Contribution of the DFTB Scheme to the Description of Molecules and Clusters at the Water/Solvant interface

Aude Simon & **Jérôme Cuny**

Laboratoire de Chimie et Physique Quantiques (LCPQ)
Université de Toulouse & CNRS
UT3-Paul Sabatier

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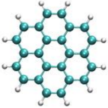
Outlook

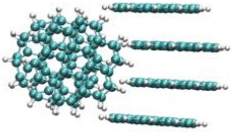
1. **Introduction**
2. Theoretical approaches
3. Towards bulk systems

Systems of interest : molecular clusters and complexes of atmospherical and astrophysical interest

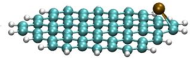
- PAH-derived species (PAH : Polycyclic Aromatic Hydrocarbon)
- The PAH population would represent 10-20 % of the interstellar carbon
- No specific PAH molecule has been identified



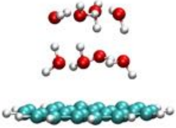
bare *PAHs*



PAH Clusters



$[XPAH]^+$ (X=Fe, Si)

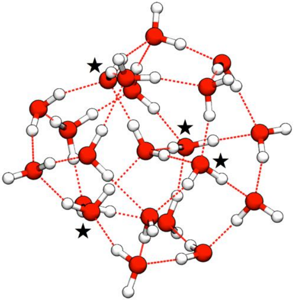


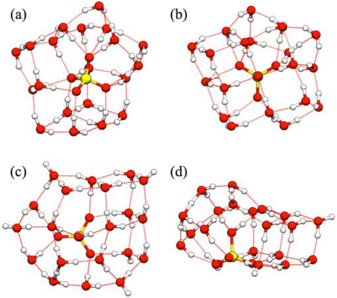
$(H_2O)_nPAH$

- Collaborations with experimentalists and astrophysicists (Groups of C. Joblin (IRAP/LCAR, ERC Nanocosmos) and P. Moretto-Capelle (LCAR, Toulouse, France))
- Structures, energetics, spectral features

Systems of interest : molecular clusters and complexes of atmospherical and astrophysical interest

- Water clusters (isolated and with impurities)





$(H_2O)_{21}H^+$ $(H_2O)_{20}SO_4^{2-}$ *(a,c)* ; $(H_2O)_{20}H_2SO_4$ *(b,d)*

from Korchagina et al. JPCA 2016 *from Korchagina et al. PCCP 2017*

- Collaborations with experimentalists (Group of J.-M. L'Hermite (LCAR, Toulouse, France))
- Structures, energetics, thermodynamic properties (heat capacities)

Systems of interest : molecular clusters and complexes of atmospherical and astrophysical interest

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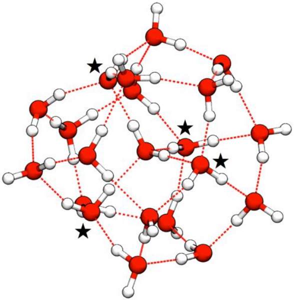

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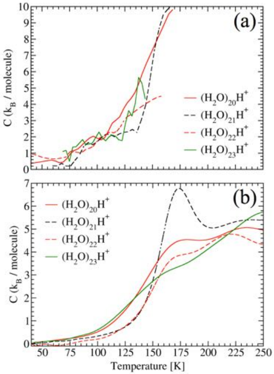

Cv(T) *from Korchagina et al. PCCP 2017*

- Collaborations with experimentalists (Group of J.-M. L'Hermite (LCAR, Toulouse, France))
- Structures, energetics, thermodynamic properties (heat capacities from MD with Replica Exchanges)

Approach : BOMD/SCC-DFTB

- Extensive "On-the-fly" Born Oppenheimer molecular dynamics simulations (BOMD, nuclei : classical, electrons : quantal) of $\sim$100 ps-1 ns
- Electronic structure described with the Self-Consistent-Charge Density Functional based Tight Binding (DFTB) method (*Elstner PRB 2008*) with the deMonNano code (http ://demon-nano.ups-tlse.fr/)
- SCC-DFTB : An approximate DFT-based approach significantly faster than DFT : parameterized functions and integrals, and reduced basis sets.

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(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 *(Rapacioli et al. Phys. Stat. Solid. B 2012)*

- 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 : charges CM3 (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)*

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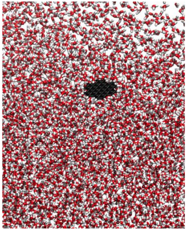
Example : Bond dissociation energies (kcal/mol)

	$C_6H_6 - H_2O$	$H_2O - H_2O$
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

System of interest : PAHs on water ice (astro. and atmosph.)

- PAHs adsorbed on water ice *(Michoulier et al. PCCP 2018 a and b)*



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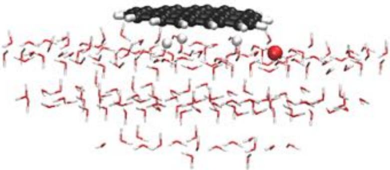


MD/FF : structures

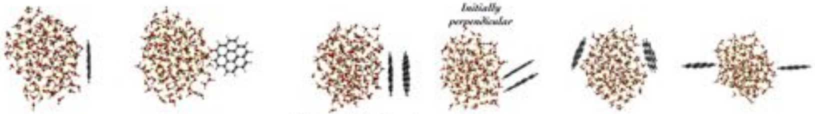
DFTB : ionisation energy of adsorbed PAHs
IR spectra

- Collaborations with C. Toubin (Lille, France) and J. Mascetti (Bordeaux, France)
- Adsorption energies (benchmark on TPD experiments)
- Influence of interface structure on the ionisation energy of PAHs (now charge transfer excited states)

Systems of interest : asphaltene molecules/clusters at the interface with water

- Collab. V. Pauchard, involving S. Darjani (PhD)
- Preliminary results : finite systems

Fig. 1 DFTB optimized geometries and interaction energies between PAH and water clusters



PAH - $(H_2O)_{200}$ interaction energy

1.00 eV	*0.38 eV*	*1.16 eV*	*0.80 eV*	*2.05 eV*	*0.65 eV*

PAH – PAH interaction energy

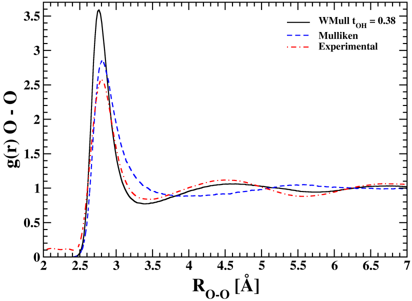
0.74 eV *0.76 eV*

- Most favorable situation (both in terms of total energy and water-PAH energy) : individual coronene molecules parallel to water surface
- Water-PAH interaction energy in line with experimental free energies of adsorption for smaller PAH (Raja et al J. Chem. Engin. Data 2002, 47, 1213-1219)

from Petrophase 2016 poster by Pauchard, Cuny and Simon

Systems of interest : asphaltene molecules/clusters at the interface with water

- Description of liquid water (and aromatic solvent)

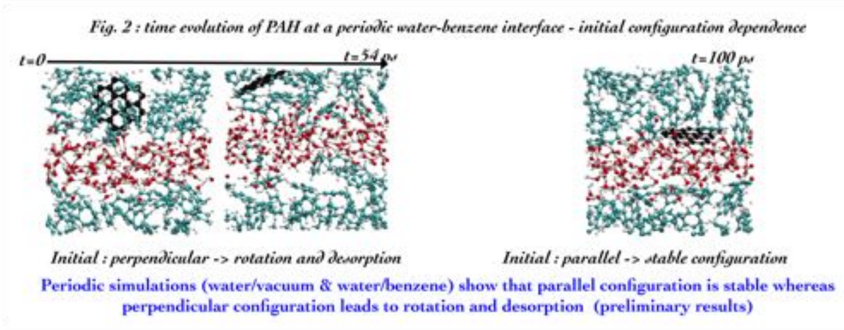


from Simon et al., Mol. Sim., submitted

- RDF for O-O for liquid water at 300 K obtained from BOMD/SCC-DFTB simulations, modified Mulliken charges (similar to CM3).
- Details : Periodic conditions, cubic box of 16 $Å^3$, 128 water molecules, chain of Nose-Hoover thermostats, 100 ps of production run
- + Nuclear quantum effects with Path Integral Molecular Dynamics simulations (PIMD, *Cuny et al, to be submitted*).

Systems of interest : asphaltene molecules/clusters at the interface with water

- Collab. V. Pauchard, involving S. Darjani (PhD)
- Current work : MD/DFTB simulations in periodic conditions



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Ongoing and Future work

Asphaltene at the water interface

- Refine theoretical description
- Chemical modifications : size, heteroatoms, akylside chains
- Change of solvant, presence of impurities
- $\rightarrow$ Influence on structures, energetics and kinetics at the interface
- $\rightarrow$ Adsorption energies and solvation energies (umbrella sampling)

Gas hydrates

- New topic (collab. LGC, Toulouse, France)
- Test on some systems (so far about 1500 atoms maximum in the cell)
- Same data as for the ashaltene project

Use of transferability and efficiency of MD/SCC-DFTB

Acknowledgments

- Mathias Rapacioli
- CALMIP (computing mesocenter in Toulouse, France)