PAHs photo-reactivity with water clusters and water ice: structures, energetics and spectra from FTIR experiments and a multi-method theoretical study

H. Leboucher[1], E. Michoulier[1,2], J.A. Noble[3], C. Aupetit[4], C. Toubin[2], N. Ben Amor[1], A. Simon[1] and J. Mascetti[4].

[1] *Université Paul Sabatier, CNRS UMR 5626, LCPQ, F-31062 Toulouse cedex 09, France*
[2] *Université de Lille, CNRS UMR 8523 PhLAM, F-59655, Villeneuve d'Ascq cedex – France*
[3] *Aix-Marseille Université, CNRS UMR 7345, PIIM, F-13397 Marseille cedex 20, France*
[4] *Université de Bordeaux, CNRS UMR 5255, ISM, F-33405 Talence cedex, France*
joelle.mascetti@u-bordeaux.fr

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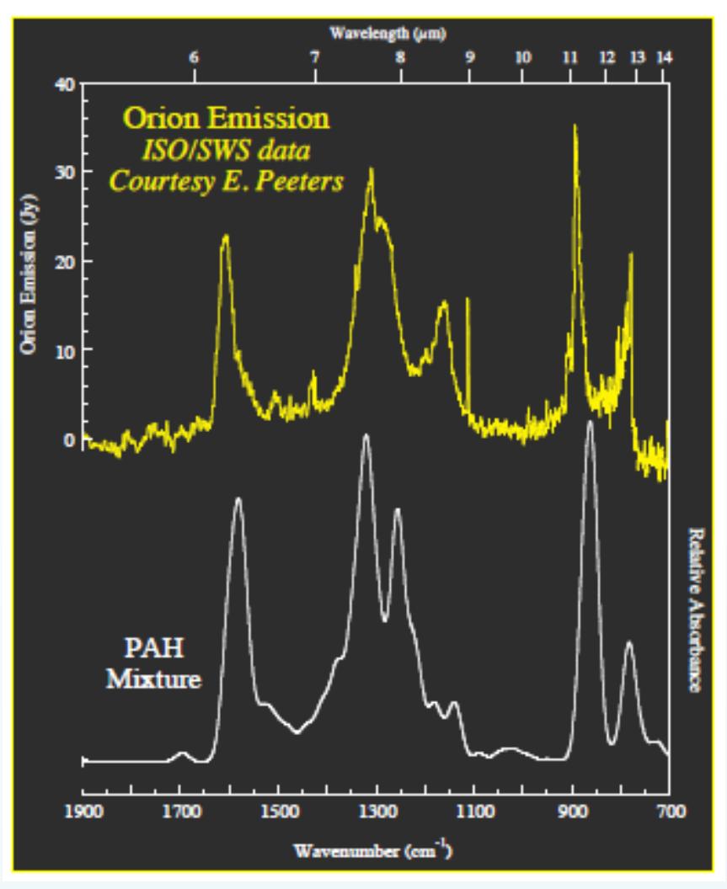
Polycyclic Aromatic Hydrocarbons (PAHs) are organic molecules representing around 20% of carbon in the Universe. They have been proposed to be the carriers of the Aromatic Interstellar Bands (AIBs), a set of infrared (IR) emission bands observed in the [3 - 15 μm] range in many regions of the interstellar medium (ISM). In dense environments, PAHs are likely to condense onto or integrate into water ice mantles covering dust grains and to contribute to the complex grain chemistry [1]. **The photochemistry of PAHs at the surface of cold, ice-covered grains** can produce a large number of aromatic species, such as alcohols and quinones.

Understanding the role of ice in the processes involving adsorbed PAHs is therefore a key issue in astrochemistry.

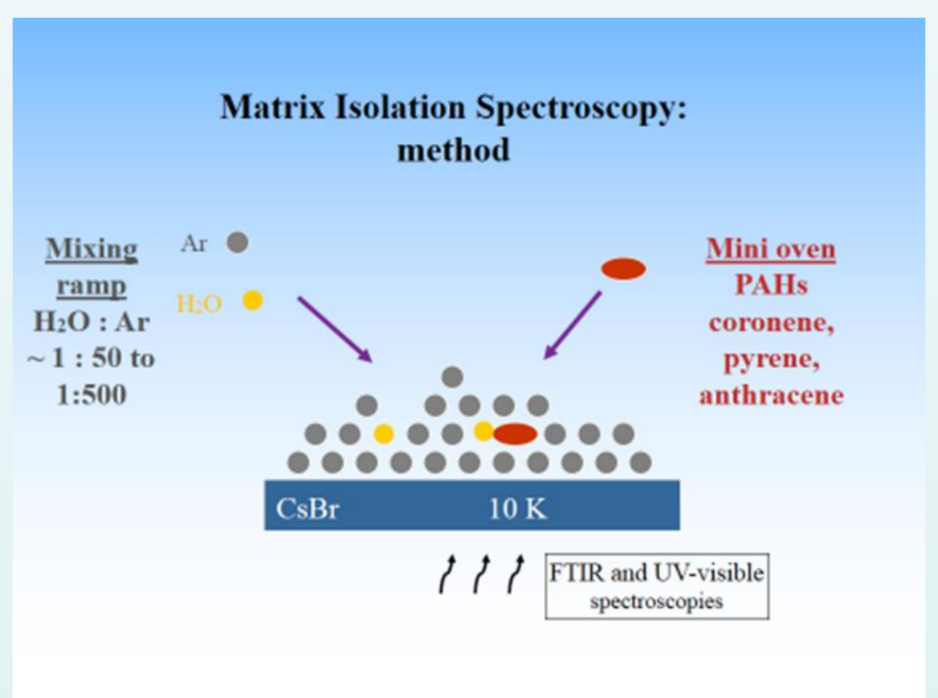
Our joint theoretical (classical molecular dynamics/force field simulations and SCC-DFTB calculations) and experimental (matrix isolation FTIR spectroscopy) study has allowed to elucidate:

- the role of water clusters and of ice structure on the photo-reactions of PAHs. [2]
- the relationship between the number of interacting dangling OH (dOH) bonds of ice and PAH ionization potential variation. [3]
- how the surface of amorphous solid water (ASW) is perturbed by the adsorption of PAHs. [4]
- the effect of the PAH structure by comparing coronene and corannulene photoreactivity with water. [5]
- the PAH-ice interaction in the ground electronic state at low temperature, providing the binding energies and barrier heights necessary to the improvement of astrochemical models. [6]

UIR/AIB spectrum compared to PAHs



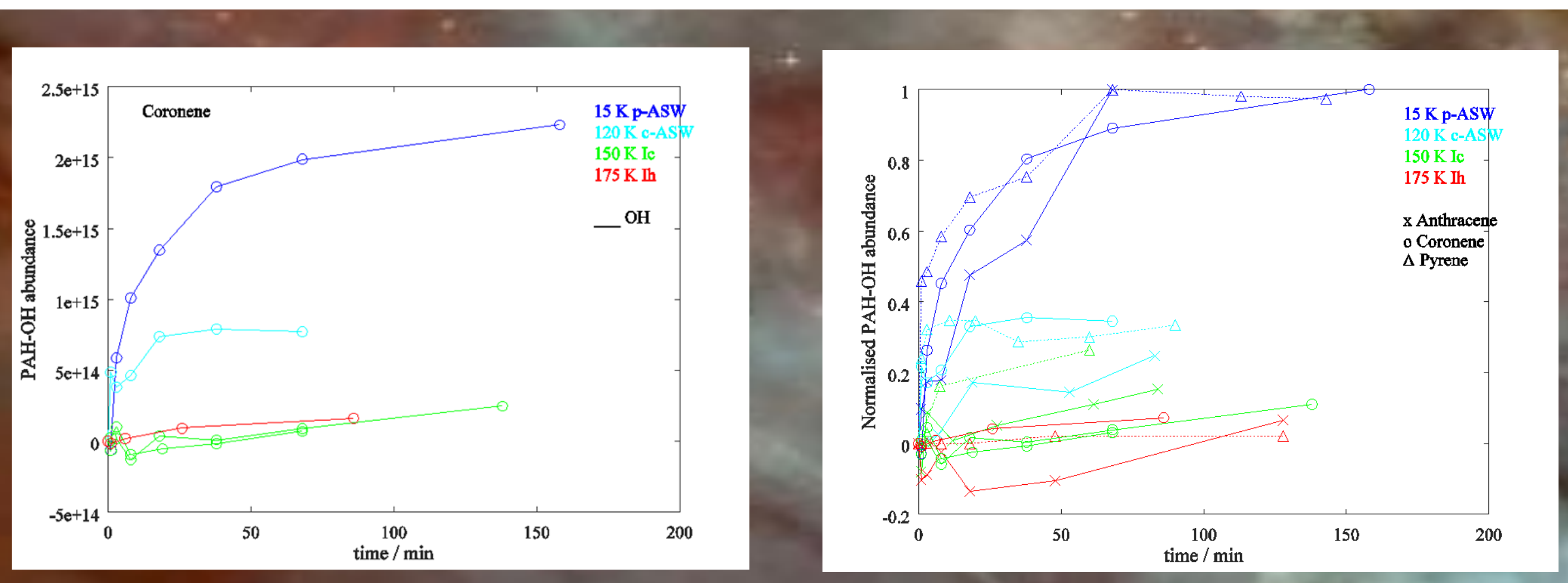
E. Peeters, 2002



Theoretical details: **a multi-method approach** :

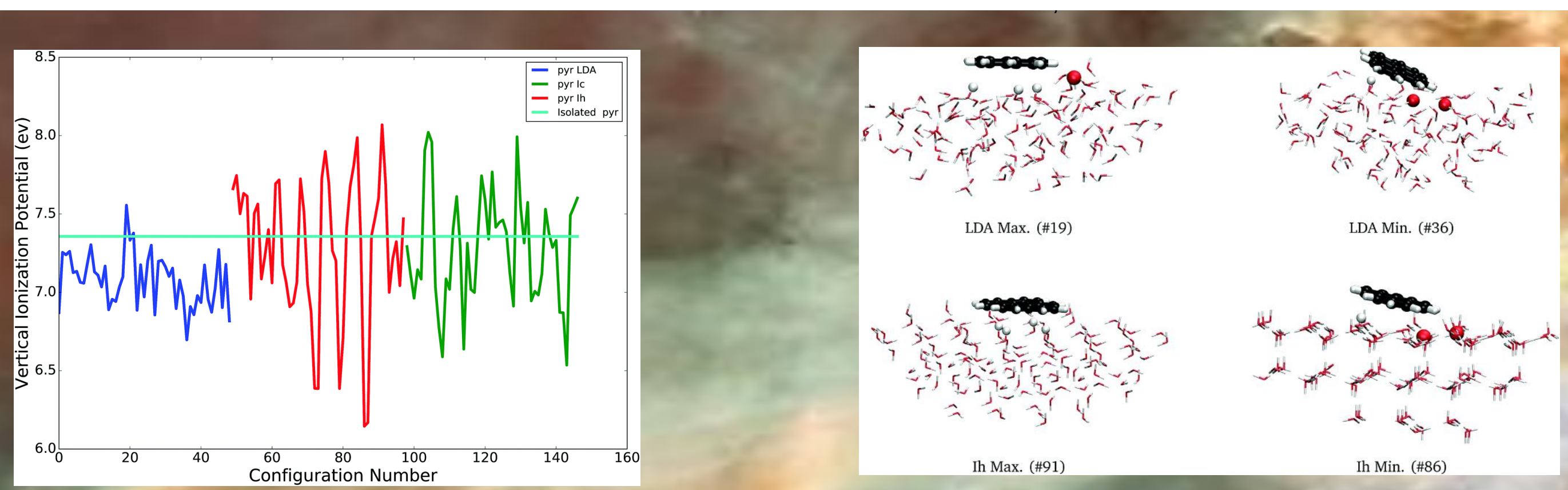
- **MD/FF simulations:** adsorption sites of PAH and binding energy maps.
- Starting from MD/FF configurations, a finite PAH-ice system is described within the Density Functional based Tight Binding **(DFTB)** scheme in its Self Consistent Charge (**SCC**) version, providing an explicit electronic structure description and the determination of the **influence of ice structure on the PAH ionization potential (IP).**

Photo-oxidation of PAHs in water ice: the role of ice structure.
The production of oxygenated PAHs is efficient only in porous amorphous water ice (ASW), where dangling OH bonds are available in pores, confirming that the reaction occurs with water in favorable geometries, similar to small water clusters, rather than crystalline ice structures.



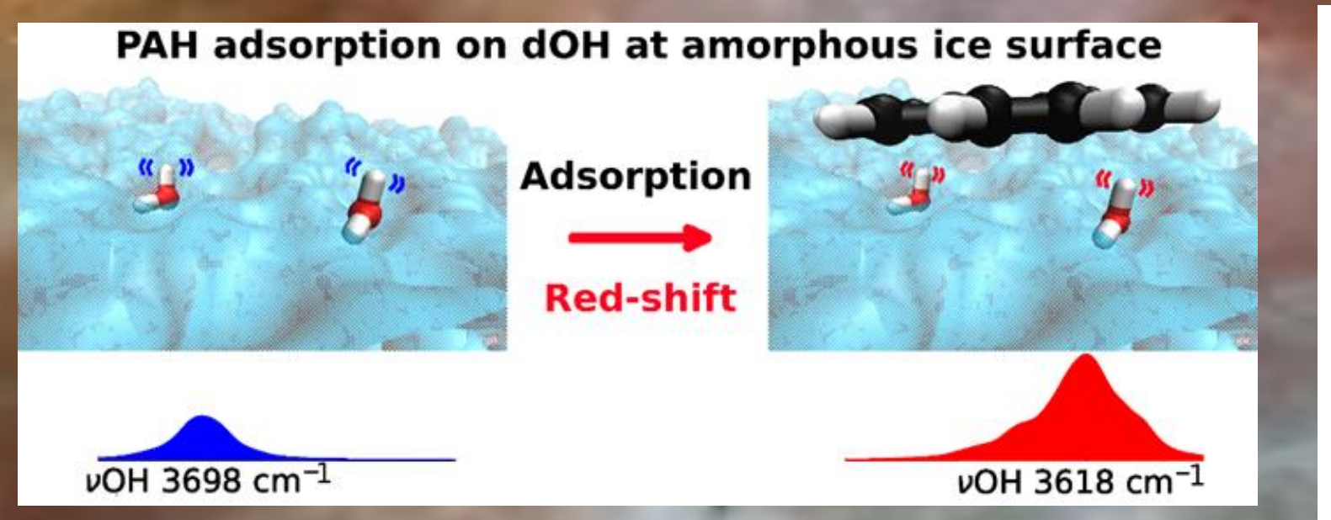
Formation of PAH-OH photoproducts in different ice structures

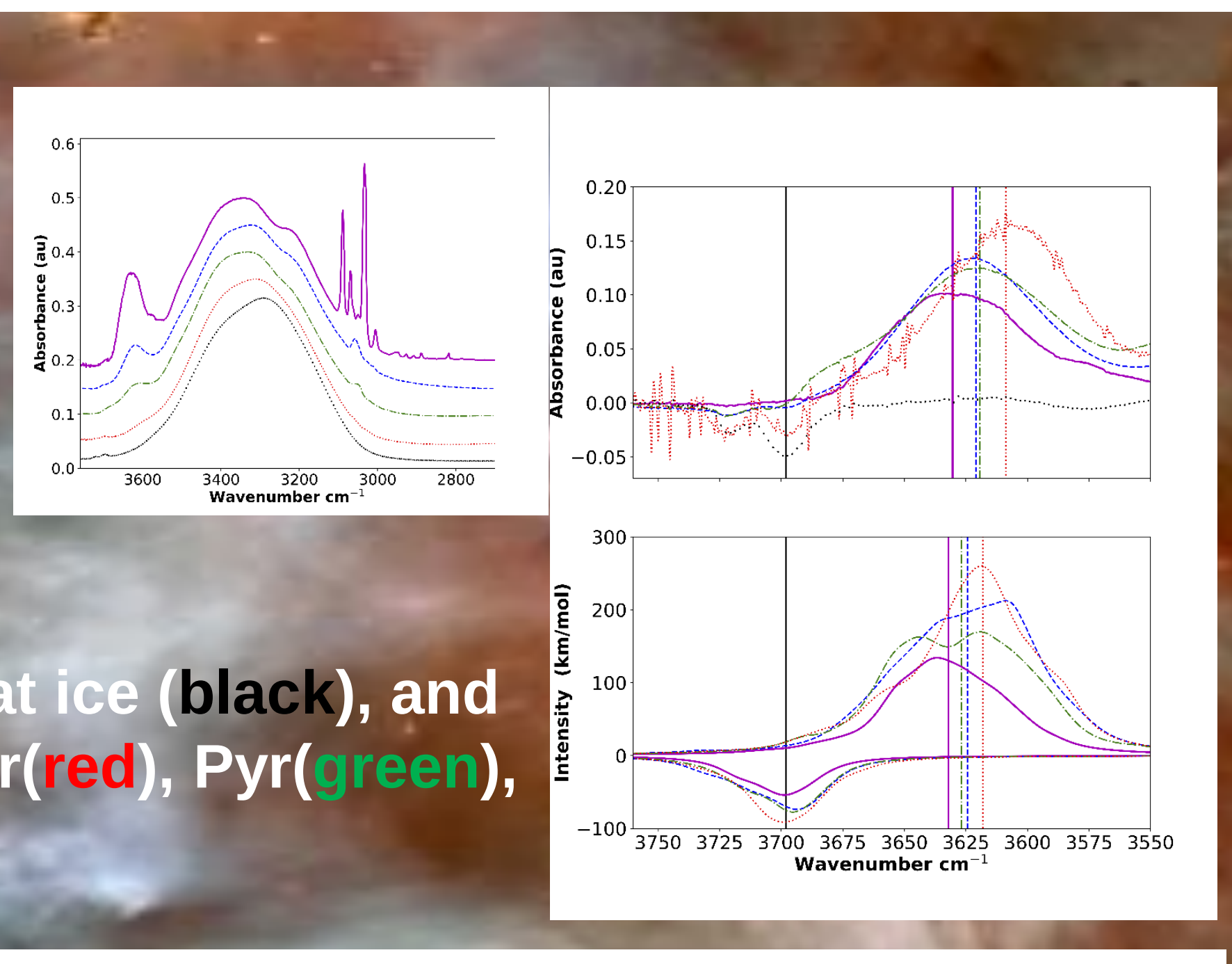
This is confirmed by the small IP variation induced by ice environment found in our SCC-DFTB calculations: 0.8 eV max. This suggests that excited states of PAHs and PAH clustering could play a role in the photo-reactivity of PAHs with water ice. This gives the possibility of the formation of oxygenated PAH molecules in interstellar environments with low water abundance or higher temperatures.



C-DFTB vertical IP of pyrene adsorbed on water ice and corresponding geometries

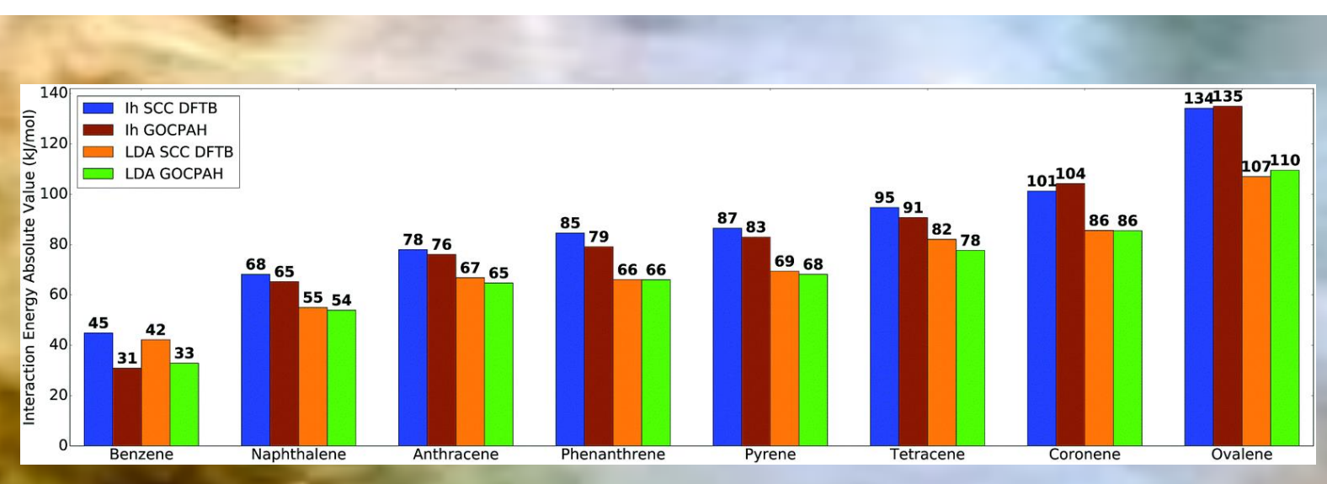
Adsorption of PAH onto the amorphous ice surface provokes a broadening and a redshift of the dangling dOH ice spectral feature, the redshift increasing with PAH size (70 to 85 cm^{-1} from benzene to coronene). Widening of the dOH feature could explain its absence heretofore in observational ice spectra.



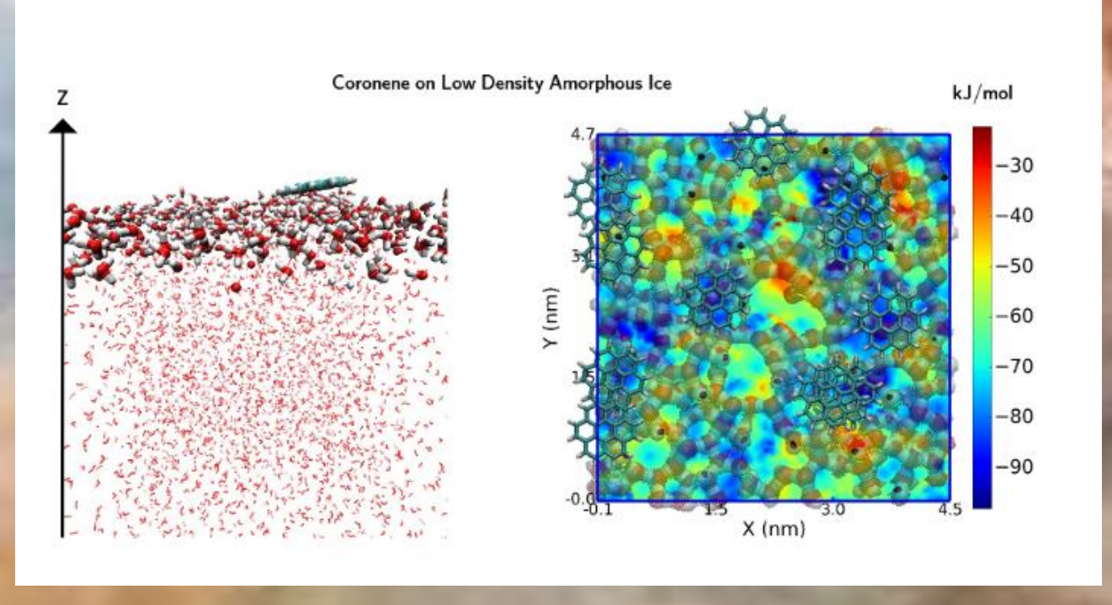


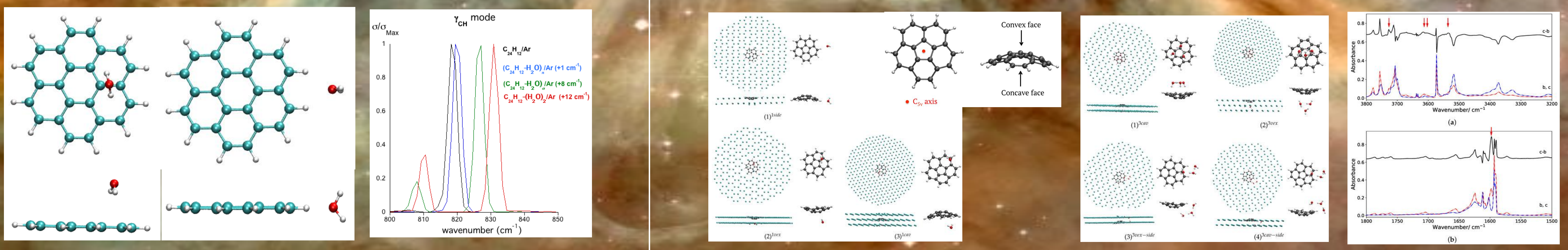
IR spectra in the dOH region.
Experimental p-ASW spectra of neat ice (black), and of PAH:pASW at 15K, with PAH=Cor(red), Pyr(green), Anth(blue) and Bz(magenta).

The adsorption of various PAHs from benzene to ovalene, on amorphous and cystalline ices has been investigated by means of classical molecular dynamics simulations. ASW offers less adsorption sites than Ih ice, for which the largest adsorption energies are found. PAHs adsorb preferentially on sites offering dangling H-bonds.



Adsorption absolute energies (kJ.mol^{-1}) of PAHs on water ices (GOCPAH model)





Comparison of the complexes formed by coronene (planar) and corannulene (curved) and water in argon matrices at 10K. Coronene forms σ-complexes with H_2O, which induces shifts of the γ(CH) mode and favors the formation of oxygenated photoproducts, whereas corannulene forms π-complexes, which leads to large shifts of water modes and hinders further photoreactivity .

Conclusions & astrophysical implications

PAH:water systems are very reactive: oxygenated PAHs are produced after short irradiation time with smooth UV radiation (>235 nm). The formation of oxygenated PAHs occurs from first H_2O interactions, with no need for icy layer. The orientation of the PAH compared to the water molecules is a key factor controling the photoreaction pathway. Oxygenation is optimal in p-ASW, where edge-on interactions are more abundant than in c-ASW or crystalline ice. So, oxygenated PAHs could be formed in dense clouds with low water abundances. Our results provide critical input data (binding energies, barrier heights, ionization potentials, dangling OH vibration mode) for astrochemical models of star-forming regions, where the implementation of gas-grain interactions is currently a high priority. The higher sensitivity of future space missions (JWST) could detect dOH spectral feature and confirm wether PAHs are indeed frozen out onto icy grains in dense regions.

References

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