

Introduction

Polycyclic Aromatic Hydrocarbons (PAH) clusters can be thought as model nanoparticles in combustion science or astrochemistry. For the latter, it is now quite well established that PAHs are present in the interstellar medium, and clusters of PAHs have been proposed to be present as well [1].

For the former, PAHs are the main constituent of soot. In both these areas of science, the interaction of these particles with water is of relevance. For instance, in the terrestrial atmosphere, the coupling of soot with water is of importance to understand the fate of these pollutants [2]. Concerning astrochemistry, it is of interest to understand as well how water molecules absorb or detach from these model nanograins as a function of their size, temperature or composition [3].

We present here the study of the attachment of water molecules onto mass-selected pyrene ($C_{16}H_{10}$) cationic clusters. Pyrene clusters are produced in a gas aggregation source and then mass-selected with a well-defined and controlled kinetic energy in the lab frame [4]. They undergo low energy collisions with water molecules in a collision cell and the products are analyzed through time of flight mass spectrometry.

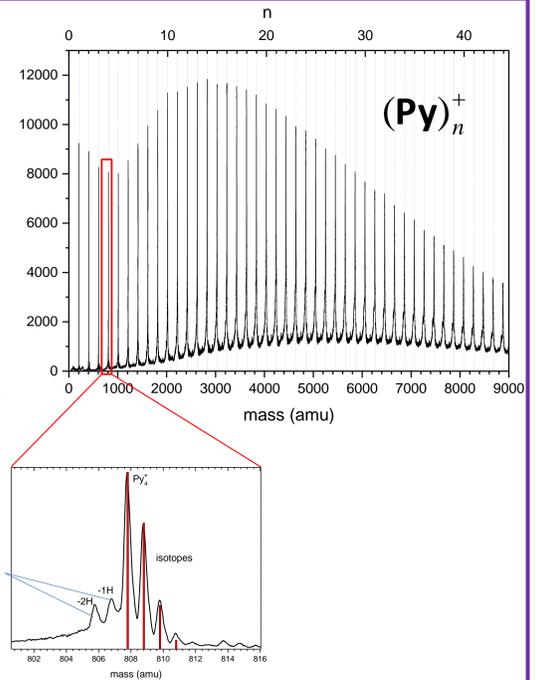
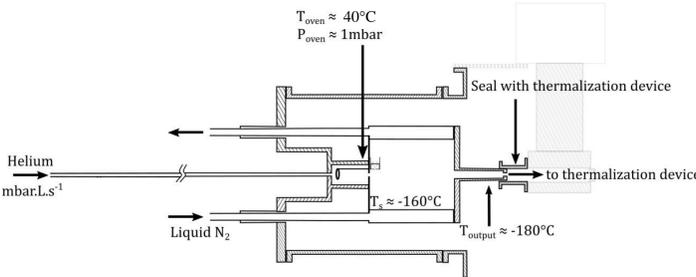
Pyrene clusters production

Source conditions

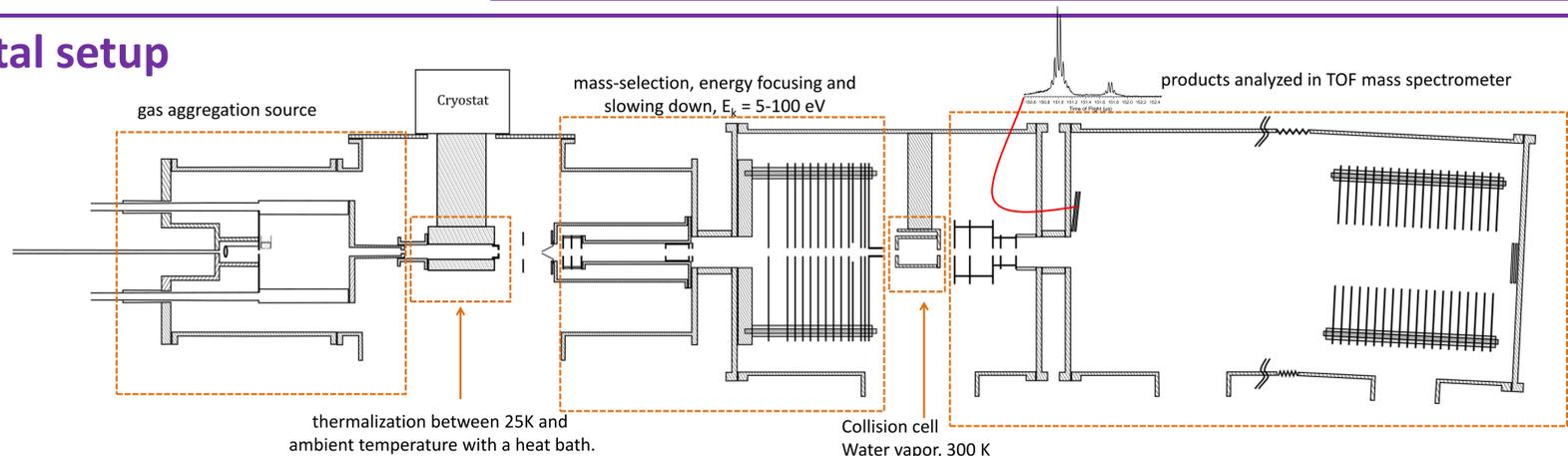
Clusters are produced in a gas aggregation source.

Ionization by either :

- a discharge electrode, $I \approx 100 \mu A$, $V \approx 1$ kV
- an electron gun, $I = 2.5$ A, $V = -100$ V



Experimental setup



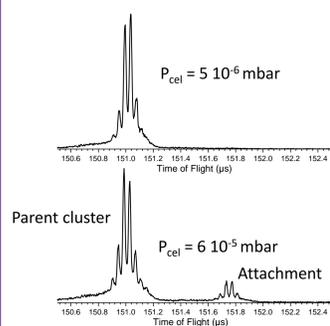
For more details see [5] and [6]

Experimental results

Principle of measurement:

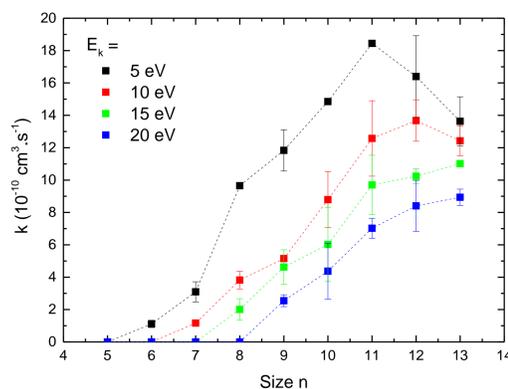
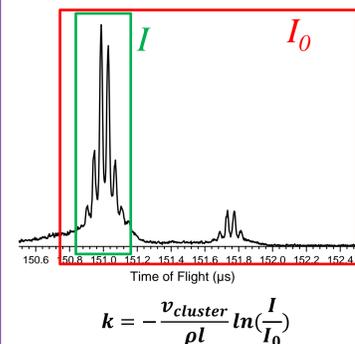
Temperature controlled pyrene clusters are mass-selected and slowed down. They fly through the collision cell where a controlled pressure of water vapor is maintained. Mass-spectra show the appearance of attachment products as the water vapor pressure is increased.

Example: $(Py)_5^+ + H_2O$ @ 5 eV

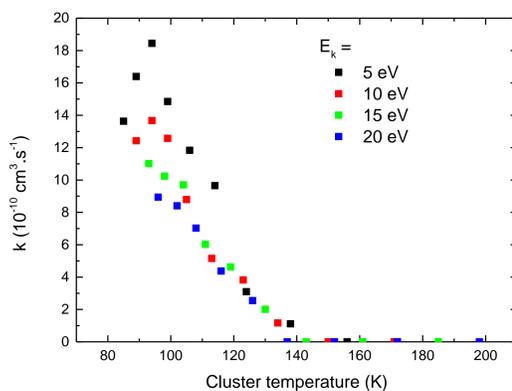


The attachment rate $k = \int \sigma(v_{rel})v_{rel}f(v_{rel})dv_{rel}$

can be directly deduced from the experimental TOF mass spectra:



When plotted as a function of the collision energy, there is a size dependent threshold for attachment: the higher the size, the higher the threshold. Not only the collision energy has to be low enough, but the cluster size has to be large enough so that the deposited energy can be absorbed among the internal degrees of freedom.

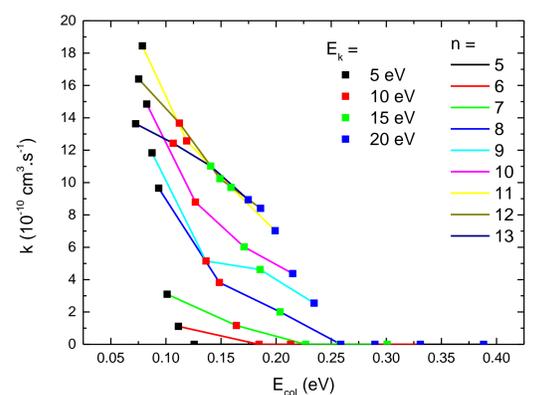


The attachment rate of water onto pyrene clusters cation increases with size up to $n=11$. For larger sizes we observe a slight stagnation and even a decrease at low E_k . The attachment rate increases when the cluster kinetic energy is decreased.

Since experiments are performed for a given kinetic energy in the lab frame, the center of mass collision energy varies when the size changes. The collision energy evolves as:

$$E_{col} = \frac{m}{M+m} E_k + \frac{3}{2} \frac{M}{M+m} k_B T$$

If the collision energy is too high, no attachment is observed: at each kinetic energy there is a size threshold for attachment. Does it correspond to a collision energy threshold?



The total internal energy after attachment is given by: $E_{int} = E_{col} + E_{th} + D_n$ Where E_{th} is the initial internal thermal energy, D_n the dissociation energy and E_{col} the collision energy. The clusters being thermalized at 25 K, the initial internal thermal energy E_{th} is rather low, about 2meV/molecule. The dissociation energy of water from the pyrene cation monomer is of the order of 0.3 eV (A. Simon, private communication).

From the normal modes calculated in DFTB, one can deduce the heat capacity of the clusters and thus determine their temperature from their internal energy [7]. Therefore the attachment rate can be plotted as a function of cluster temperature.

On the left figure, one can see that the attachment of H_2O is not observed for cluster temperatures above 150 K. This is consistent with the water desorption peak observed at 170-180 K in Temperature Programmed Desorption (TPD) experiments both for H_2O ices [8] and for an H_2O sub-monolayer adsorbed on small dust particles (carbon and silicates) [9].

Perspectives

In the future, we still have to elucidate the fact that the attachment rate decreases for large sizes: is it due to a geometrical effect? Charge density distribution changes (as the size increases the charge is more and more diluted [10] and polarization effects on the H_2O molecule decrease)?

We would like to see the effect of the initial internal energy on the attachment: as the cluster initial temperature is increased we should observe a decrease of the collision energy threshold for attachment.

Since our gas aggregation source allows to produce mixed water-pyrene clusters we would like also to explore the attachment of water onto these mixed clusters.

- [1] M. Rapacioli *et al*, *A&A* **429**, 193-204 (2005)
- [2] S. O. Baek *et al*, *Water, Air, Soil Pollut.*, **60**, 279-300 (1991)
- [3] F. Dulieu *et al*, *Sci Rep* **3**, 1338 (2013).
- [4] S. Zamith *et al*, *J. Chem. Phys.* **153**, 054311 (2020)
- [5] F. Chirof *et al*, *Rev. Sci. Instrum.* **77**, 063108 (2006)
- [6] I. Braud *et al*, *Rev. Sci. Instrum.* **88**, 043102 (2017)
- [7] S. Zamith *et al*, *J. Chem. Phys.* **151**, 194303 (2019)
- [8] R. Martín-Doménech *et al*, *A&A* **564**, A8 (2014)
- [9] A. Potapov *et al*, *ApJ* **865** 5 (2018)
- [10] Dontot *et al*, *J. Phys. Chem. A*, **123**, 9531-9543 (2019)