

Collision-induced dynamics of PAH-water clusters

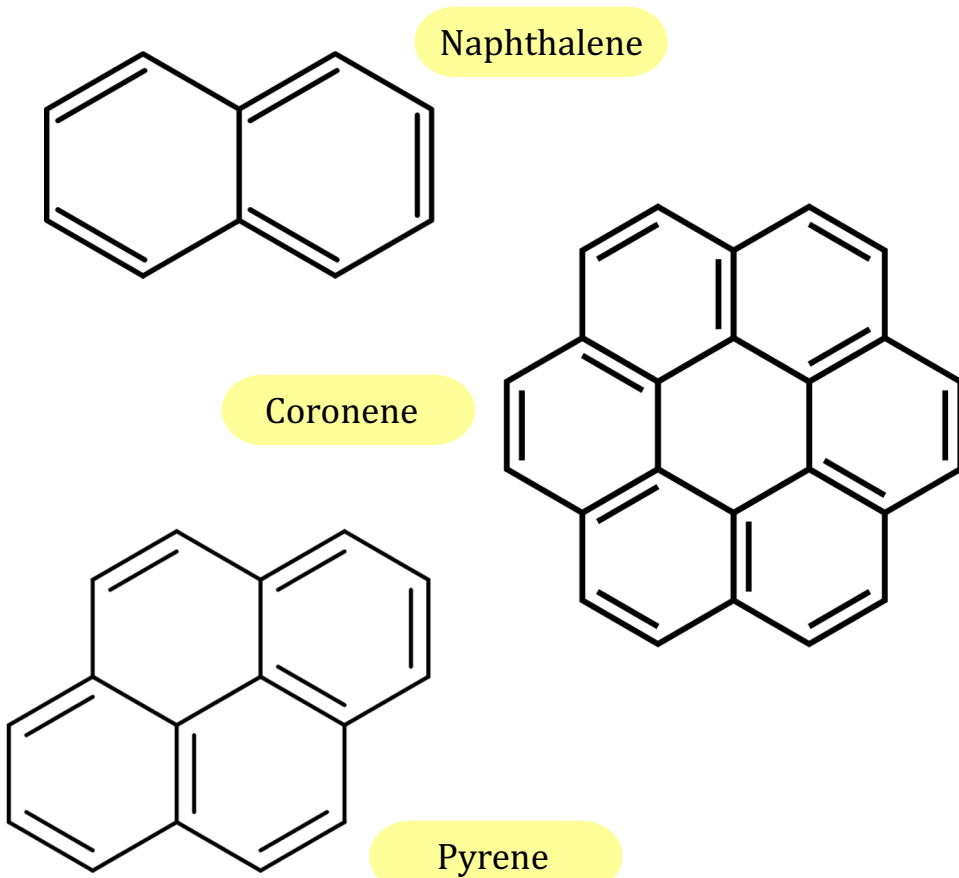
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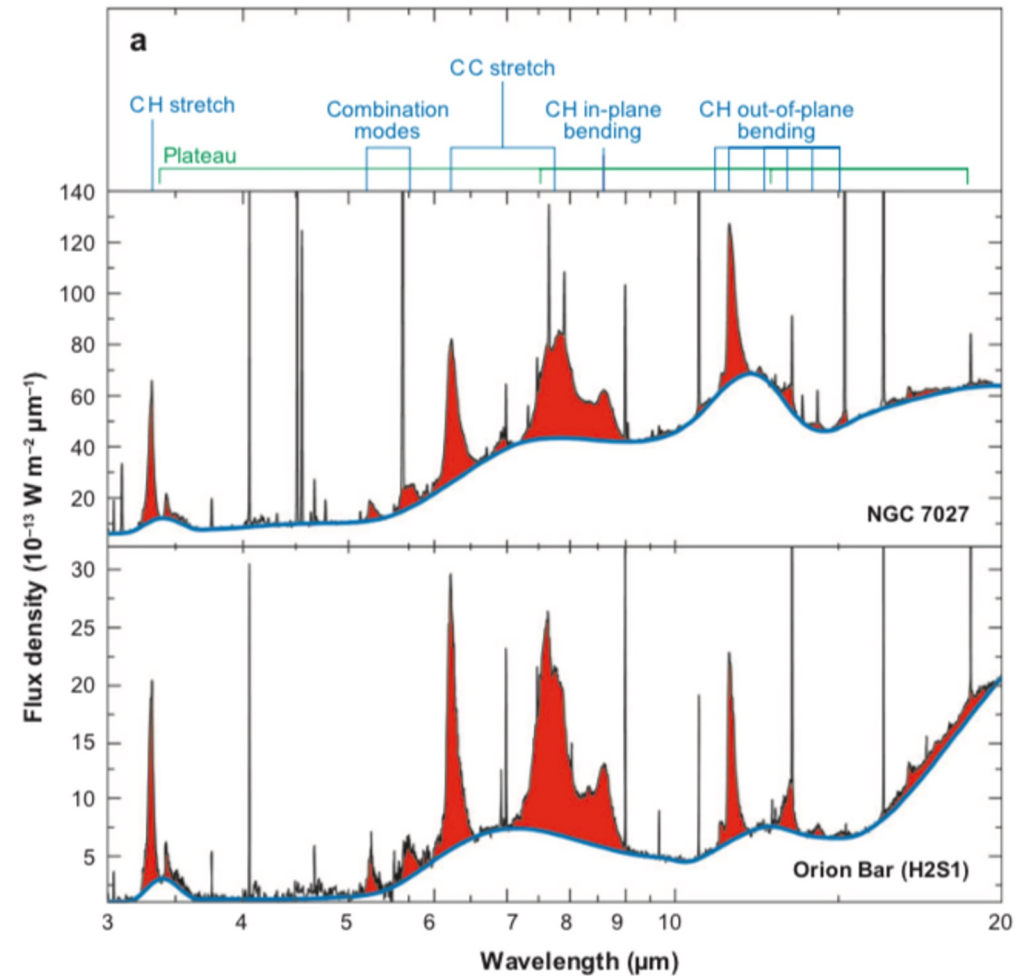
PCMI 2024, Bordeaux, October 30th 2024

What's a PAH?

PAH = Polycyclic Aromatic Hydrocarbon

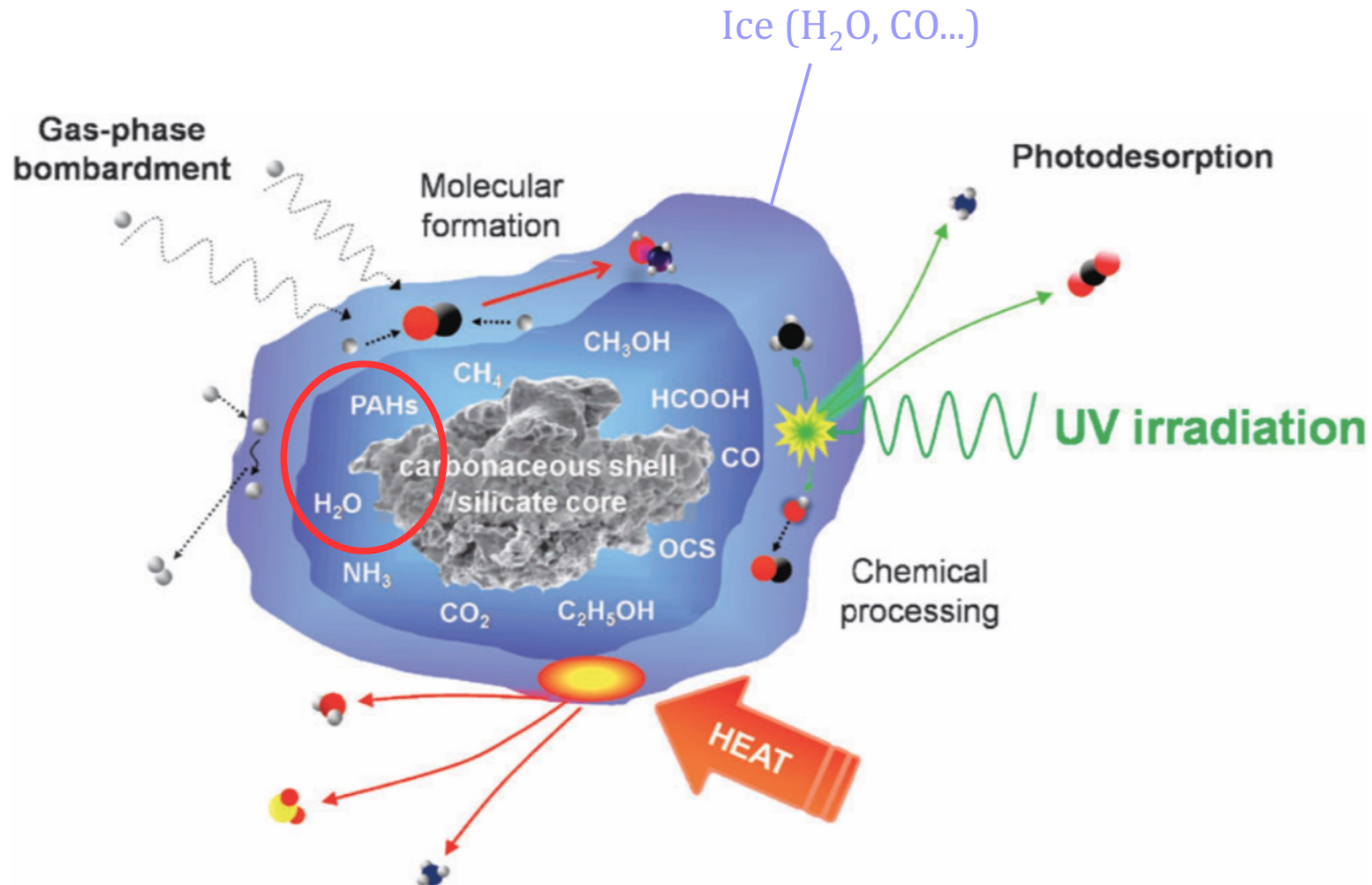


Strong and ubiquitous aromatic emission IR bands in space:



Tielens, *Ann. Rev. Astron. Astrophys.* 2008

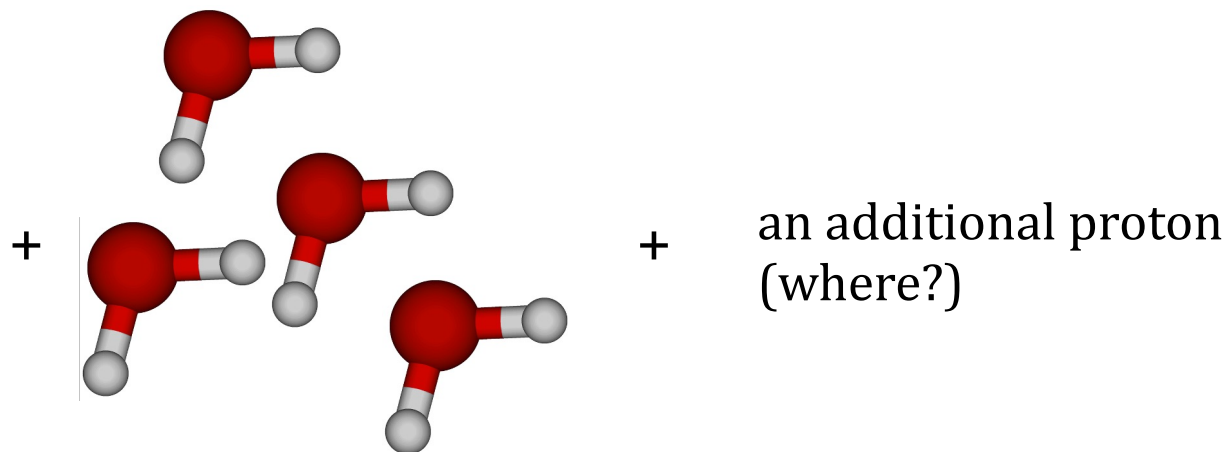
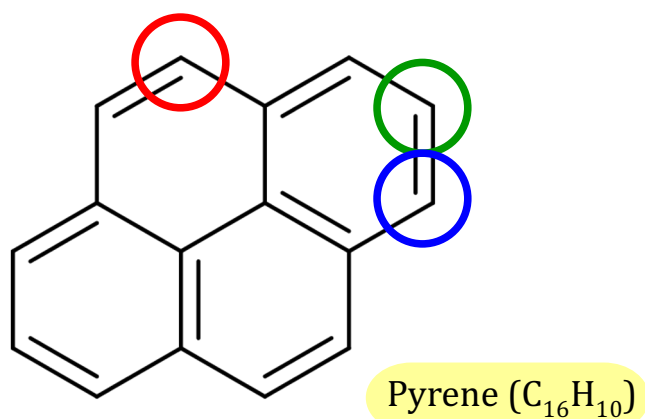
PAHs on interstellar ices



Burke and Brown, Phys. Chem. Chem. Phys. 2010

→ Large diversity of molecules!
 // Missing data for gas-grain models

Goal

**Molecular dynamics simulations:**

→ Low-energy collisions (50 meV)

→ High-energy collisions (7.5 eV)

1) Self-Consistent Charge Density-Functional based Tight-Binding (SCC-DFTB)

= Approximate DFT method

$$\rho(\vec{r}) = \rho_0(\vec{r}) + \delta\rho(\vec{r})$$



2nd-order Taylor expansion

$$E^{\text{SCC-DFTB}} = \sum_i^{\text{occ}} n_i \langle \Psi_i | h_0 | \Psi_i \rangle + V_{\text{rep}} + \frac{1}{2} \sum_{ab} \gamma_{ab} \Delta q_a \Delta q_b + V_{\text{disp}}$$

→ Parametrised: **inexpensive calculations**

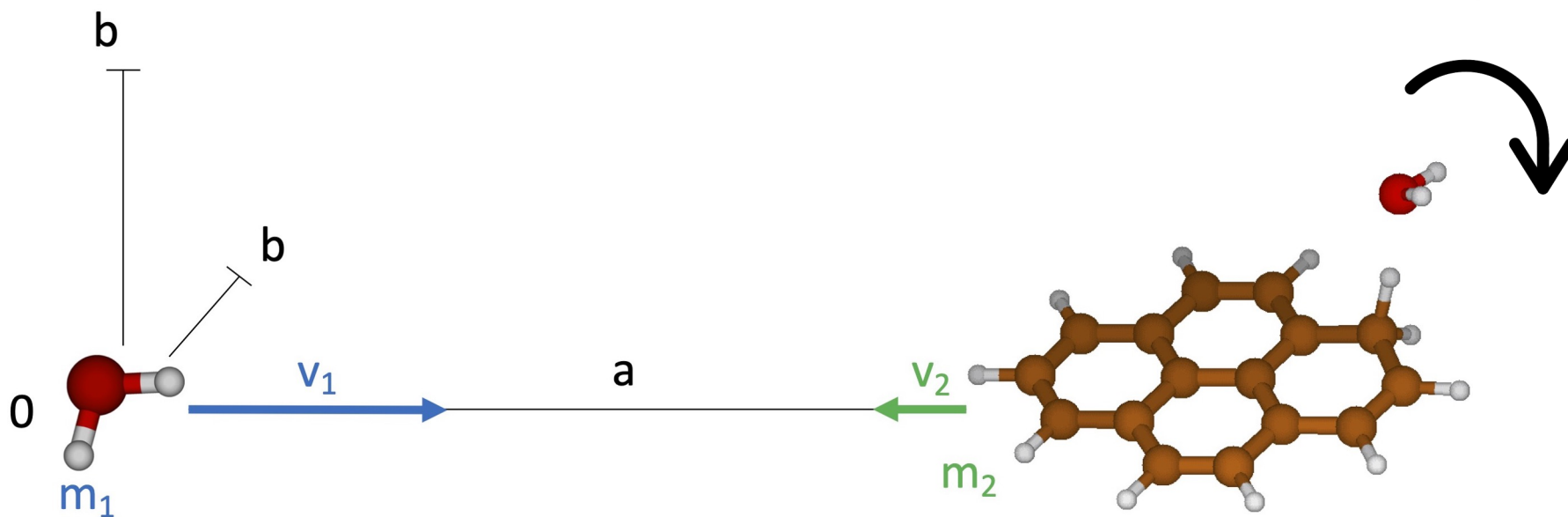
→ Implemented in deMonNano package

deMonNano experiment, <http://demon-nano.ups-tlse.fr/>
Rapacioli et al. 2023

2) Collision simulations

→ Born-Oppenheimer MD (BOMD) / SCC-DFTB

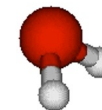
→ **Random initial conditions:** lots of simulations (of a few ps)



Successive growth of water cluster (n=1-4) on protonated pyrene

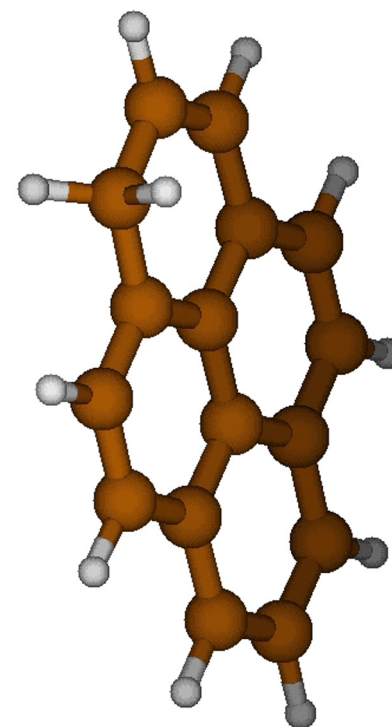
Parameters:

- 50meV
- 9ps (timestep=1fs)
- 1,080 starting geometries
- No charge constraint (proton transfer?)

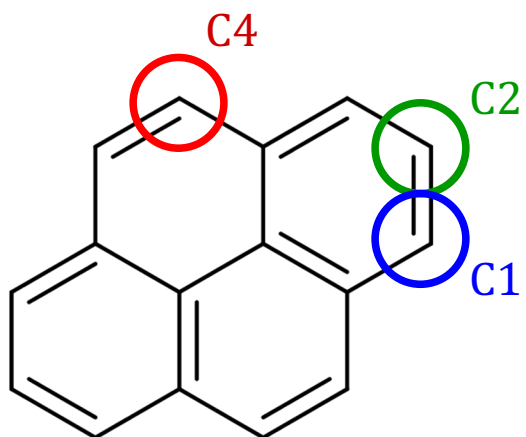


- 1) Collision
- 2) Identification of largest fragment
- 3) New collision

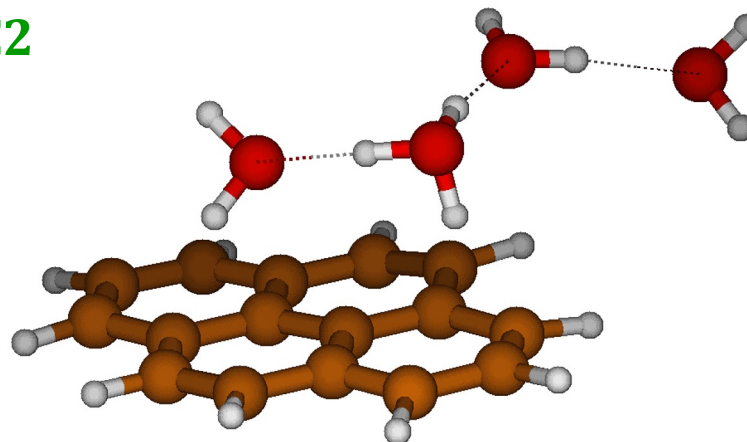
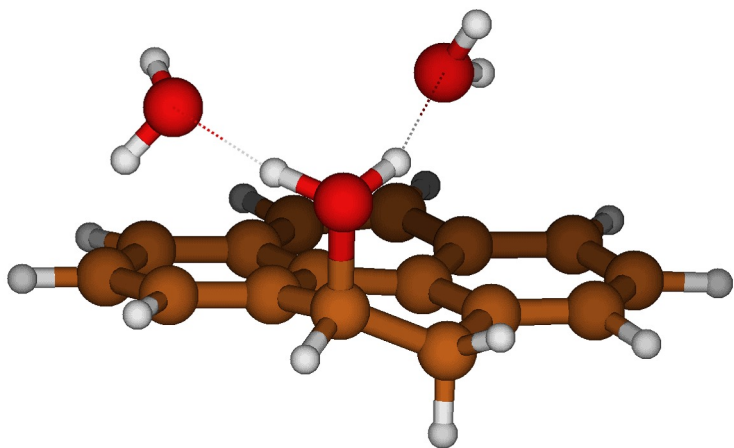
x4



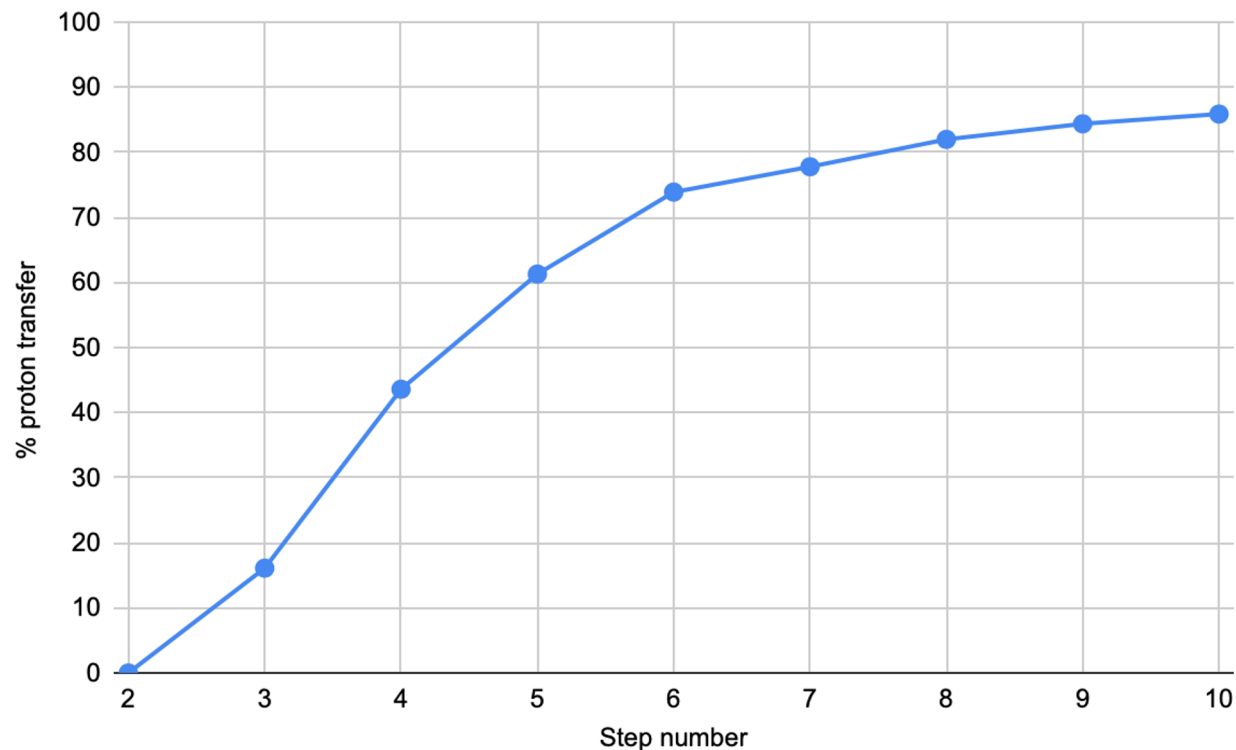
Results

**C1**

Progressive growth

C2**C4**

Step 4: 35%



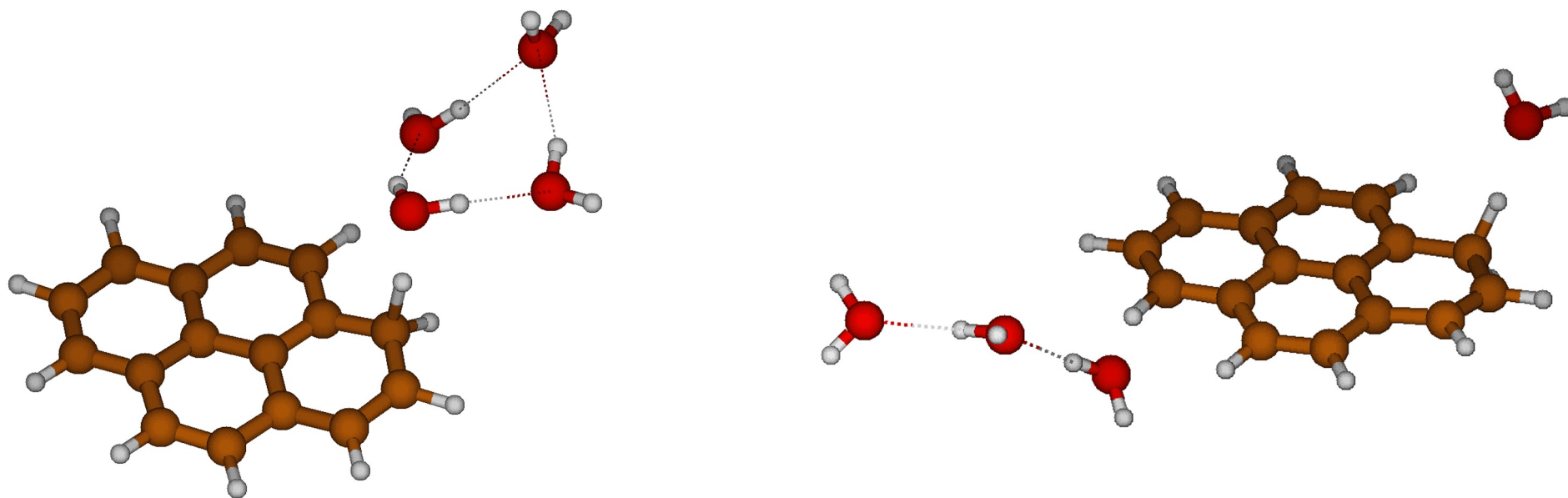
With a longer simulation time? 0.25ns

- The “special behaviours” are slightly facilitated
- **Structures**: with a longer simulation time → convergence of the geometries

How many water molecules are bound? (close to each other)

→ The most stable and compact water cluster geometries are more rarely found

→ **Dependence on the growth conditions**



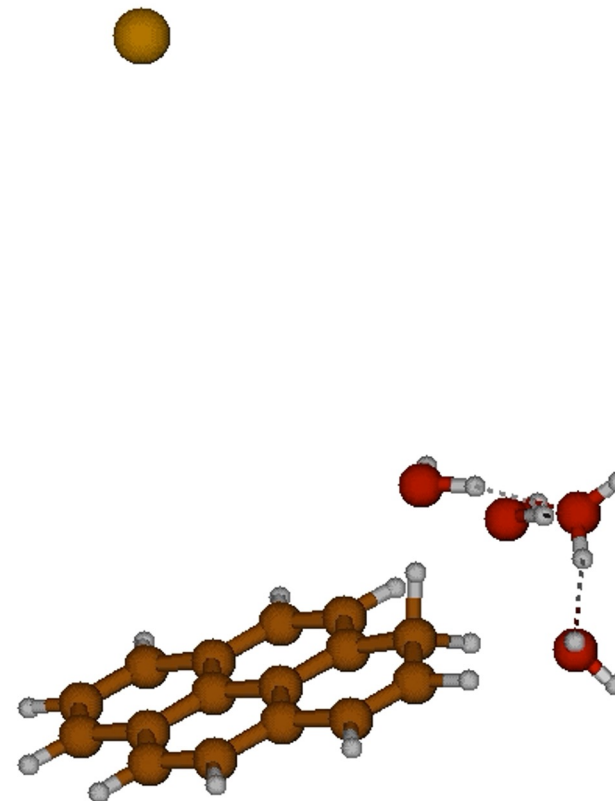
Let's break them!

Parameters:

- 7.5eV
- 3ps (timestep=0.5fs)
- 1,080 starting geometries
- No charge constraint (proton transfer?)
- Argon atom = MM

To obtain theoretical **mass spectra**
(charged fragment)

→ Comparison with experiments

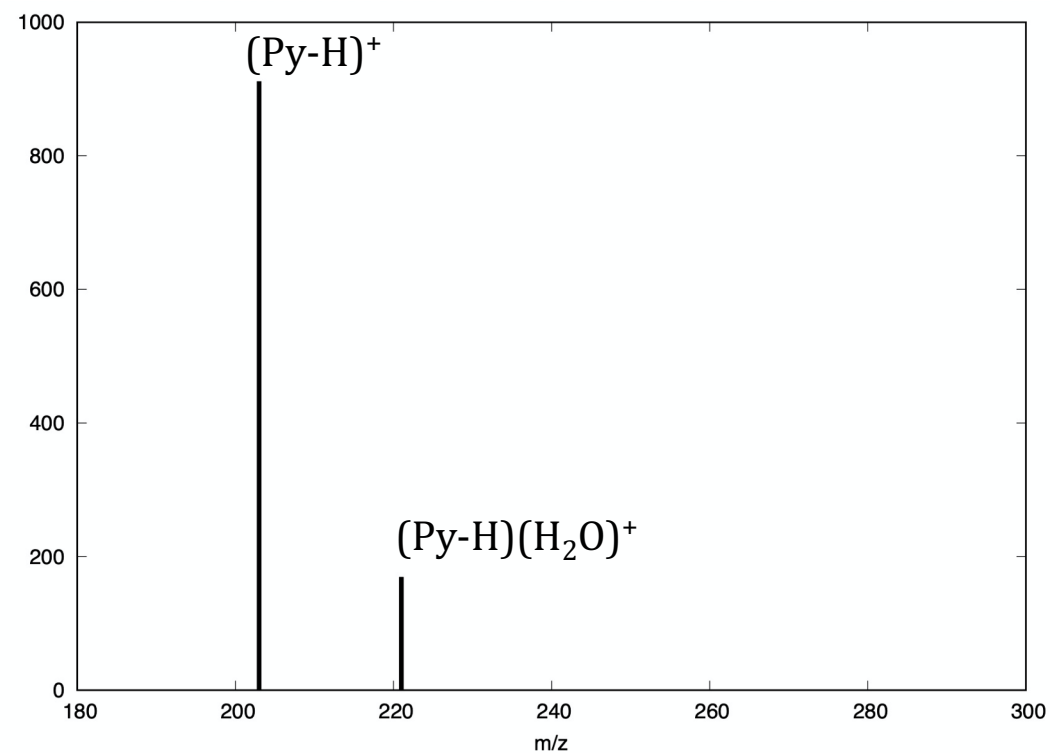
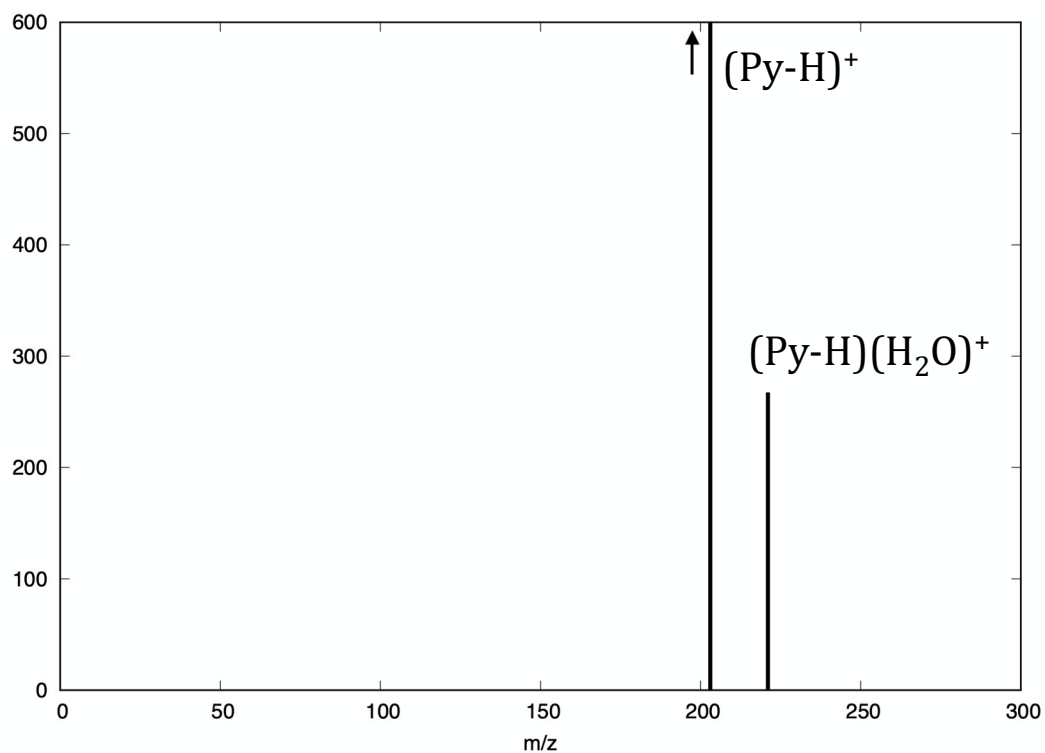


Proton on pyrene (C2)

Proton on pyrene (C1)

n=1

Loss of water in both cases

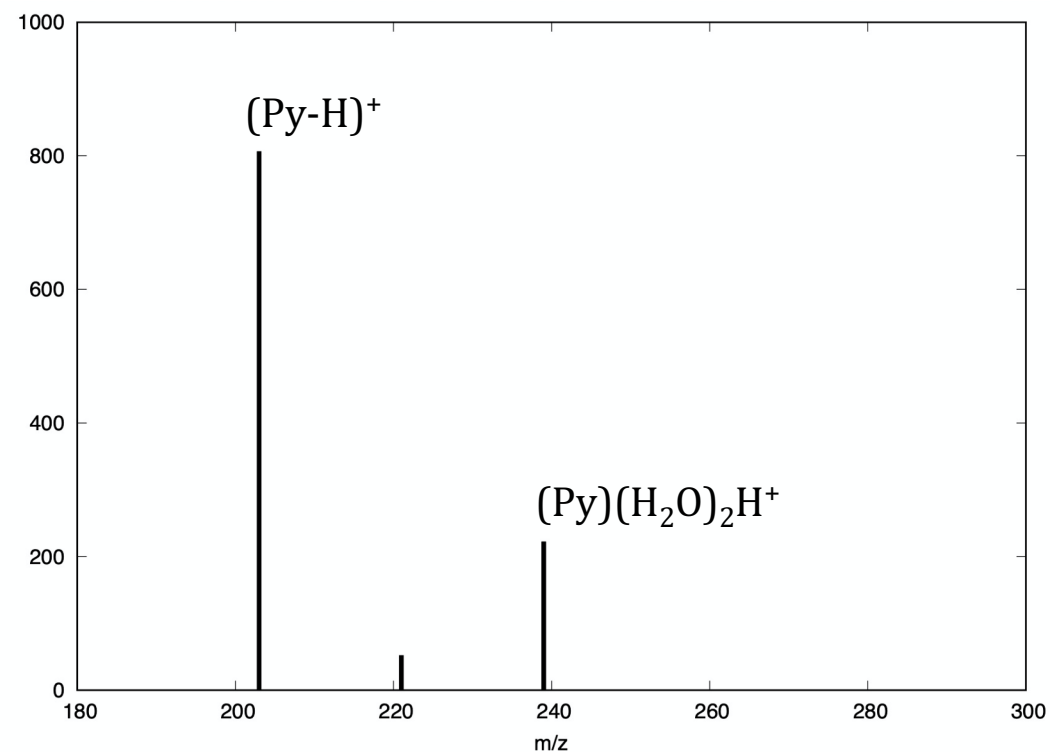
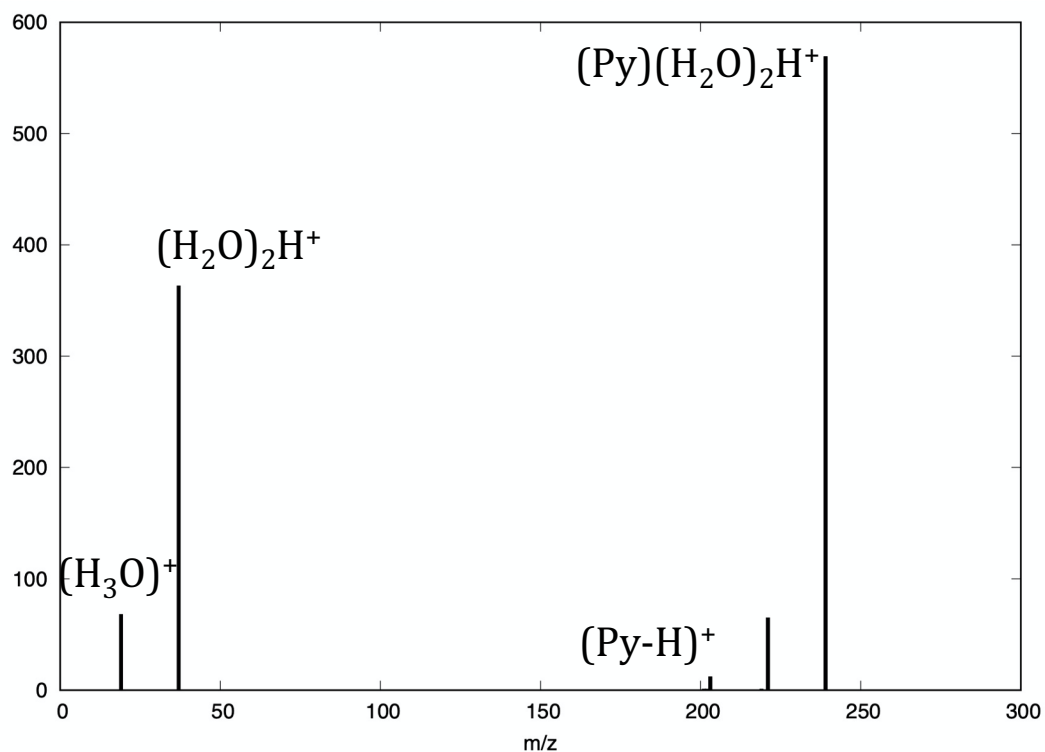


Proton on water

Proton on pyrene (C1)

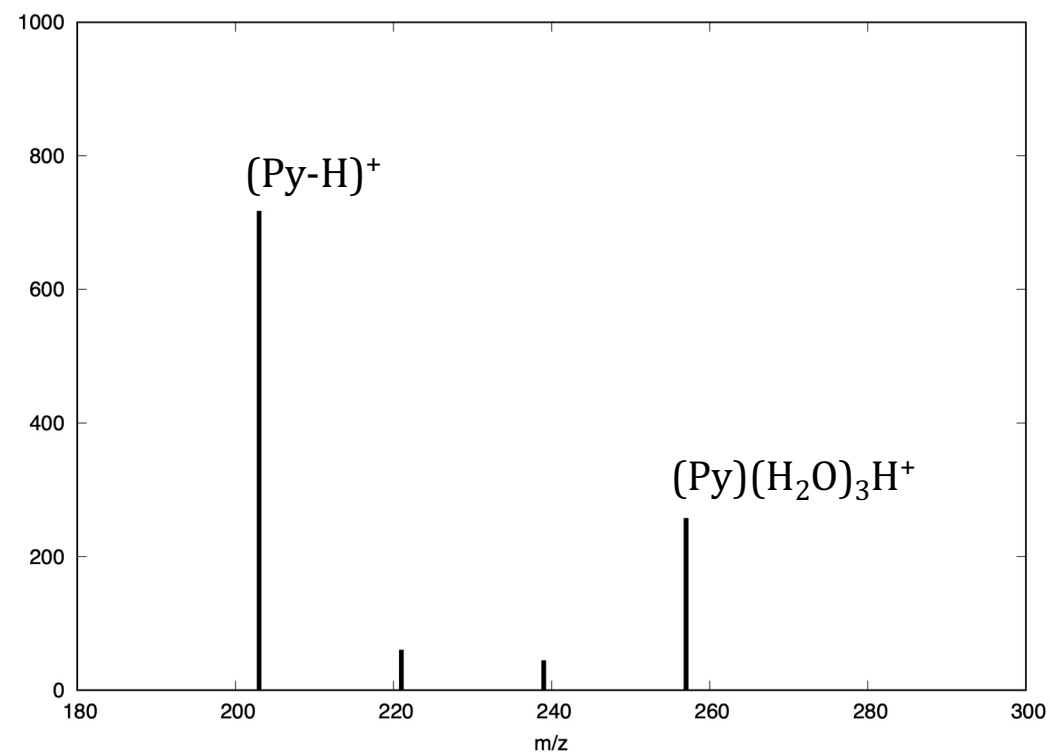
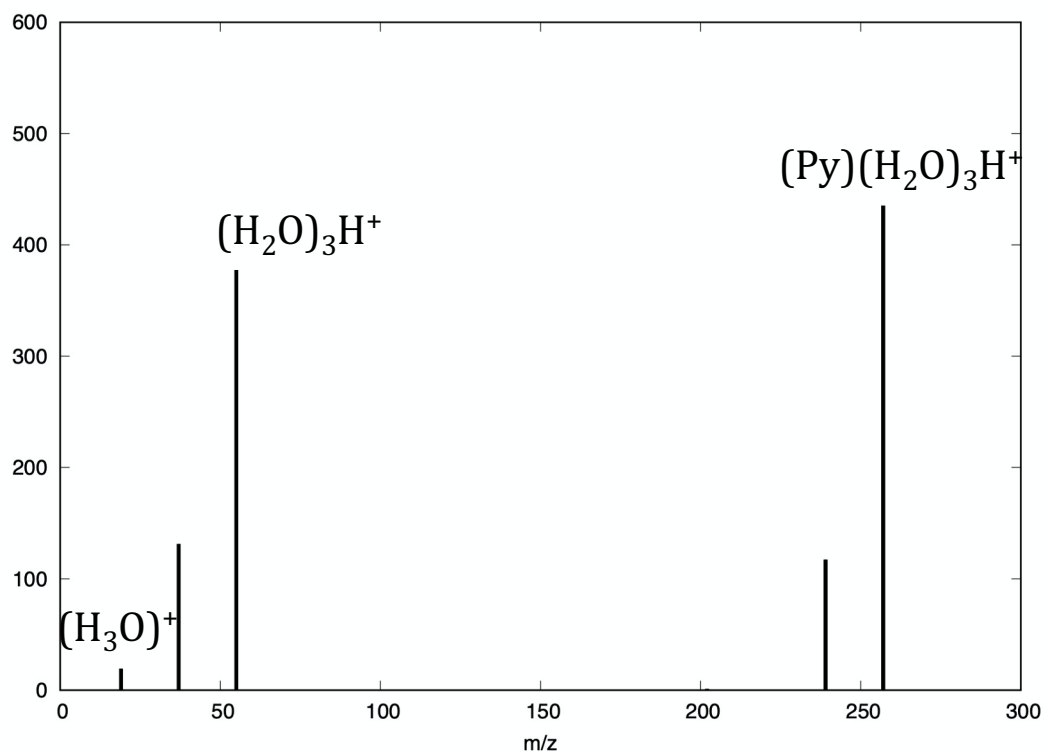
n=2Loss of pyrene
+ water

Loss of water

Loss of water (Py-H⁺)

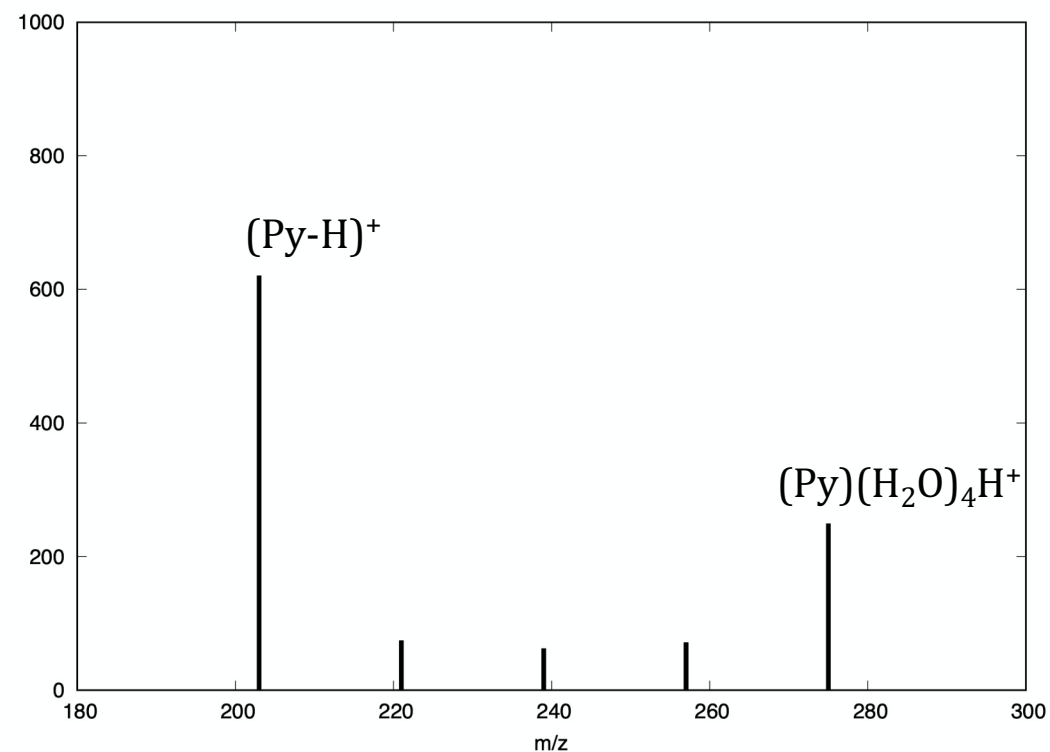
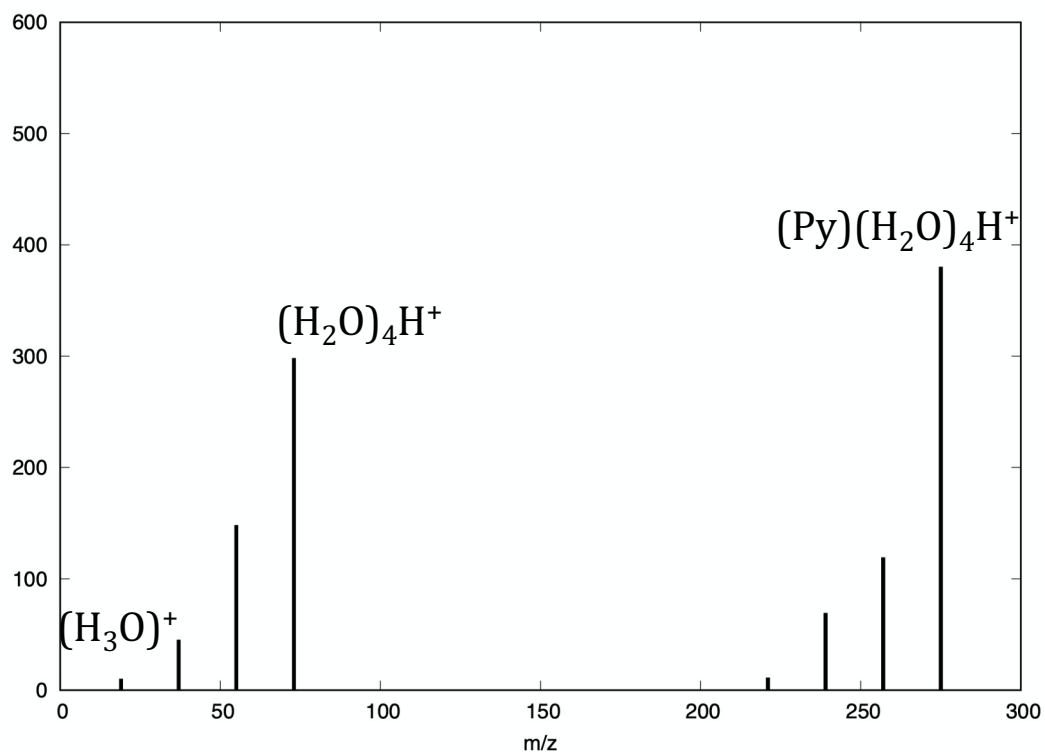
Proton on **water**Proton on **pyrene (C1)****n=3**Loss of pyrene
+ water

Loss of water

Loss of water (Py-H⁺)*+ Some rare cases of proton transfer*

Proton on **water**Proton on **pyrene (C1)****n=4**Loss of pyrene
+ water

Loss of water

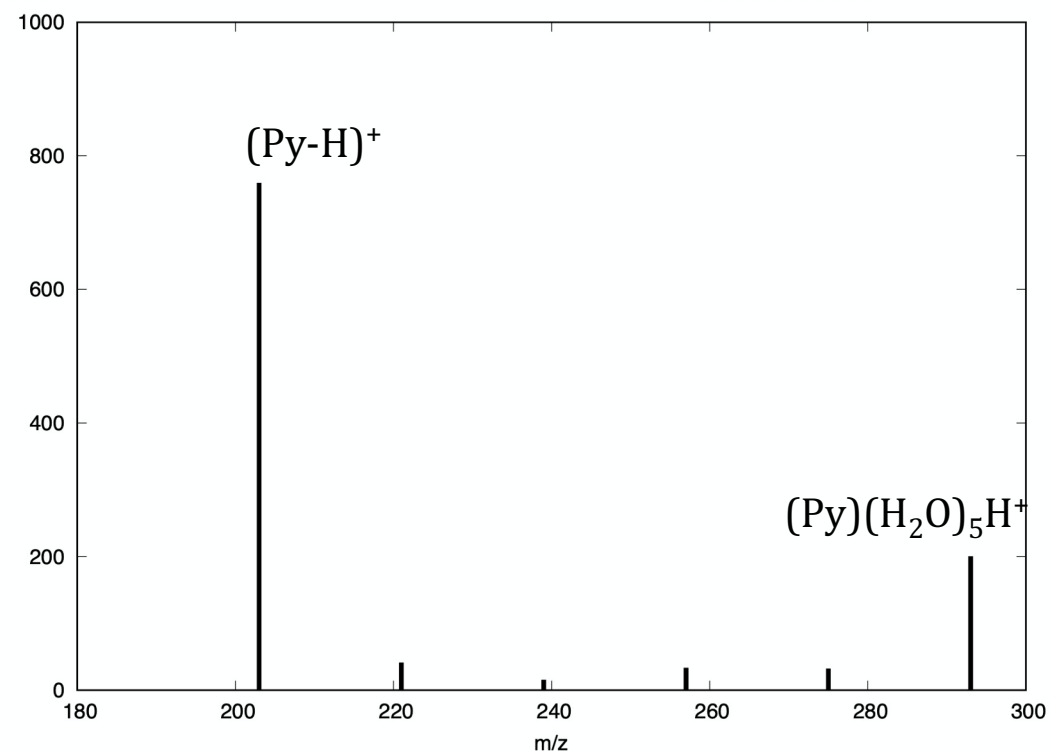
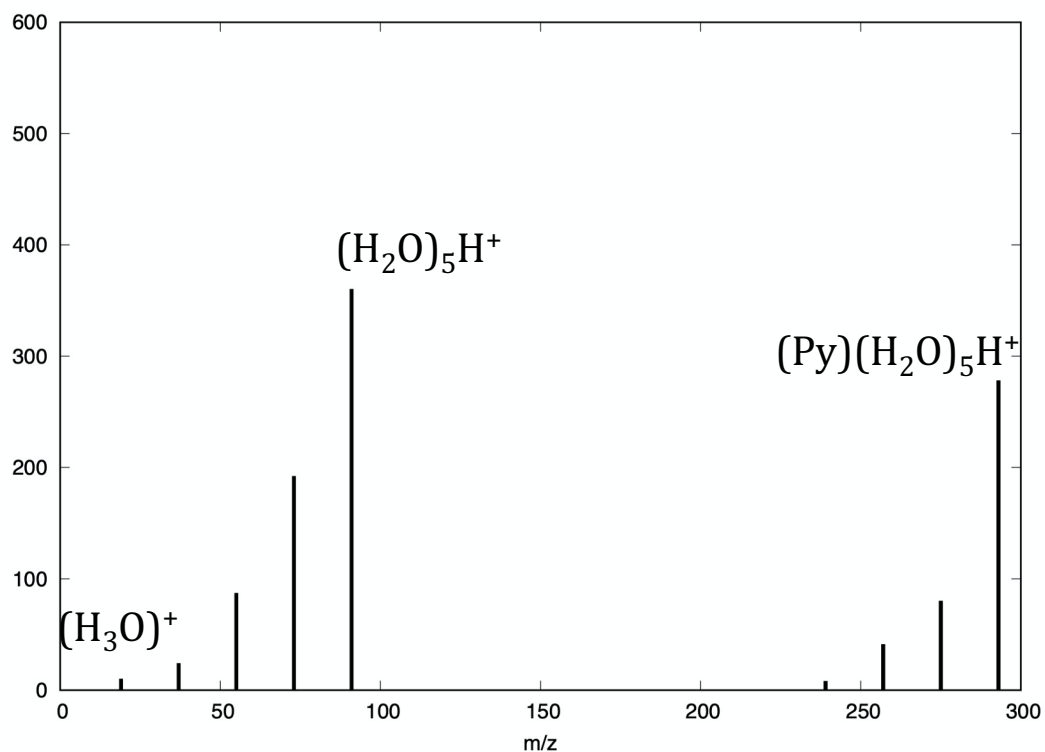
Loss of water (Py-H⁺)*+ Some rare cases of proton transfer*

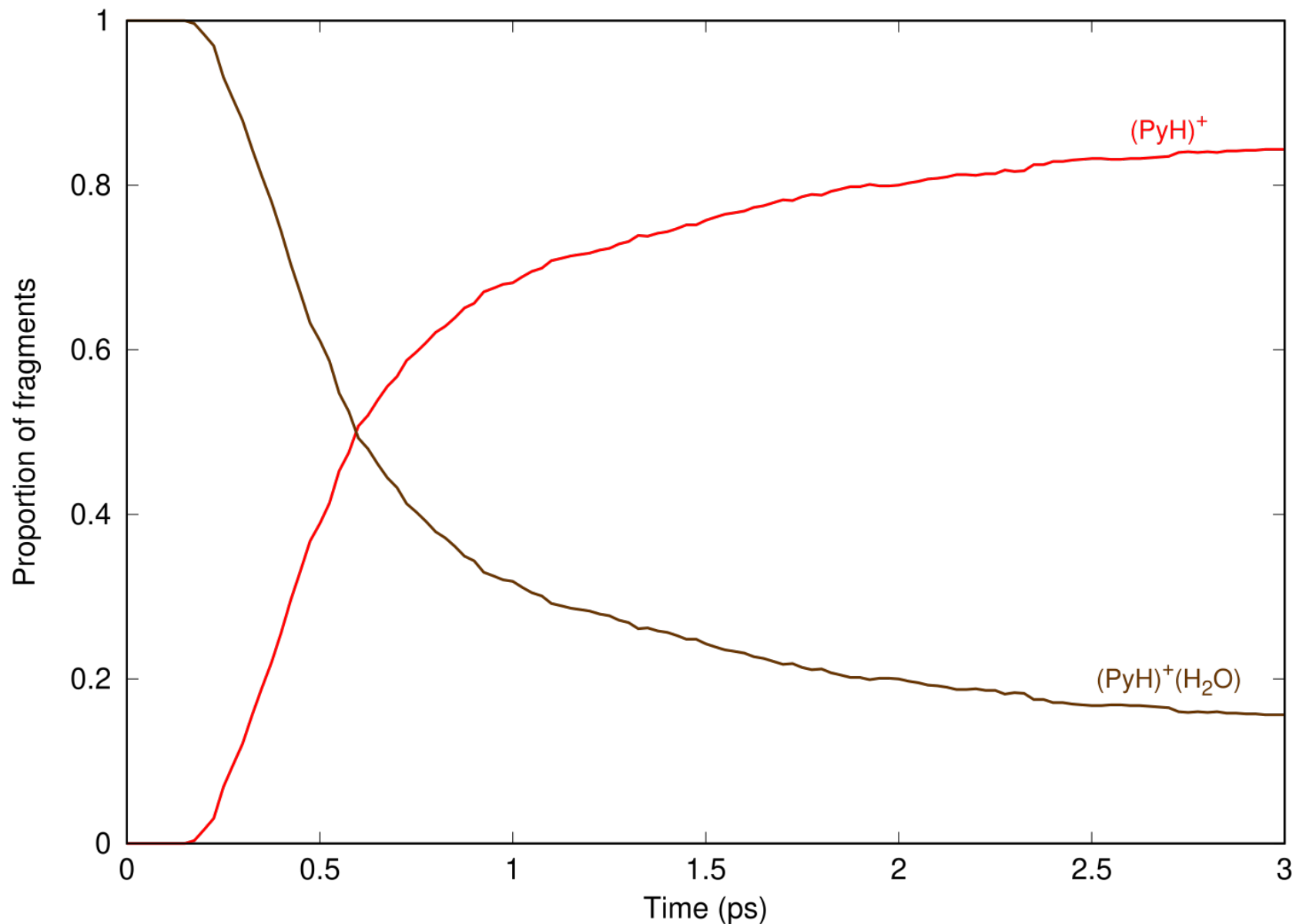
Proton on water

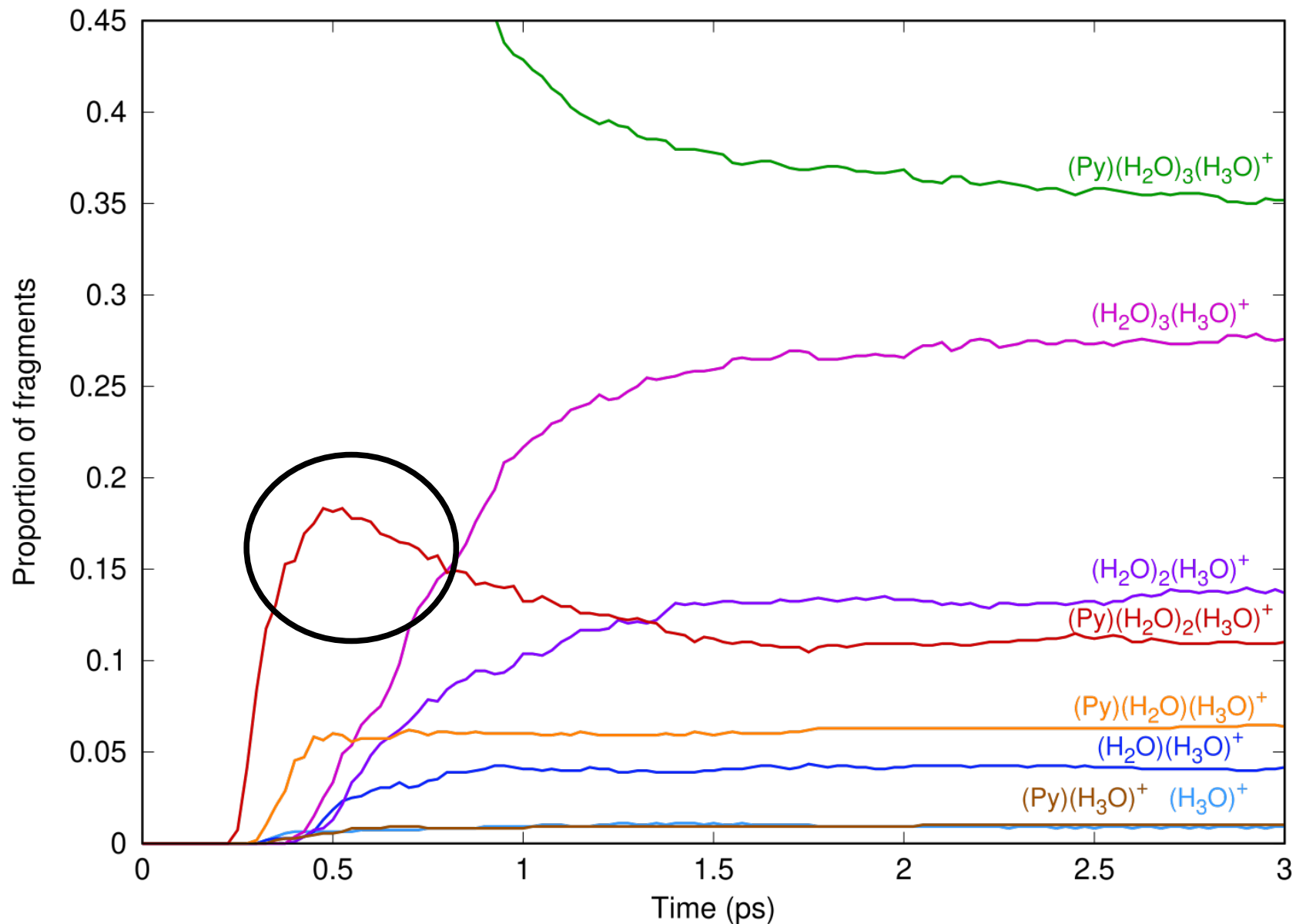
Proton on pyrene (C1)

n=5Loss of pyrene
+ water

Loss of water

Loss of water (Py-H⁺)

n=1

n=4

→ Goal

To study collision-induced dynamics of $(\text{Py-H})(\text{H}_2\text{O})_n^+$ clusters with BOMD/SCC-DFTB simulations

→ Results

Low-energy collisions } The dependence on the protonation site
High-energy collisions } was clearly established

Importance of the collision process in itself

→ Perspectives

- Other SCC-DFTB parameters: new reactions?
- Collisions with the protonated dimer of pyrene → charge delocalisation question



Computing mesocenter
(projects P0059 and P17002)



ANR-17-EURE-0009

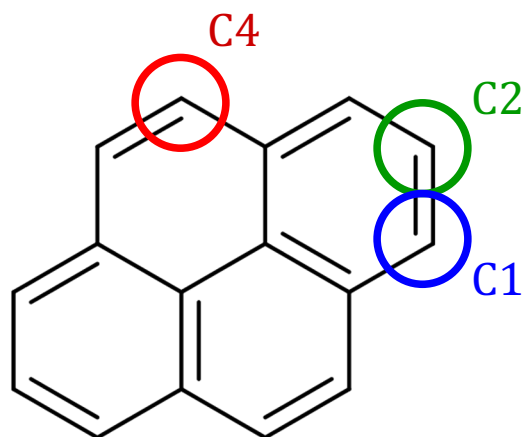


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Thank you for your attention!

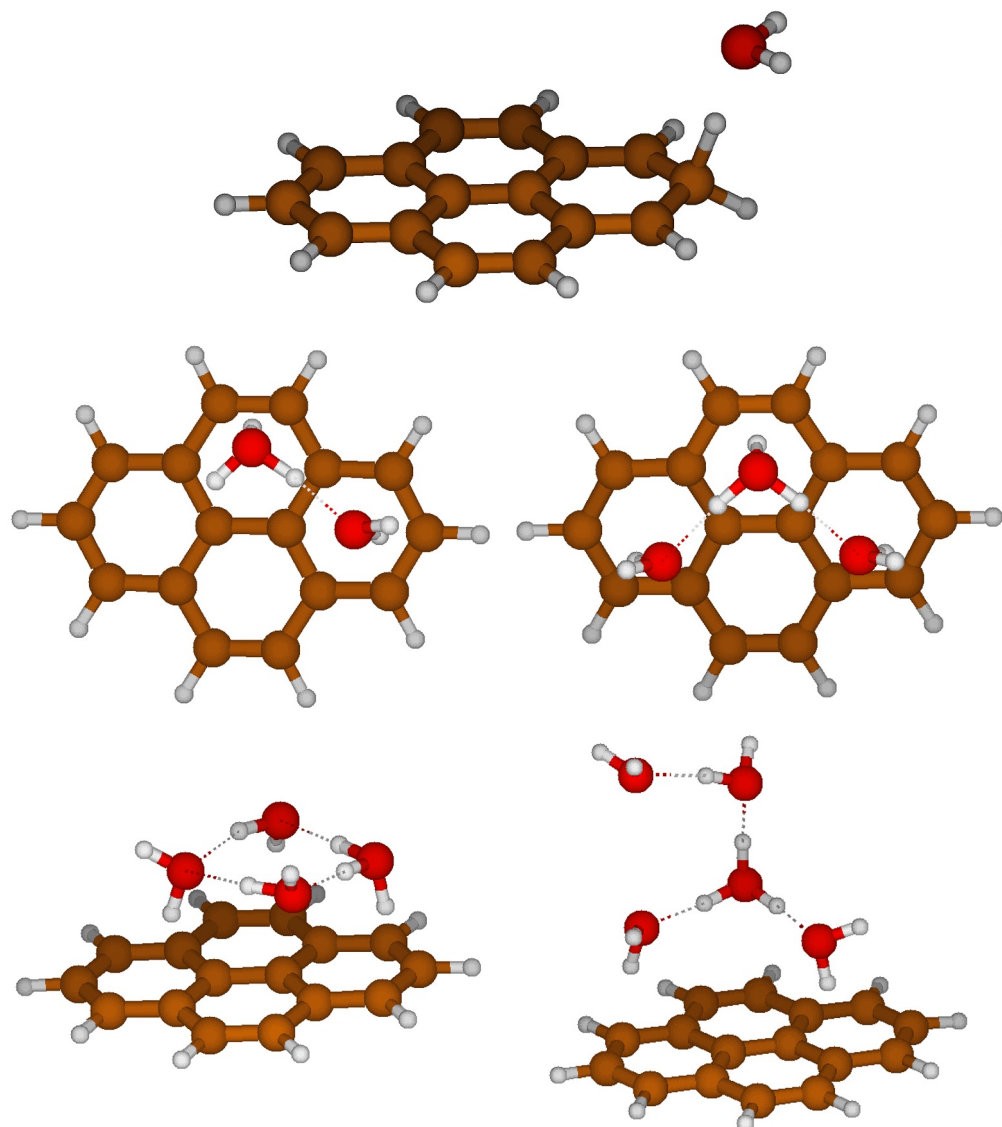
Results

**C1**

(Py-H) ⁺	1080	760	133	60	9
+ H ₂ O		320	678	187	89
+ 2 H ₂ O			269	589	205
+ 3 H ₂ O				244	552
+ 4 H ₂ O					225
	Step number	1	2	3	4

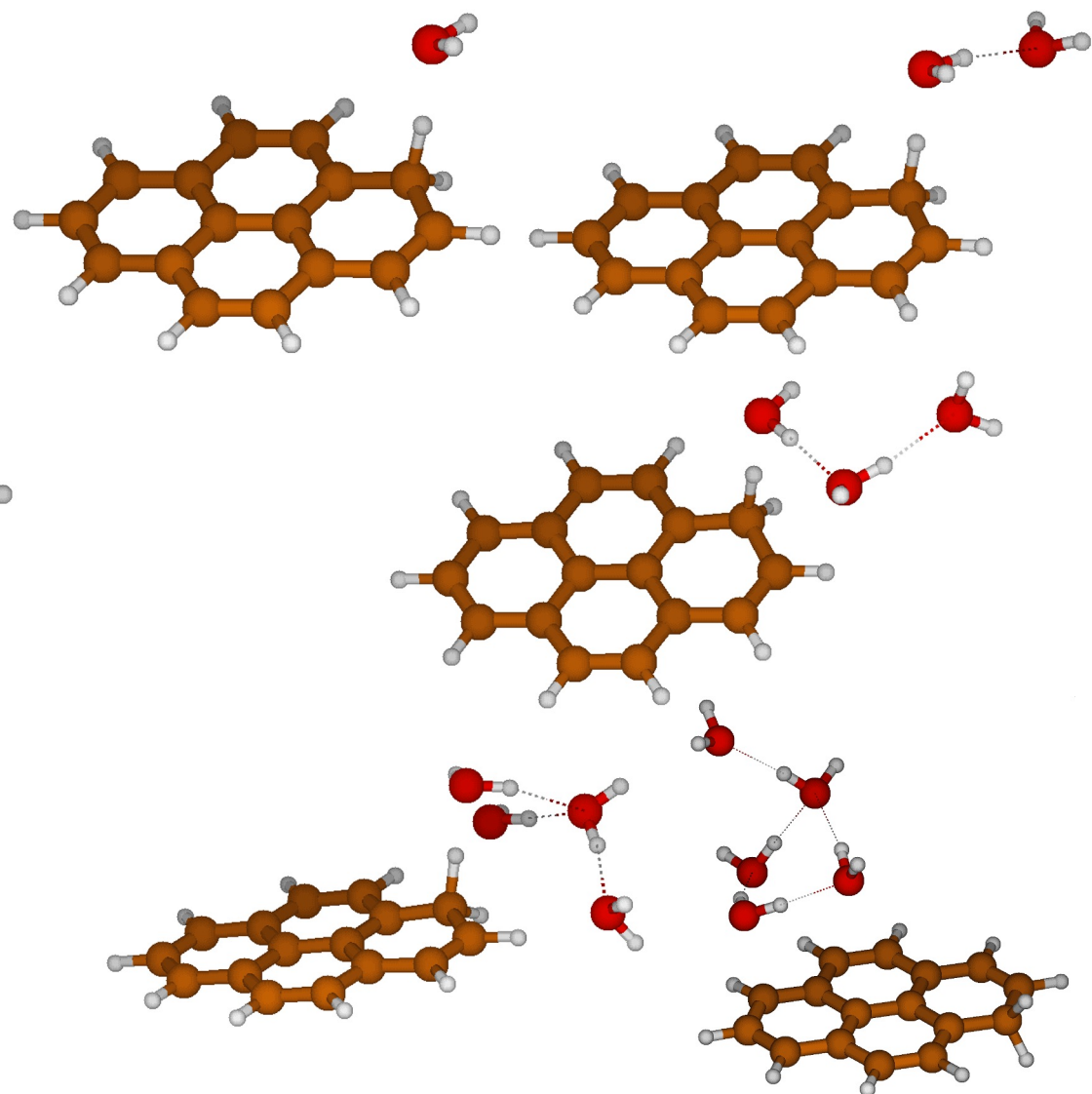
Annotations: A blue arrow points from 1080 to 320 with the label "29.6%". A blue arrow points from 552 to 225 with the label "92.2%". Purple boxes highlight the values 760, 133, 60, 9, 320, 678, 187, 89, 269, 589, 205, 244, 552, and 225.

Proton on water (or C2)



30/10/2024

Proton on pyrene (C1)



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