VUV photo processing of large cationic PAHs in astrophysical conditions: coupling a VUV source to the PIRENEA setup

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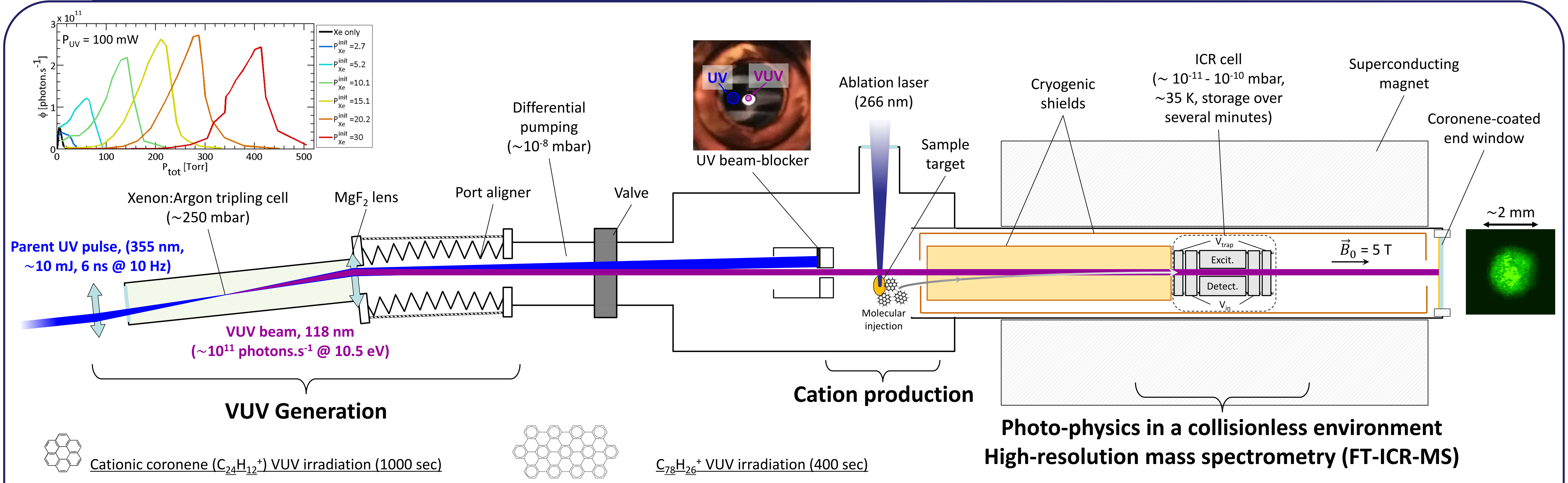
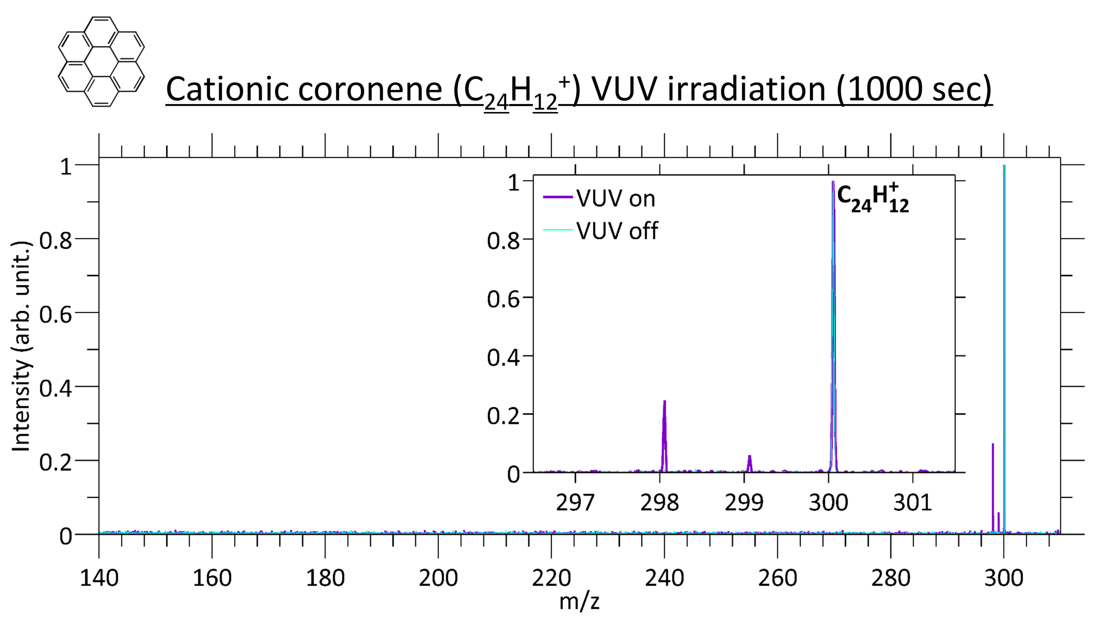
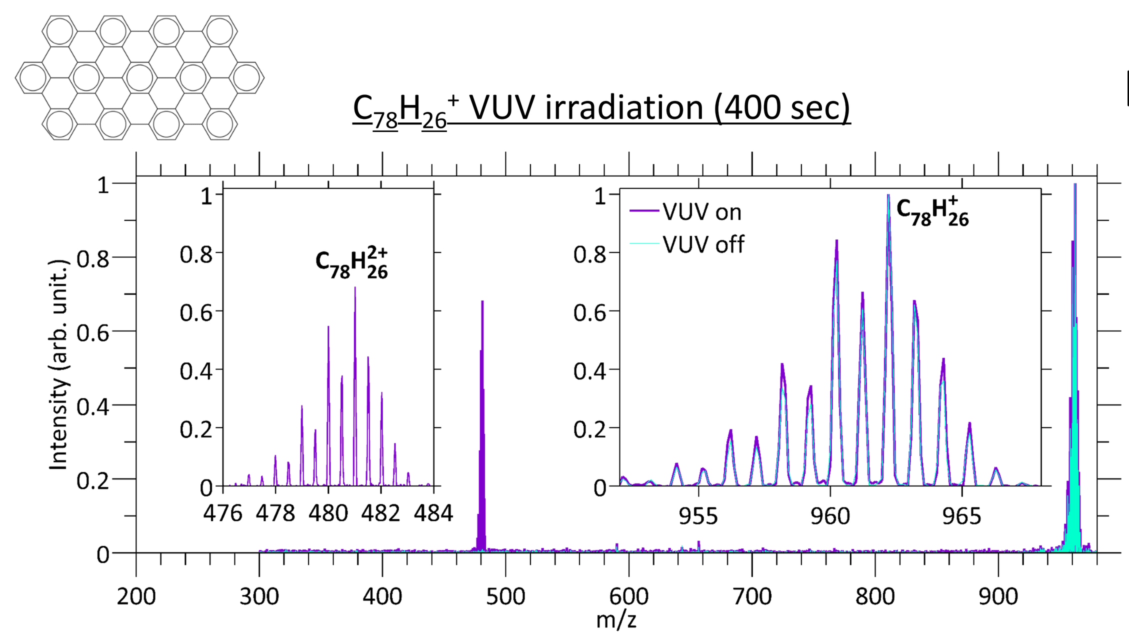
Abstract

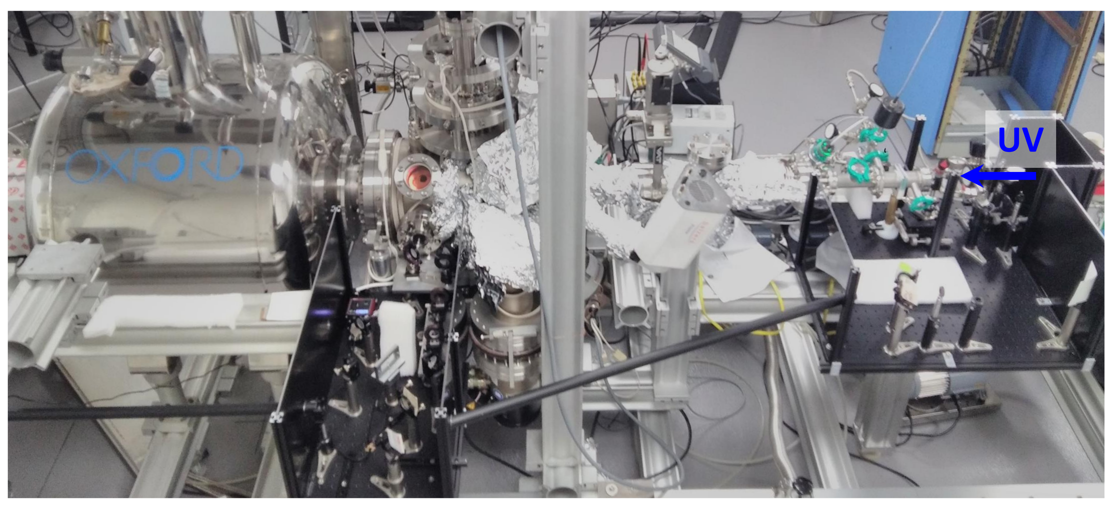
Studying the interaction of polycyclic aromatic hydrocarbons (PAHs) with UV and VUV light is crucial for the understanding of the physical and chemical evolution of the interstellar medium. Photo-processing by VUV irradiation leads to variation of the hydrogenation and ionization states of PAHs [1] and plays an important role in the heating of the gas [2]. Recent laboratory studies have shown that the VUV photoexcitation of large PAHs rather induces further ionization than fragmentation [3,4] and, more surprisingly, it can also induce non-statistical dissociation [5]. We have recently coupled a VUV source based on a Xe-Ar tripling cell to the PIRENEA (Piège à Ions pour la Recherche et l'Etude de Nouvelles Espèces Astrochimiques) setup which consists of a cryogenic (35 K) ion cyclotron resonance cell that is especially well suited to investigate ionization and dissociation on long timescales [1,5]. The produced VUV photons (10.5 eV) are sufficiently energetic to trigger dissociation in small/medium-size PAHs [6] and ionization in large PAH cations [4]. We present first measurements of VUV processing of several PAHs in a cryogenic and collisionless environment which is appropriate for interstellar conditions.

Experimental Method : VUV photo-processing of isolated PAH molecules





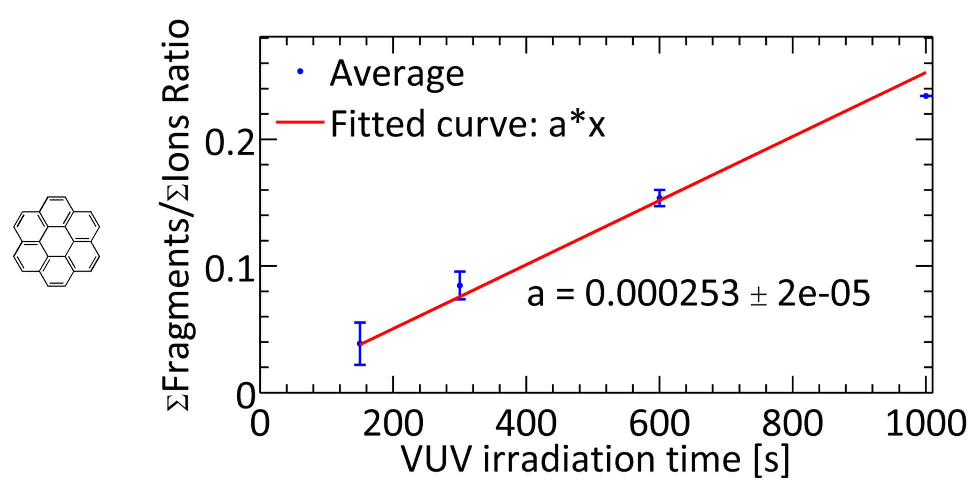


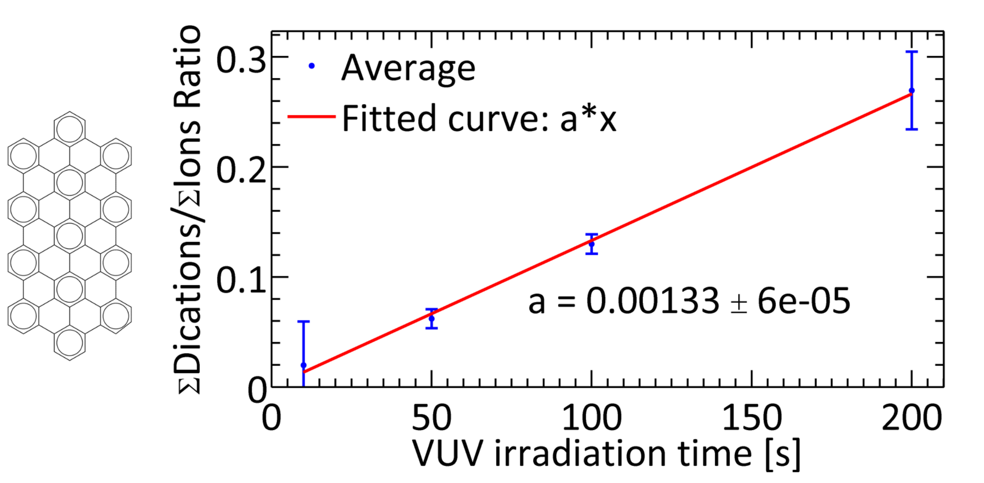


- ➢ **Only fragments [Cor-H]⁺ and sequentially [Cor-2H]⁺**
- ➢ **Only dications with the same initial distribution of isotopes and fragments**

Preliminary results

Study as a function of the VUV irradiation time





Implications in VUV photo-processing of PAHs

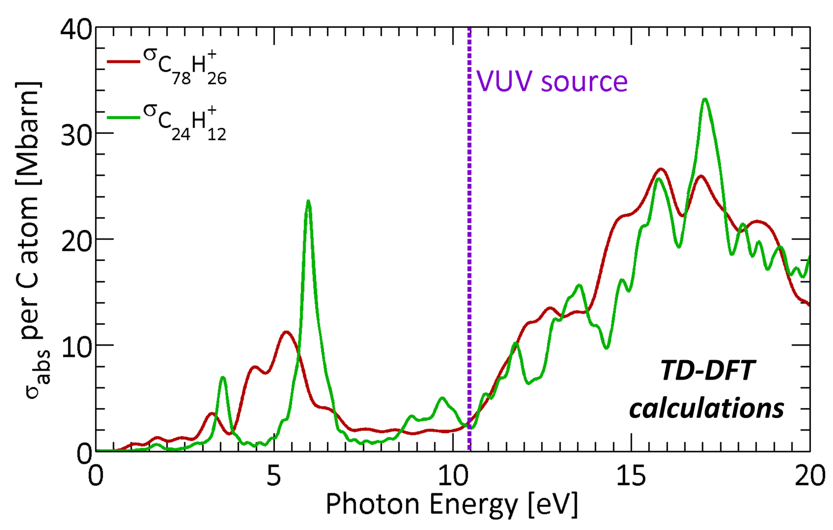
- The measured photo-products formation rate of $C_{78}H_{26}^+$ is **5.25 times** larger than the one of $C_{24}H_{12}^+$.
- The absolute VUV photo-absorption cross-section of $C_{78}H_{26}^+$ is about **3.25 times** larger than the one of $C_{24}H_{12}^+$ (ratio of C atom number).
- A simple model for the photo-ionization yield of large PAH has been derived from measurements in a previous study [4] : ~**0.23** at 10.5 eV for $C_{78}H_{26}^+$.

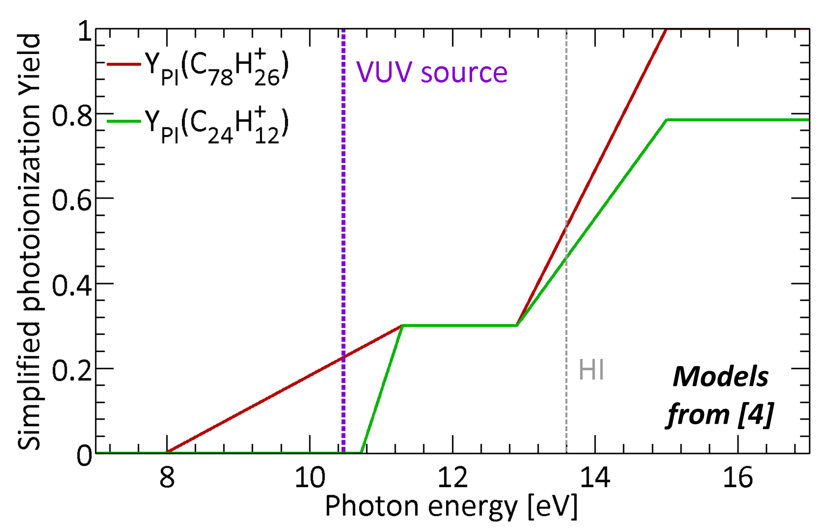
$$\text{Absorbed photons per second} = \begin{cases} \sigma_{abs}(C_{24}H_{12}^+) \times \phi_{VUV} = \dfrac{a(C_{24}H_{12}^+)}{Y_{diss.}(C_{24}H_{12}^+)} \\ \sigma_{abs}(C_{78}H_{26}^+) \times \phi_{VUV} = \dfrac{a(C_{78}H_{26}^+)}{Y_{ion.}(C_{78}H_{26}^+)} \end{cases}$$

if ϕ_{VUV} is constant

$$\Rightarrow Y_{diss.}(C_{24}H_{12}^+) \approx \frac{a(C_{24}H_{12}^+)}{a(C_{78}H_{26}^+)} \times \frac{\sigma_{abs}(C_{78}H_{26}^+)}{\sigma_{abs}(C_{24}H_{12}^+)} \times Y_{ion.}(C_{78}H_{26}^+) \approx 0.14$$

- ➢ The retrieved dissociation yield at a VUV energy close to the threshold is consistent with the results found by Zhen and coworkers [6].
- ➢ This shows that a large fraction of the 10.5 eV photons absorbed by C24H12+ are relaxed by radiative cooling.





Perspectives

- Calibration to determine robust values of the dissociation yield combining experiments on smaller PAHs.
- Molecular systems from strongly dissociative to intermediate case where dissociation and ionization are in competition.
- VUV photo-chemistry by molecular gas injection.

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