GDR 3533 EMIE

PAHs on/in water ice: structures, energetics and spectra from FTIR experiments and a multi-method theoretical study

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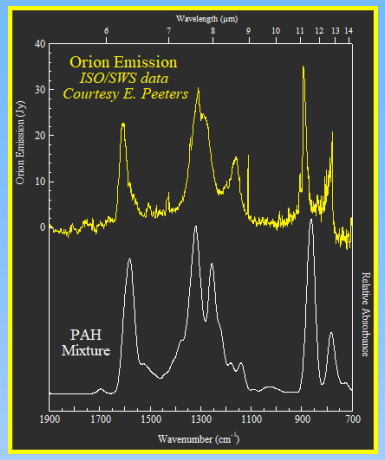
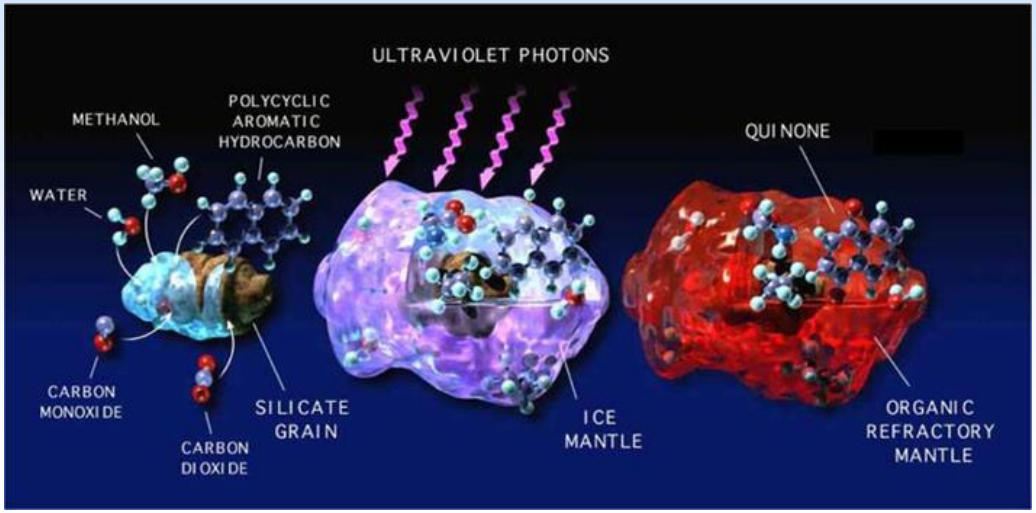
Celebrating the first 40 years of Alexander Tielens contribution to Science

The Physics and Chemistry of the Interstellar Medium, Avignon, France, 2-6 September 2019.



The “AIB” spectrum can be roughly reproduced by IR features of mixtures of neutral, ionized, hydrogenated or **oxygenated** PAHs.

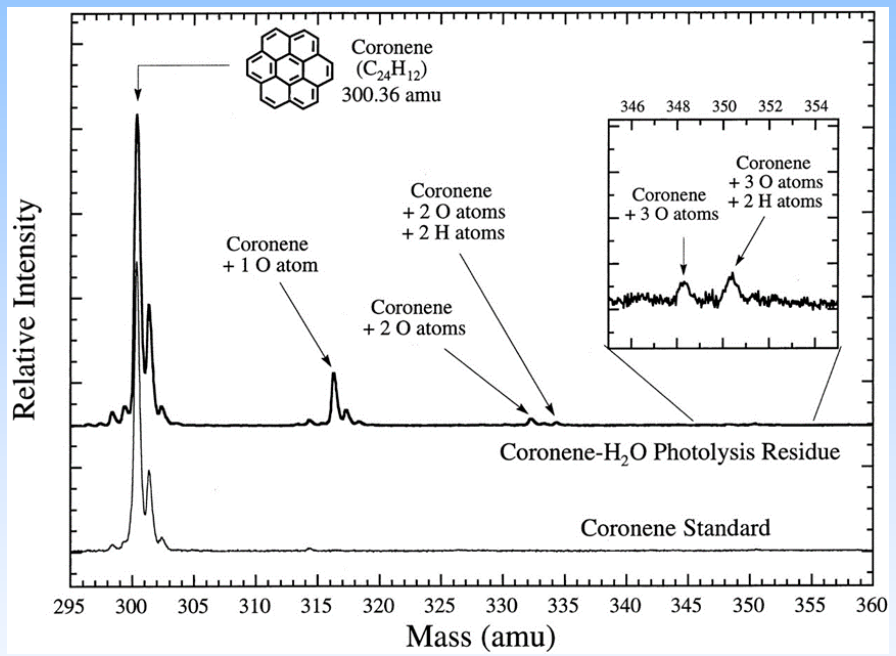
PAHs can condense on/in water ice mantles in cold dense regions and contribute to complex grain chemistry. Understanding the role of ice in the processes involving adsorbed PAHs is therefore a key issue in astrochemistry



A.G.G.M. Tielens, Annu. Rev. Astron. Astrophys. 2008

Photoreactivity of PAHs in amorphous water ices (ASW)

1. VUV irradiation studies (Ly-α)



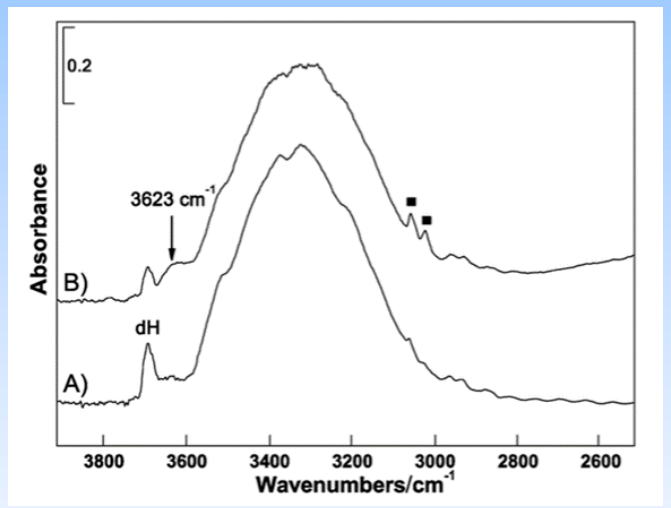
- **PAHs are efficiently ionised by VUV irradiation to form cations**
- **PAH^+ cations react with H_2O**
- **Photoproducts are alcohols and ketones**

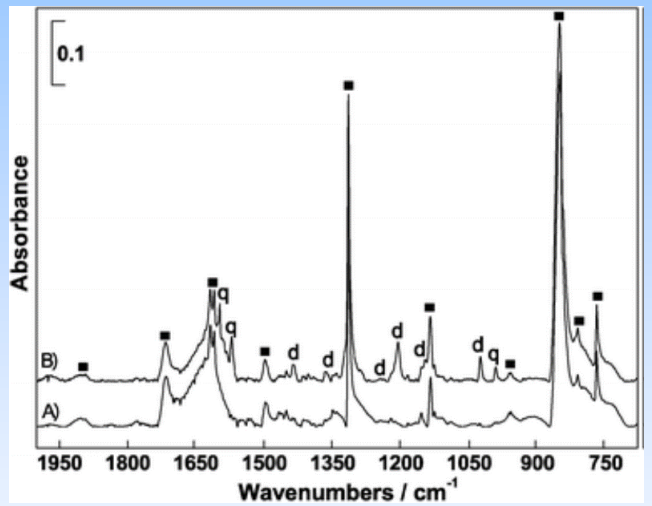
Bernstein et al, Science 1999
Bernstein et al, ApJ 2002
Bouwman et al, A&A 2011
Cook et al, ApJ 2015

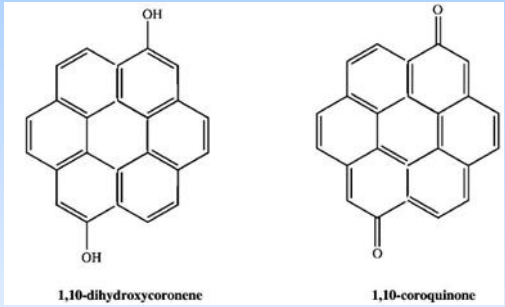
Photoreactivity of PAHs in amorphous water ices (ASW)

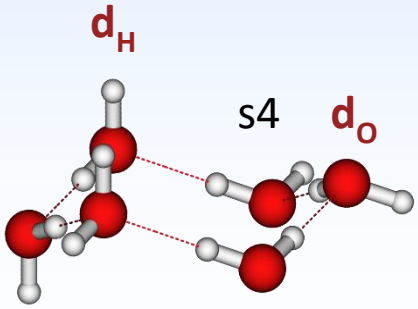
2. UV irradiation studies (λ > 235 nm)

FTIR spectra of Coronene ($C_{24}H_{12}$) adsorbed on ASW at 10K and after irradiation









d_H: 3699 cm^{-1}

s4: 3503 cm^{-1}

d_O: 3549 cm^{-1}

- *ca* 5 eV *vs* IP coronene 7 eV / water 12 eV

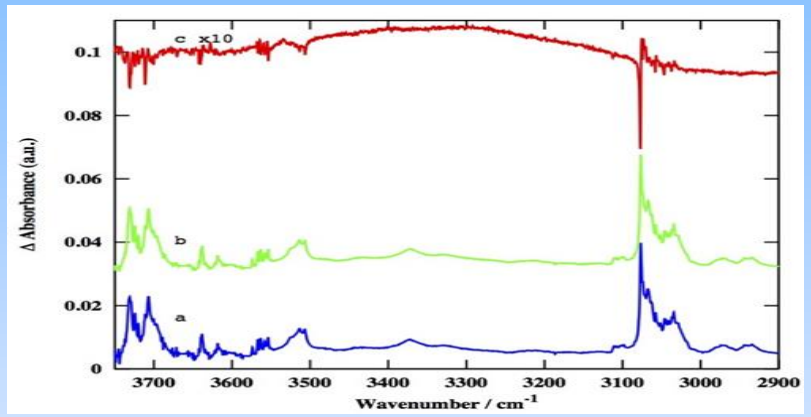
- does ASW lower ionisation barrier?

- is there previous formation of a PAH-H_2O complex?

Gudipati & Allamandola, ApJ 2004
Guennoun et al, PCCP 2011
Guennoun et al, JPCA 2011

Photochemistry of coronene:H_2O complexes in Ar matrices

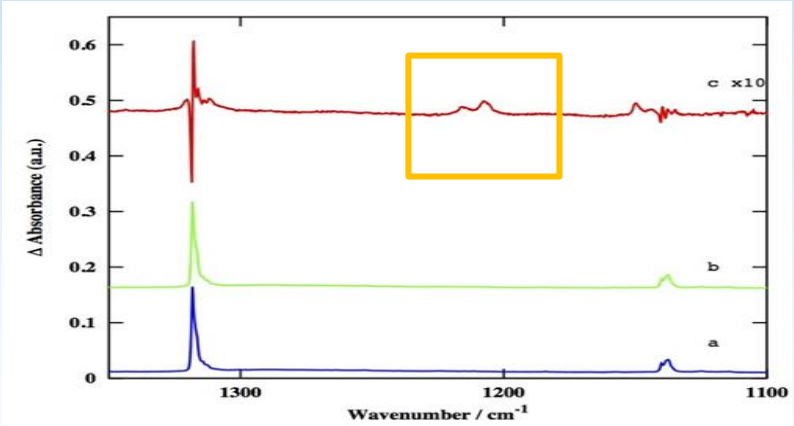
UV irradiation of a coronene:H_2O:Ar matrix (Hg lamp, $\lambda > 235$ nm)

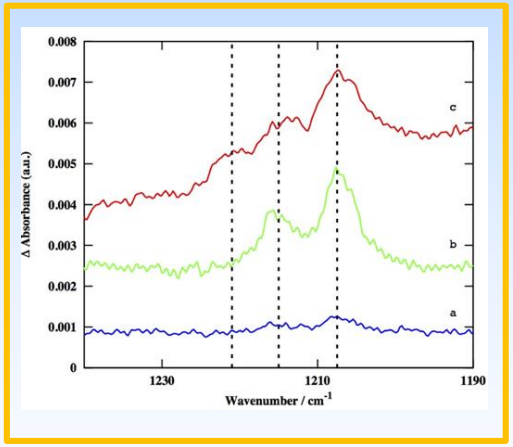


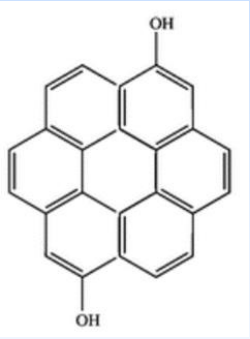
difference spectrum

3' irradiation

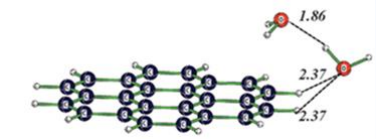
deposition





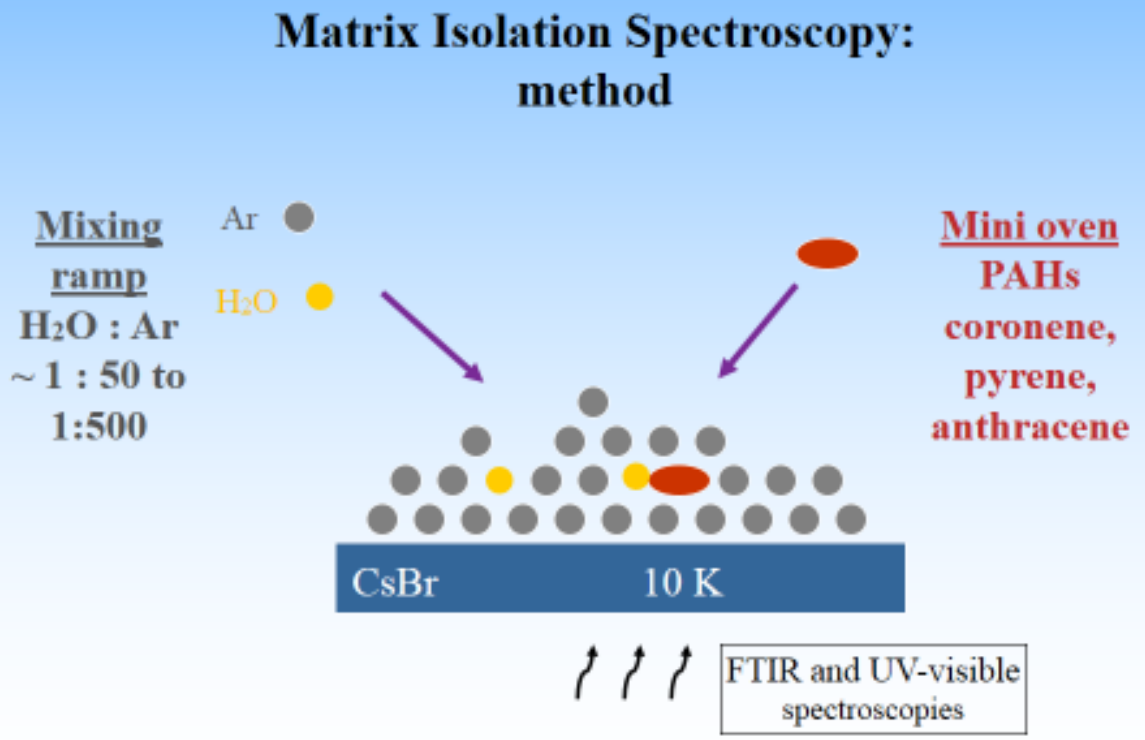


- **Water ice is not necessary for reactivity**
- **Small edge-on PAH:water complexes produce alcohols**
- **Reactivity possible at low H_2O abundances**



Noble, Jouvet, Mascetti et al, A&A 2017

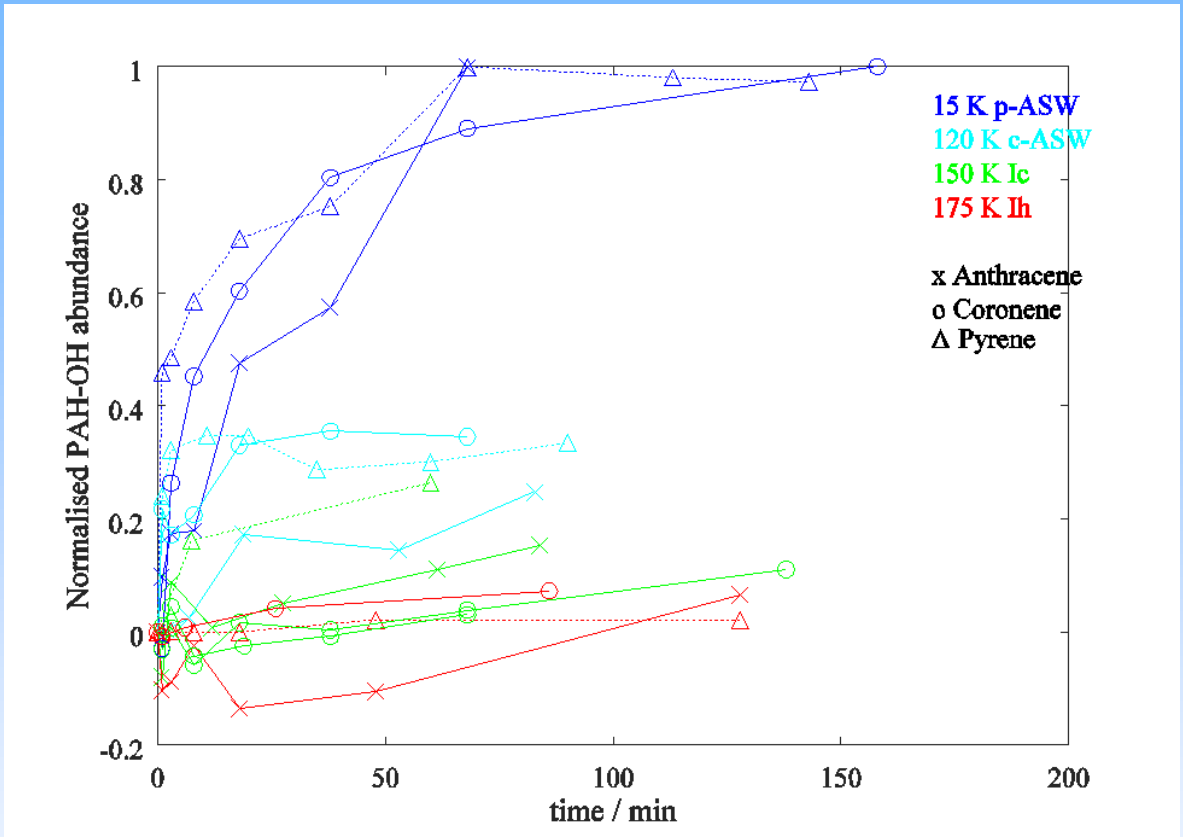
Experimental method: matrix isolation spectroscopy



- **Study of PAH:H_2O complexes**
- **Simple model for the interaction of PAHs on dust grain surfaces or in interaction with water**

Pressure: 10^{-7} mbar, T surface: 10K, irradiation with Hg lamp ($\lambda > 235$ nm)

UV irradiation of PAHs in different types of water ices



Production of oxygenated PAHs efficient only in p-ASW, where dangling OH bonds are available in pores.

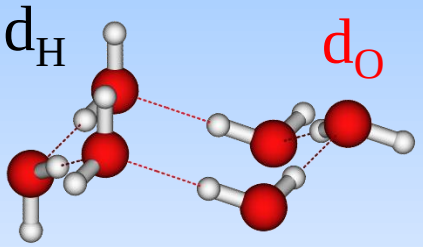
The reaction occurs with water in favorable geometries, similar to small water clusters: **role of the initial orientation of molecules.**

J.A. Noble et al, submitted.

- **Photoreactivity restricted to porous ASW:** what are the roles of water clusters and of the ice structure?

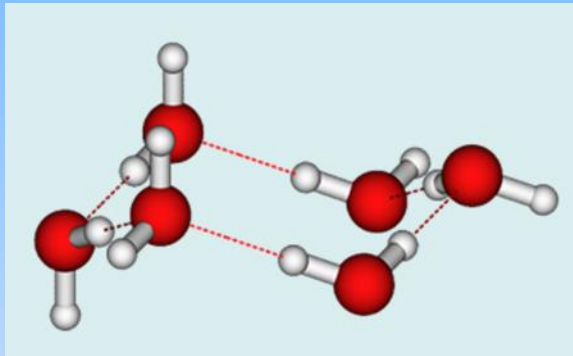
- **The type of interaction with H_2O seems to be the key** : what is the role of dOH dangling bonds? How the surface of ASW is perturbed by the adsorption of PAHs?

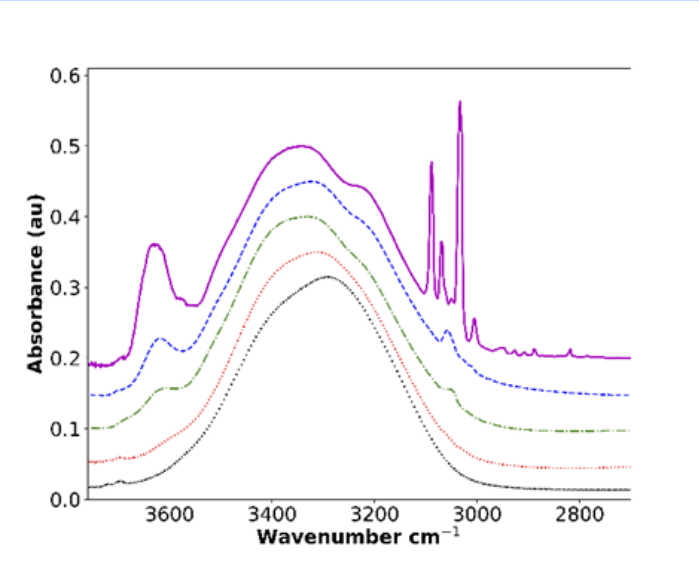
- **Soft UV irradiation: no direct ionisation of coronene nor water photolysis**: what is the influence of ice (water) on the IP of PAHs?



Multi-method theoretical approach :
Molecular dynamics/force-field (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 ionisation potential (IP).**

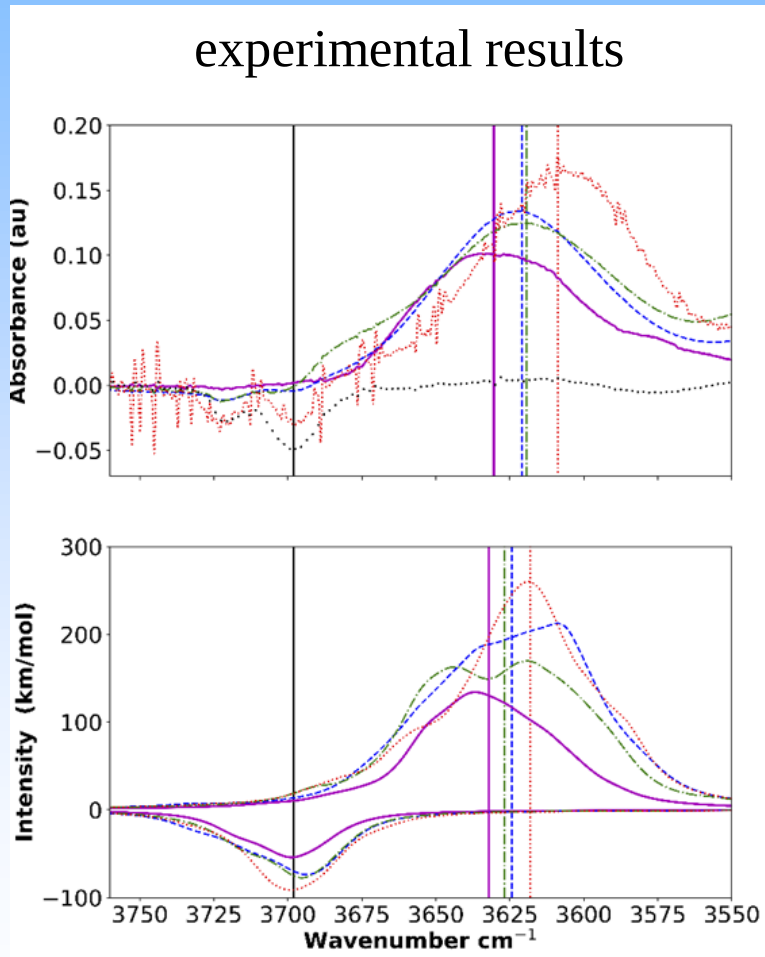
PAH (Bz, Anth, Pyr, Coro) adsorption on d_{OH} at ASW surface





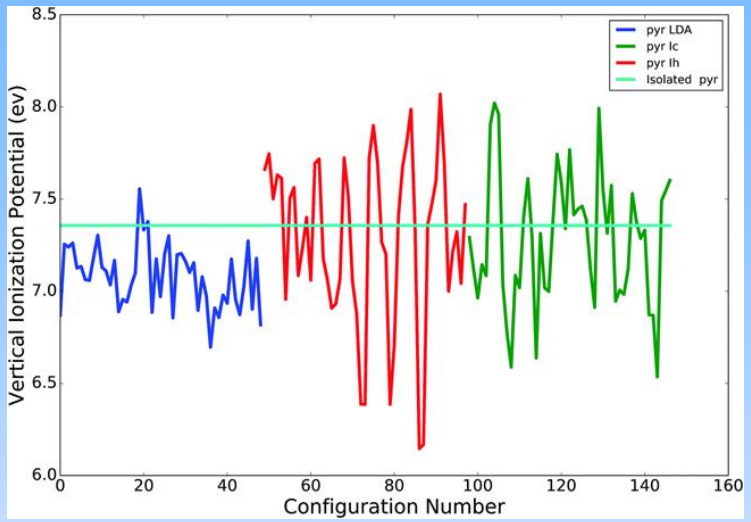
d_{OH} redshift from 70 to 85 cm^{-1}

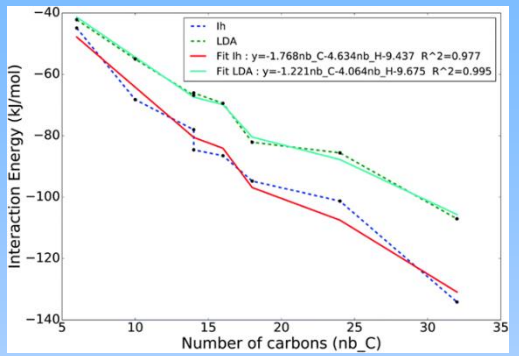
experimental results



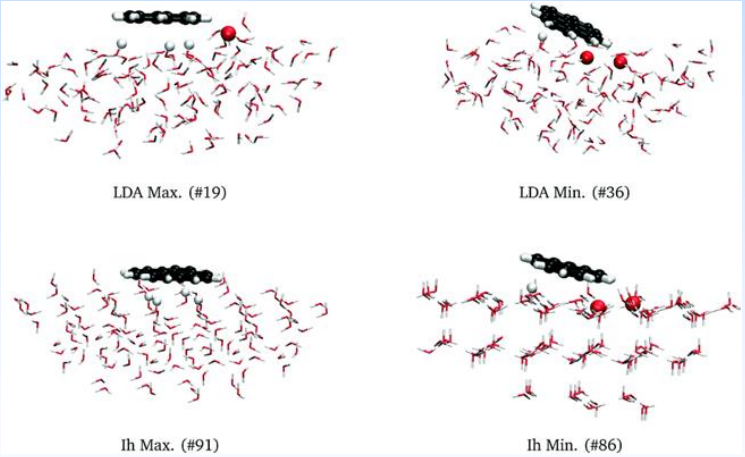
calculated (SCC-DFTB) difference spectra

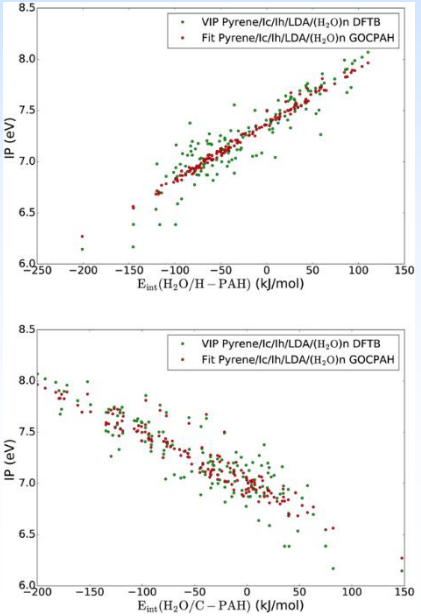
Adsorption and ionisation energies of PAHs on ice





1st-order dependence of the DFTB derived PAH-ice adsorption energy as a function of the number of C and H atoms and correlation laws between VIP values (DFTB) and pair interaction energies (FF)





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

CONCLUSIONS AND ASTROPHYSICAL IMPLICATIONS

PAH:water systems are very reactive: oxygenated PAHs are produced after short irradiation time with smooth UV radiation.
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 or higher temperatures.

Our experimental results, MD/FF simulations and SCC-DFTB calculations provide input data (binding energies, barrier heights, ionisation potentials, dangling OH vibration mode) for astrochemical models of gas-grain interactions.
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.

Thank you for your attention

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