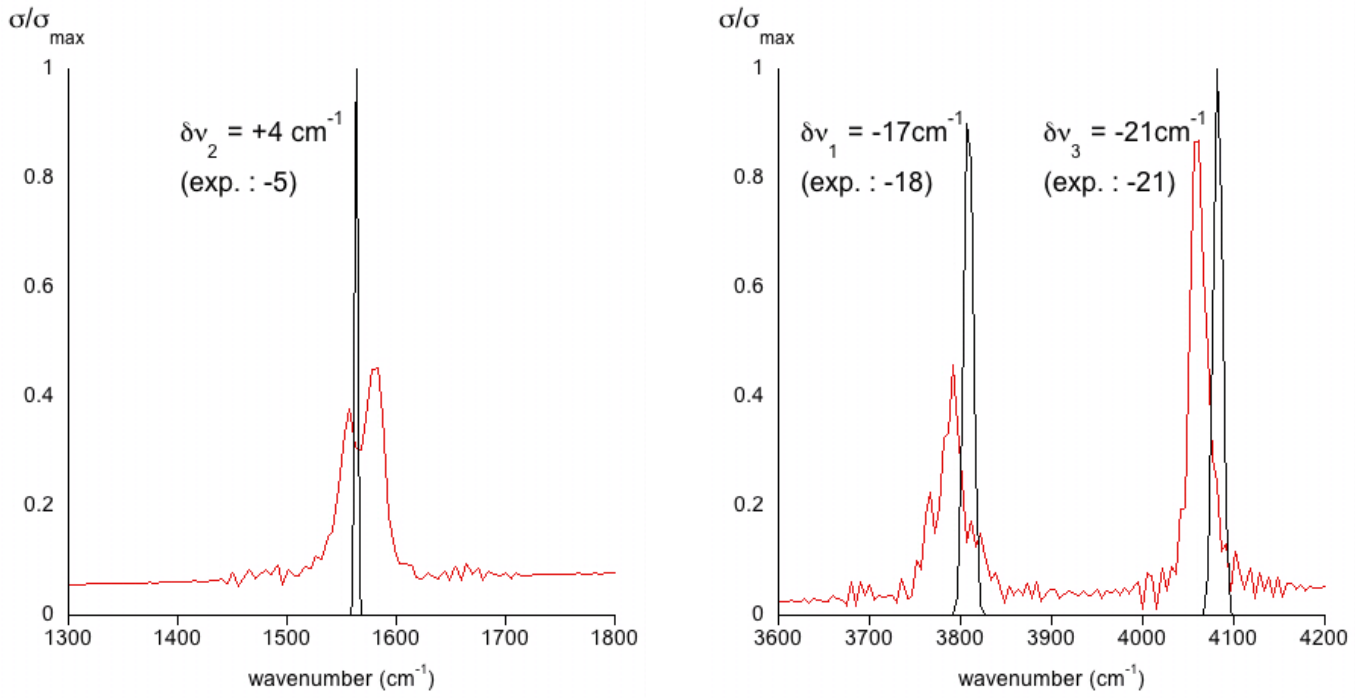
H_2O/Ar in an Ar matrix (H_2O/Ar) : model system

- QM (DFTB)/FF model (*Iftner et al. JCP 2014*)
- Matrix : finite-size system, organized in a face centered cubic crystalline structure, frozen atoms at the border.
- Experimental IR spectra available *(Perchard et al. Chem. Phys. 2001, Michaut et al. Vib. Spect. 2004)*





H_2O/Ar (substitution site) : IR spectra at 10 K in line with experimental results

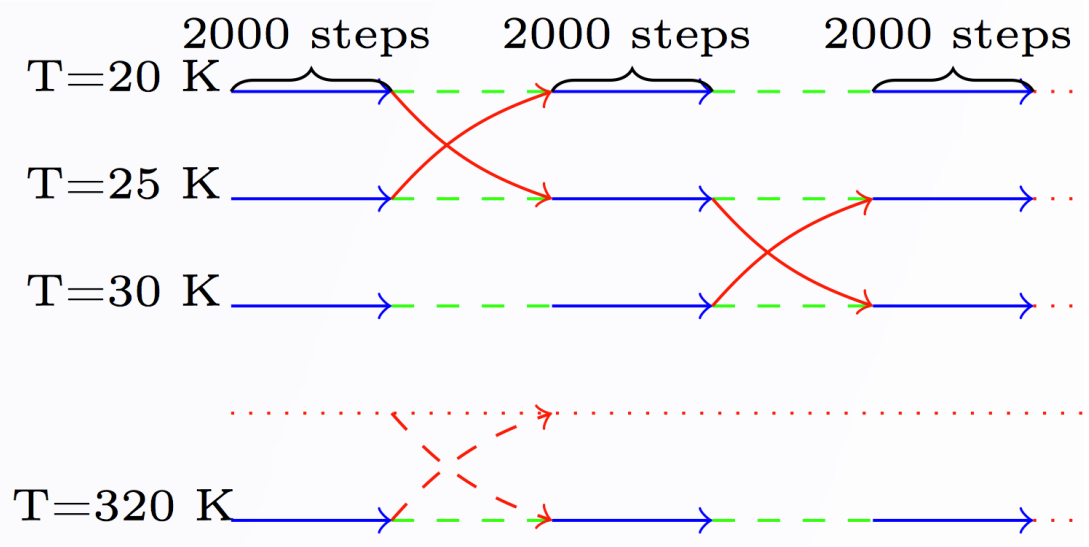


(a) (b)

Water IR spectra : gas phase (black), in *Ar* matrix (428 *Ar* atoms, red)

- H_2O/Ar with H_2O substituting one *Ar* atom : broadening + shifts in good agreement with experiment (*Perchard et al. Chem. Phys. 2001, Michaut et al. Vib. Spect. 2004*)

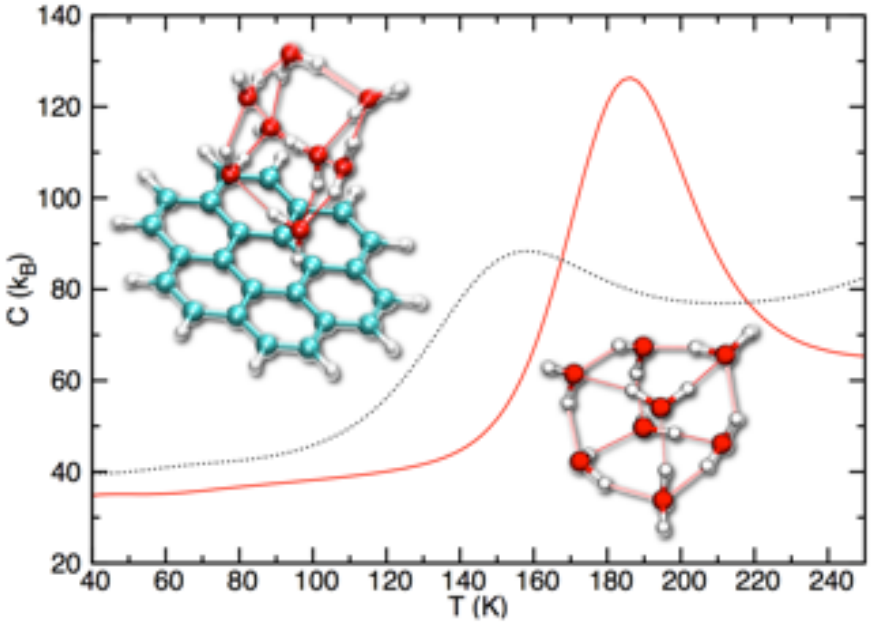
Ex. 3 Replica exchange molecular dynamics (REMD)



- N replica with independent trajectories
- Exchange probability (between T_i and T_j , $j = i + 1$)
- Metropolis criterium : $W(C_i\text{-}C_j) = \min(1, e^{\Delta E \Delta\beta})$
  with $\Delta E = E_i - E_j$ and $\Delta\beta = \frac{1}{k_B T_i} - \frac{1}{k_B T_j}$

PES exploration and thermodynamic data

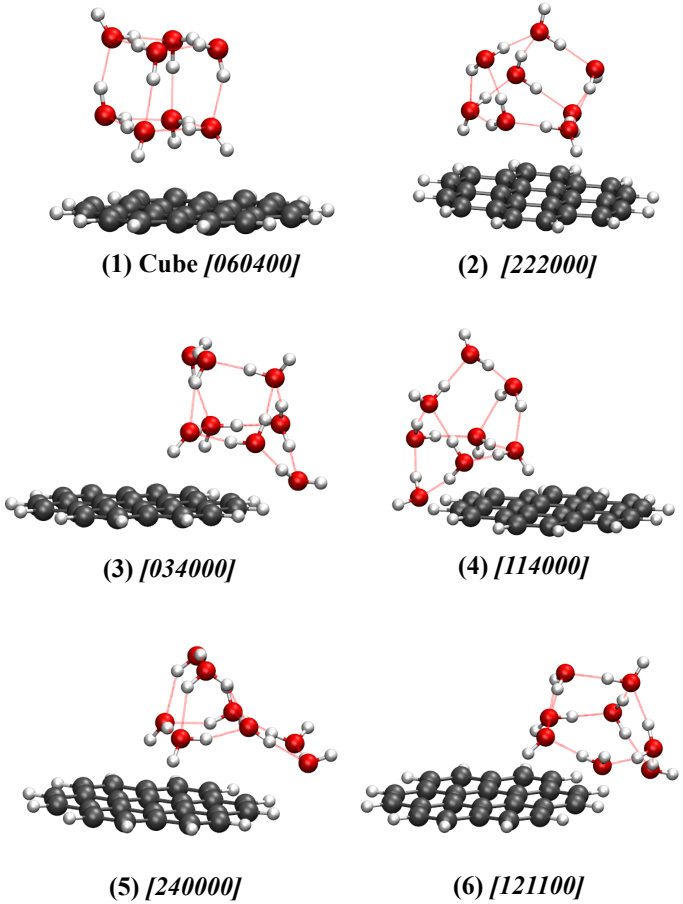
Thermodynamics : heat capacities



$$C(T) = \frac{3Nk_B}{2} + \frac{\langle V^2 \rangle - \langle V \rangle^2}{k_B T^2}$$

Oliveira et al. PCCP 2015

Labastie & Whetten PRL 1990



PAH-$(H_2O)_8$: phase change at lower temperature than $(H_2O)_8$: PAH surface favors "2D structures" : π_C–H and σ_H–OH_2 interactions

Summary and outlook

- Bridge the gap between DFT and force field approaches
- Transferability : solvation of a variety of systems
- Review : *Simon et al. Mol. Sim. Special Issue, 2019, 45, Issue 4-5 : "Water", 249-268*

- Nuclear quantum effects with PIMD (*Cuny et al. to be submitted*)
- Effect of solvation on electronic excited states with TD-DFTB : static and non adiabatic dynamics (Tully Surface Hopping)
- Liquid phase : modeling of interfaces - multiscale approach (PhD N. Cinq 2019-2022)