Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for "Theoretical determination of adsorption and ionisation energies of polycyclic aromatic hydrocarbons adsorbed on water ice"

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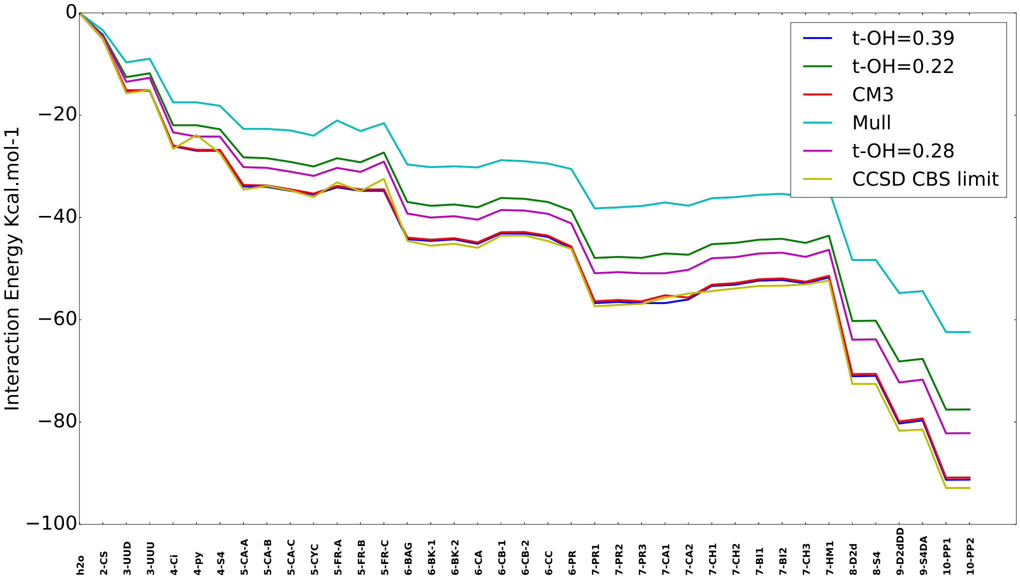


Figure S1: Interaction energies within water clusters : comparison between wavefunction results (CCSD-CBS limit),[1] DFTB results using CM3 charges (DOH=0.13)[2] and several t_{OH} trial values. The x-axis represnet water clusters with increasing size, under different isomeric forms using the acronyms of ref.[1]

Table S1: Interaction energy in kJ.mol^{-1} for $(H_2O)_2$ and various isomers of $(C_6H_6)(H_2O)$ and $(C_{24}H_{12})(H_2O)$ clusters. The nature of the isomers (min., lat., cent.) refers to those mentionned in Fig. 3 of ref.[2] for coronene. The geometries were optimized at the SCC-DFTB level using the CM3 charges of ref.[2] (DOH=0.13, DCH=0.098 and DOC=0.0), the WMull charges determined in the present paper and the Mull values of the original SCC-DFTB hamiltonian.

System	Isomer	CM3	WMull	Mull
$(H_2O)_2$		12.9	13.0	7.3
$(C_6H_6)(H_2O)$	min	10.8	10.7	5.8
	lat	5.8	5.8	2.7
$(C_{24}H_{12})(H_2O)$	min	11.3	11.2	7.4
	cent.	9.8	9.7	6.5
	lat.	8.8	8.8	4.8

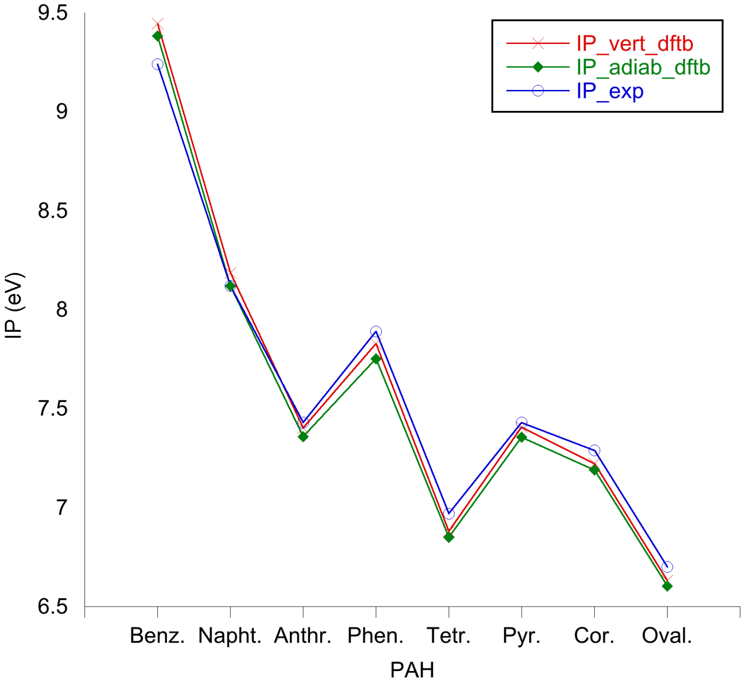


Figure S2: DFTB computed vertical (red) and adiabatic (green) ionisation potentials vs experimental values[3] for bare PAHs.

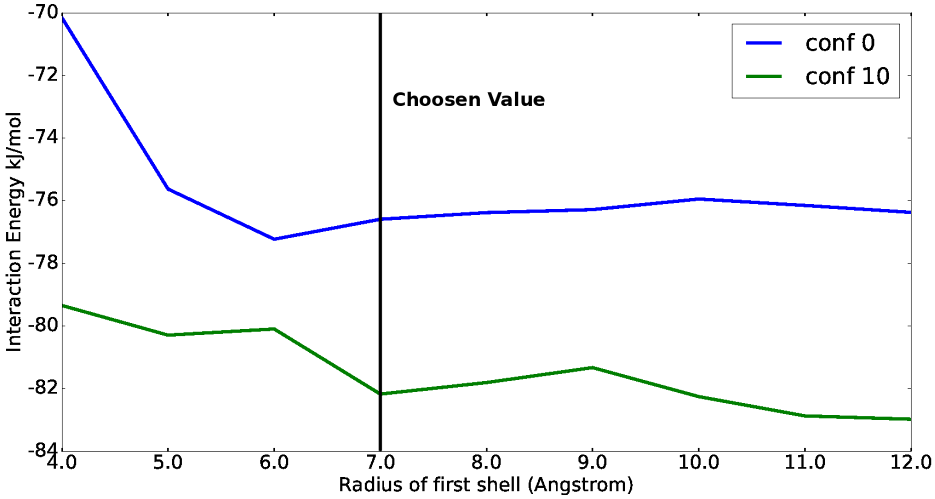


Figure S3: Convergence of the DFTB interaction energy of pyrene-LDA ice for two examples of configurations, as a function of R1, with a constant R2-R1 difference of 3.5 Å

References

(1) Temelso, B.; Archer, K. A.; Shields, G. C. Benchmark Structures and Binding Energies of Small Water Clusters with Anharmonicity Corrections. *J. Phys. Chem.A* **2011**, *115*, 12034–12046.

(2) Simon, A.; Rapacioli, M.; Mascetti, J.; Spiegelman, F. Vibrational spectroscopy and molecular dynamics of water monomers and dimers adsorbed on polycyclic aromatic hydrocarbons. *Phys. Chem. Chem. Phys.* **2012**, *14*, 6771–6786.

(3) Lias, S. "Ionization Energy Evaluation" in the WebBook of Chemistry NIST number 69 Eds. P.J. Linstrom et W.G. Mallard,National Institute of Standards and Technology, Gaithersburg MD, 20899.

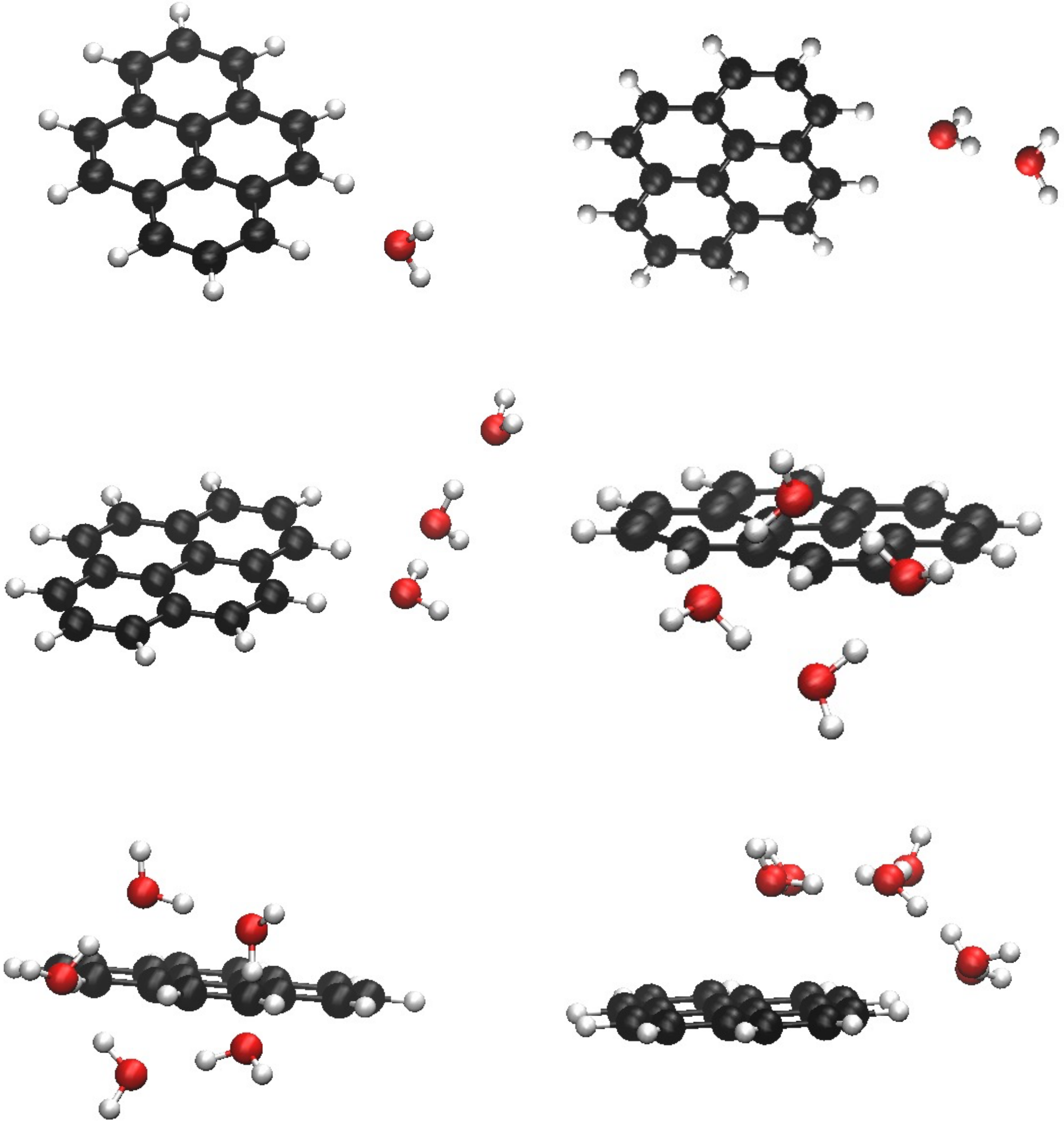
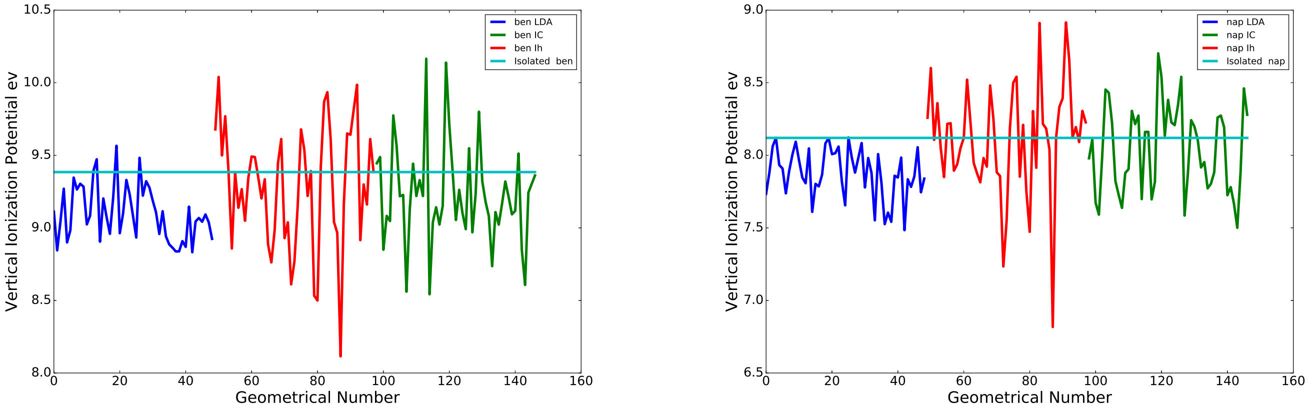
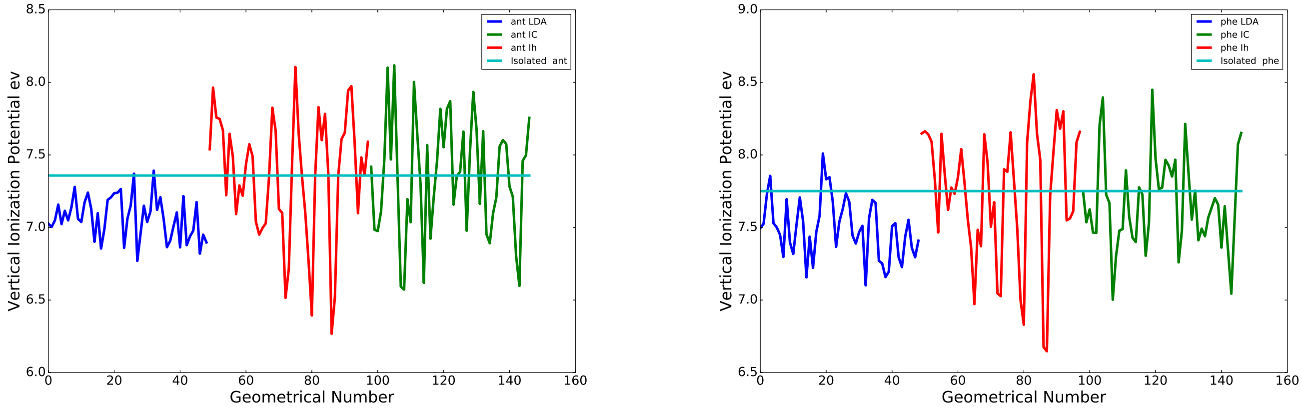


Figure S4: C-DFTB optimized geometries of cationic pyrene solvated by water clusters ($n_{H_2O} = 1 - 6$)



Benzene

Naphthalene

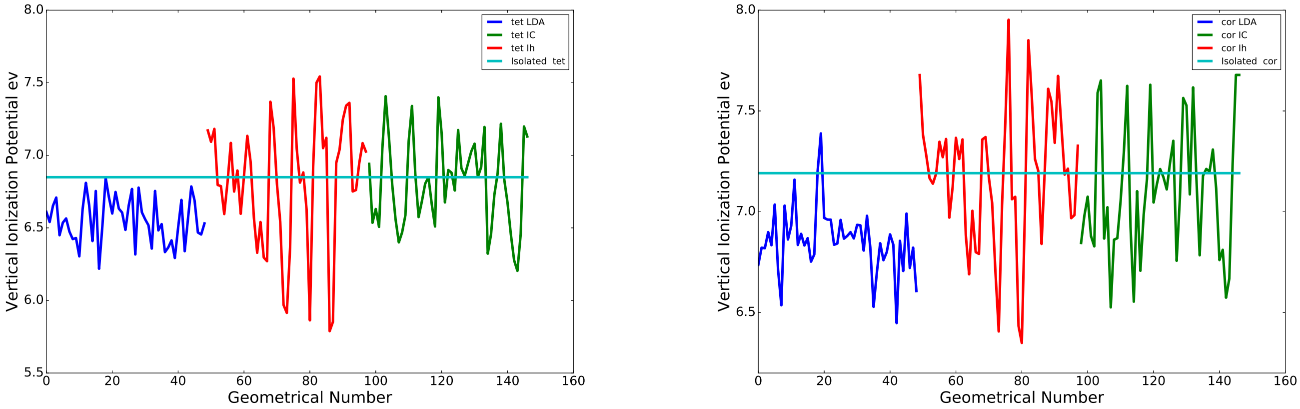


Anthracene

Phenanthrene

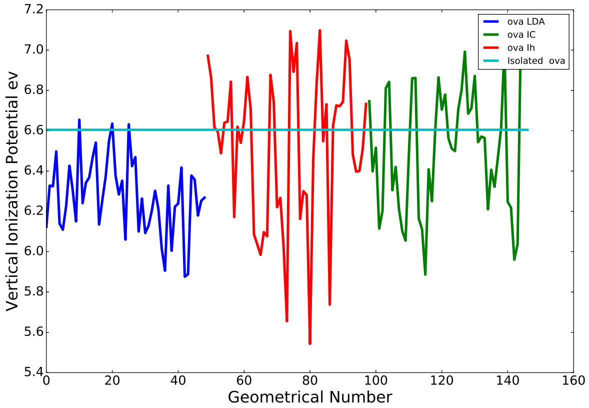
(a) First Part

Figure S5: Evolution of VIPs with PAH configuration for all studied PAH, from benzene to ovalene (increasing size from top to bottom), on the three ices types.



Tetracene

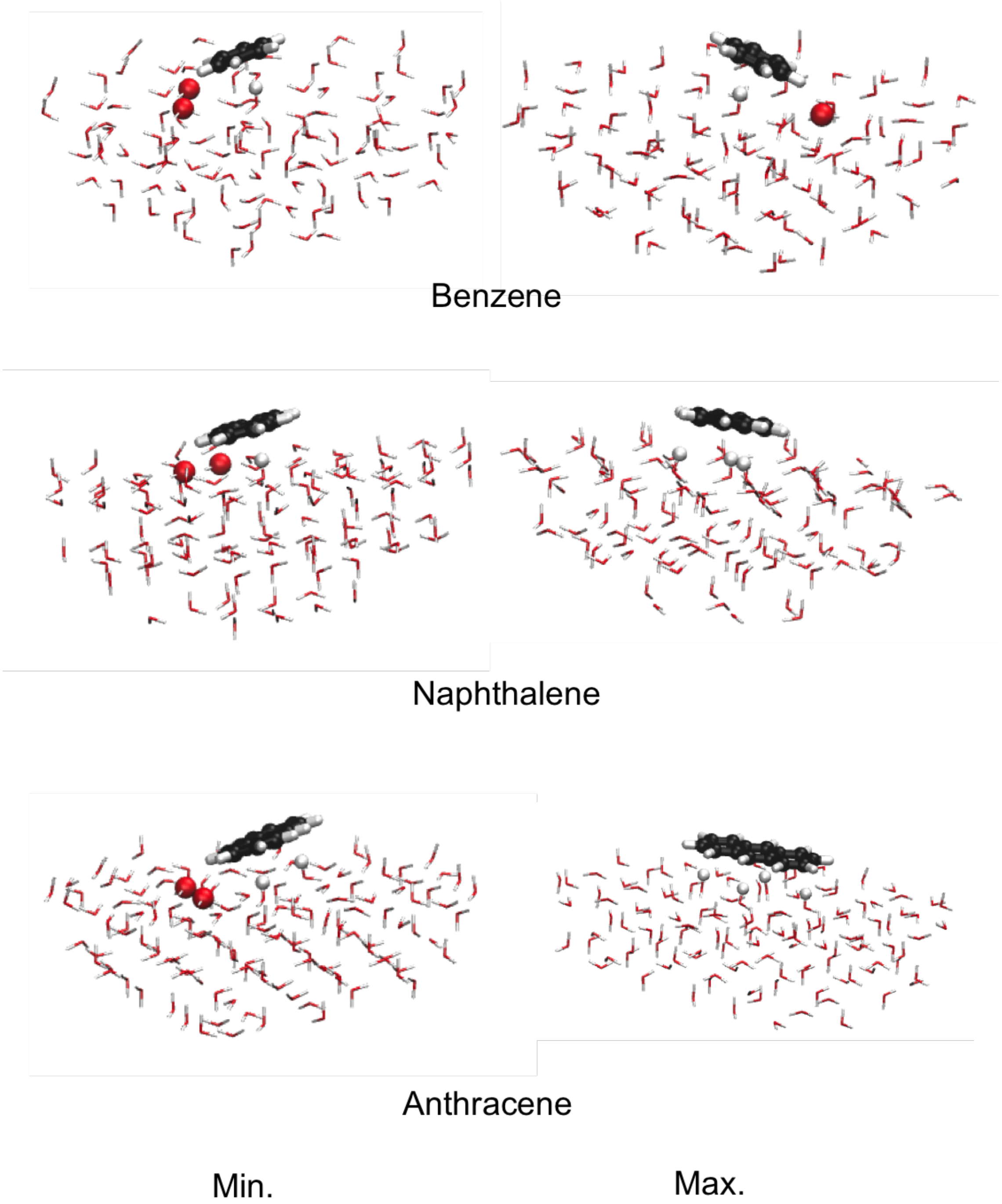
Coronene



Ovalene

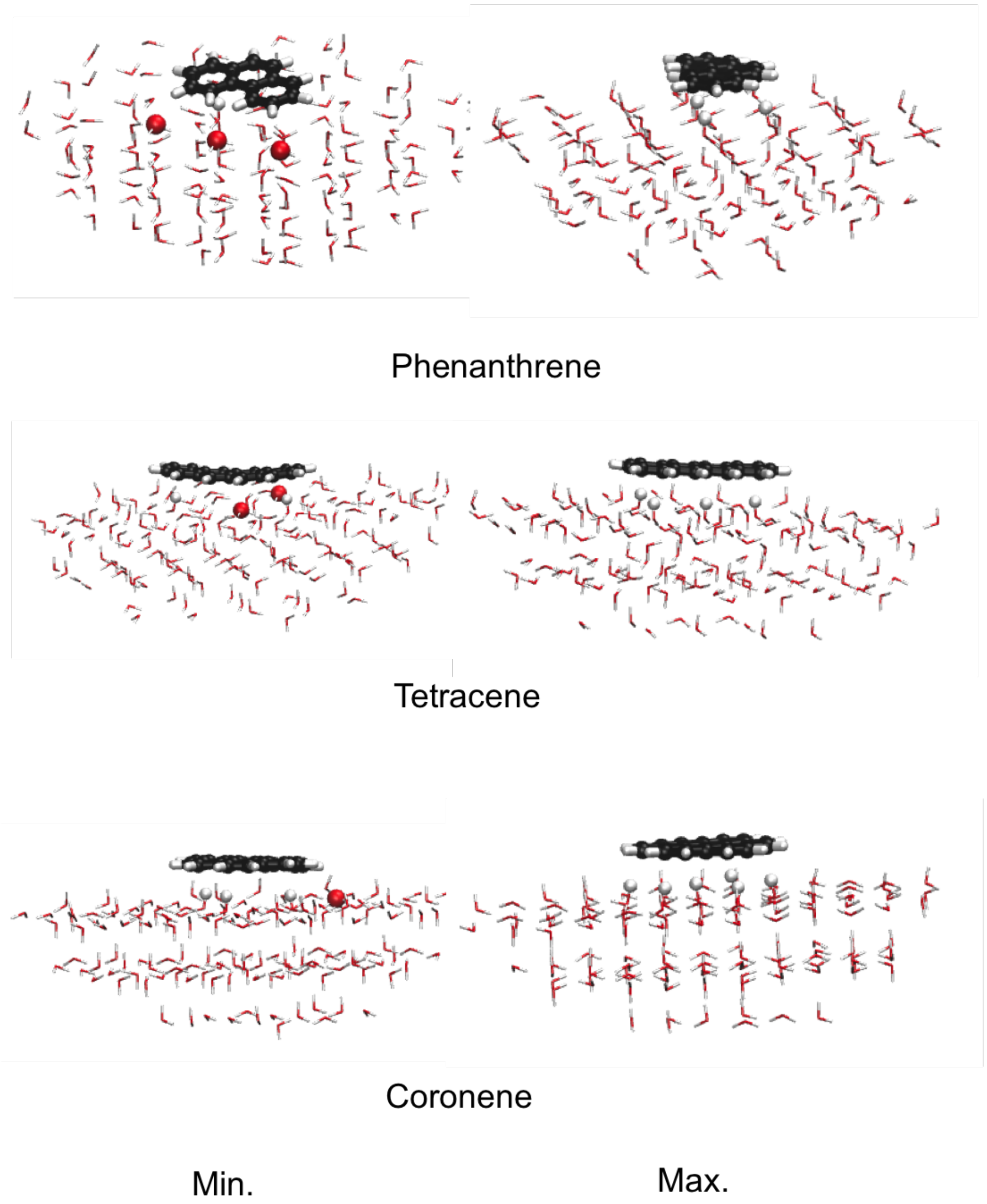
(b) Second Part

Figure S5: Evolution of VIPs with PAH configuration for all studied PAH, from benzene to ovalene (increasing size from top to bottom), on the three ices types (con't).



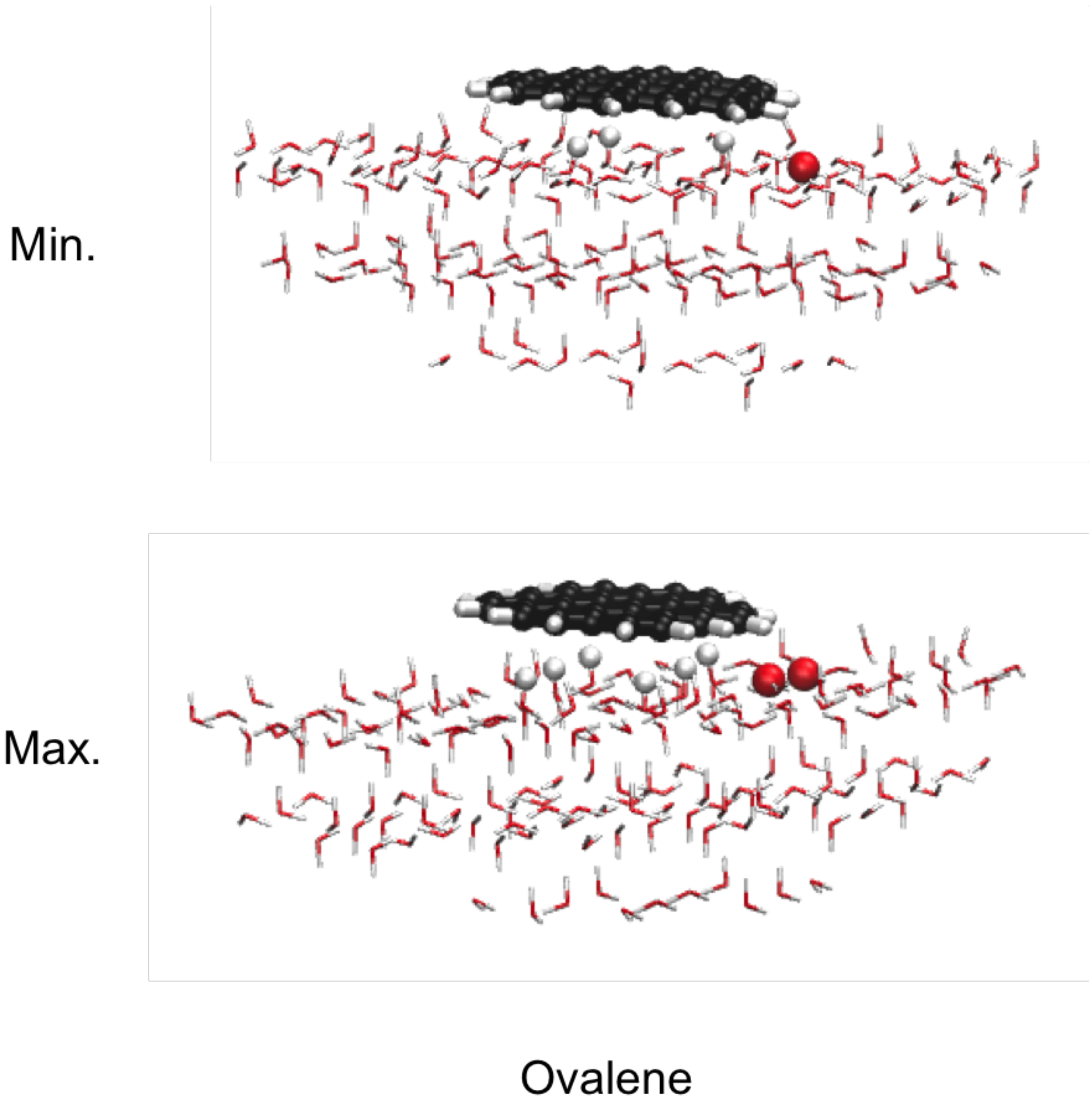
(a) First Part

Figure S6: PAH-ice configurations corresponding to the lowest (”Min.”) and highest (”Max”) vertical ionization potential , for hexagonal ice, for all studied PAHs (except pyrene)



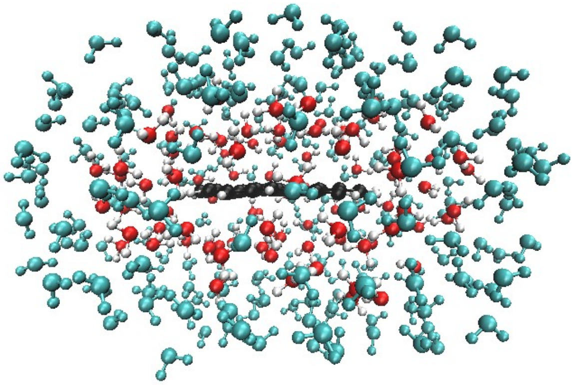
(b) Second Part

Figure S6: PAH-ice configurations corresponding to the lowest (”Min.”) and highest (”Max”) vertical ionization potential , for hexagonal ice, for all studied PAHs (except pyrene), con’t

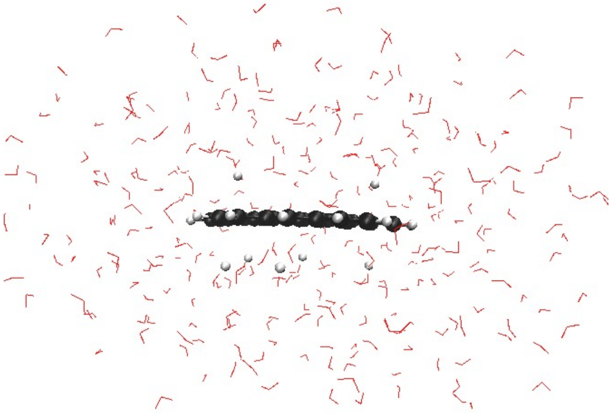


(c) Third Part

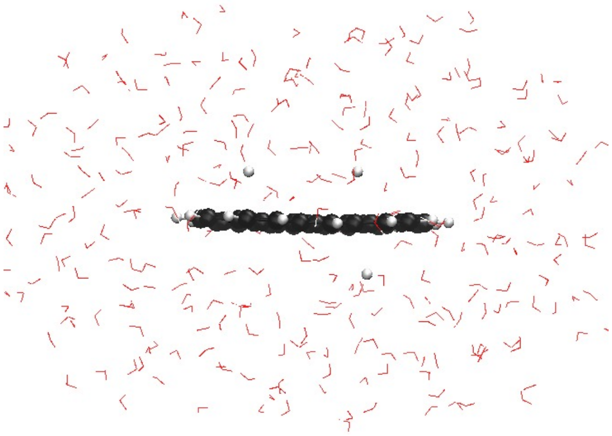
Figure S6: PAH-ice configurations corresponding to the lowest (”Min.”) and highest (”Max”) vertical ionization potential , for hexagonal ice, for all studied PAHs (except pyrene), con’t



(a) Example of solvated ovalene. The molecules in blue are frozen, the others are relaxed during the optimization.



(b) Configuration 1 of the ovalene for which the energy of interaction is -295 kJ.mol^{-1}. The VIP is 6.45 eV.



(c) Configuration 2 of the ovalene for which the energy of interaction is -213 kJ.mol^{-1}. The VIP is 6.38 eV.

Figure S7: Solvated ovalene geometries. Dangling OH bonds of water molecules interacting with carbons are represented with white balls. Configuration 1 (resp. 2) contains 96 (resp. 96) water molecules allowed to relax during the relaxation process), and 196 (resp. 208) frozen water molecules (the shell).