PAH 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. BenAmor[1], A. Simon[1], and J. Mascetti[4]*.

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

The interaction of polycyclic aromatic hydrocarbons (PAHs) with water is of paramount importance in atmospheric and astrophysical context. PAHs are believed to be a significant reservoir of carbon in the interstellar medium (ISM) and have been proposed to be the carriers of the Aromatic Interstellar Bands (AIBs), a set of infrared emission bands observed in many regions of the ISM. In dense and cold 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] Understanding the role of water in the photo-processes involving adsorbed PAHs is therefore a key issue in astrochemistry.

Our joint theoretical (classical MD / force field simulations and SCC-DFTB calculations) and experimental (matrix isolation FTIR spectroscopy) studies have revealed the key role of mutual orientation in PAH-water interactions and reactivity. Both PAH (planar or not), and ice (amorphous or crystalline) structures play a role in the formation of PAH-water complexes and on their photo-reactivity. Various results from this wide-ranging study and their astrophysical implications will be presented:

- 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 vertical ionization potential (VIP) variation. [3]
- how the surface of amorphous solid water (ASW) is perturbed by the adsorption of PAHs, leading to a redshift and a broadening of the dOH ice spectral feature. [4]
- the effect of the PAH structure by comparing coronene and corannulene photoreactivity with water. [5]
- the description of PAH-ice interaction in the ground electronic state at low temperature, providing the binding energies and barrier heights necessary to the on-going improvement of astrochemical models. [6]

Funding: French Research National Agency (ANR), CNRS-INSU National Program PCMI, CNRS Research Network GDR EMIE. [1]

---

[1] Hama, T.; Watanabe, N. Surface processes on interstellar ASW *Chem. Rev*. **2013**, *113*, 8783.
[2] Noble J.A. *et al* Efficient photochemistry of coronene:water complexes *A&A* **2017**, *599*, A124.
[3] Michoulier E. *et al*, Theoretical determination of adsorption and ionization energies of PAHs on water ice *PCCP* **2018**, *20*, 11941.
[4] Michoulier E. *et al* Perturbation of the surface of ASW by the adsorption of PAHs *JPCC* **2020**, *124*, 2994.
[5] Leboucher H. *et al* Water clusters in interaction with corannulene in a rare gas matrix: structures, stability and IR spectra *Photochem* **2022**, *2*, 237.
[6] Michoulier E. *et al* Adsorption of PAHs on interstellar ice viewed by classical MD *PCCP* **2018**, *20*, 8753.