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Impact of aliphatic bonds on the stability of VUV photo-processed PAHs under relevant astrophysical conditions

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Abstract

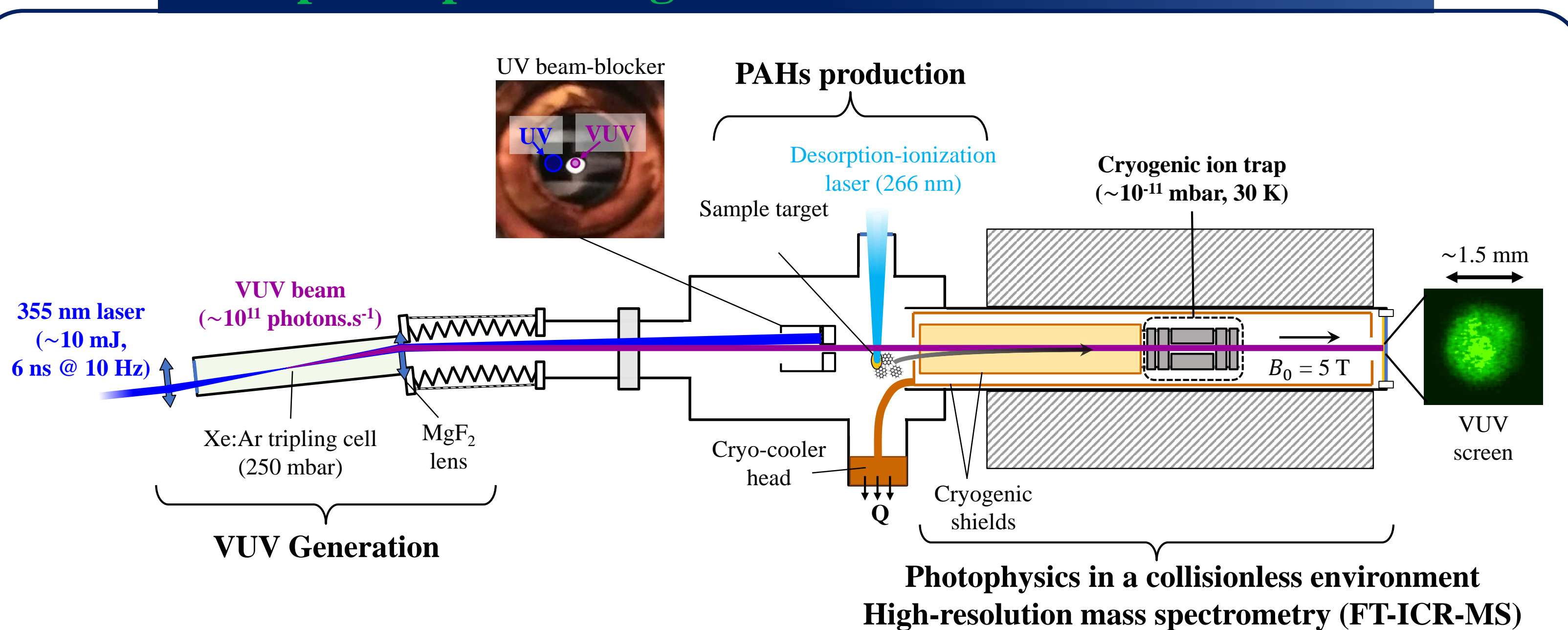
Studying the interaction of polycyclic aromatic hydrocarbons (PAHs) with VUV light is crucial for the understanding of the physical and chemical evolution of photodissociation regions (PDRs). In particular, this interaction induces the well-known aromatic infrared bands (AIB) emission [1] but other mechanisms such as fragmentation [2] can be involved, leading to selection effects favoring specific sizes and structures. In this context, despite their lower stability, PAHs containing aliphatic C-H bonds are considered as good candidates for the 3.4 μm AIB [3,4].

We have recently combined a 10.5 eV photon source with our dedicated cryogenic ion trap PIRENEA [5] in order to investigate the impact of aliphatic bonds on the VUV photo-stability of PAH cations with conditions applicable for PDRs [6]. The coronene cation ($\text{C}_{24}\text{H}_{12}^+$) and its alkylated derivatives (with methyl or ethyl sidegroups) were VUV photo-processed over long timescales (~ 1000 s). Their fragmentation cascades were analyzed with a simple kinetics model which enabled to derive fragmentation pathways, rates and branching ratios.

Alkylated coronene derivatives are found to have a higher fragmentation rate and carbon loss compared to the bare coronene. However, their VUV fragmentation cascade also leads to the formation of species carrying a peripheral pentagonal cycle, which is as stable as coronene. The stability of each detected species is quantified and the most stable ones, for which there is an effective competition of fragmentation with isomerization and radiative cooling, are identified.

This work supports a scenario in which the evaporation of nanograins with mixed aliphatic and aromatic composition followed by VUV photo-processing results in both the production of the carriers of the 3.4 μm AIB by methyl sidegroups and in an abundant source of smaller hydrocarbons at the border of PDRs. This process also results in the formation of PAHs containing pentagonal ring. Finally, our study supports the role of isomerization processes in PAH photofragmentation, including the H-migration process [7], which could lead to an additional contribution to the 3.4 μm AIB.

VUV photo-processing in astro-relevant conditions

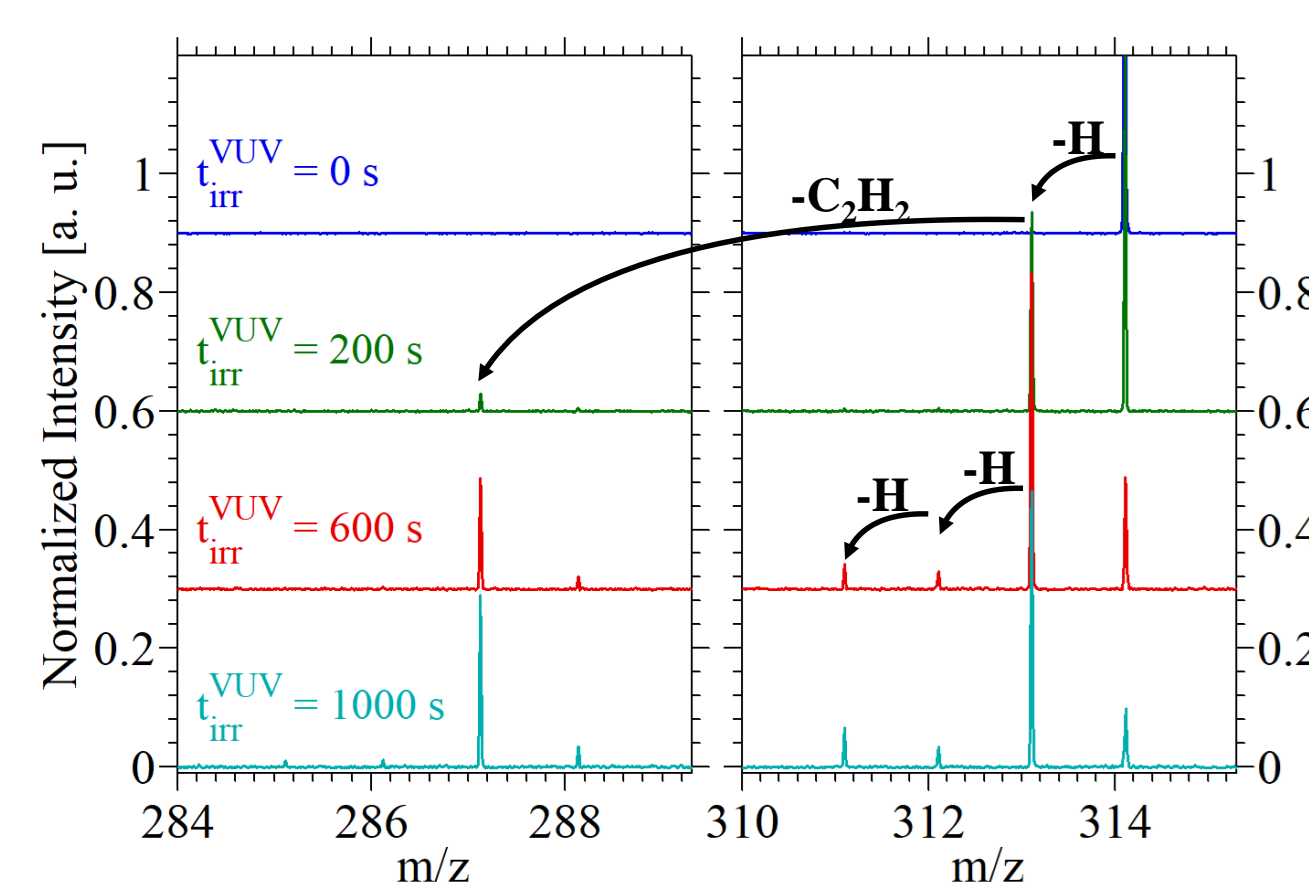


Method

1. VUV beam generated by tripling a 355 nm laser
2. Cationic PAHs produced by laser desorption-ionization
3. Isolation of the parent cations
4. 10.5 eV irradiation of the ion cloud up to 1000 s
5. Measurement of the photoproducts by FT-ICR-MS

Experimental conditions

- Low photon flux (estimated to $\sim 10^{13}$ photons \cdot s $^{-1}$ \cdot cm $^{-2}$)
- Ions have time to relax between two VUV photons absorption
- Sequential cascades of fragmentation

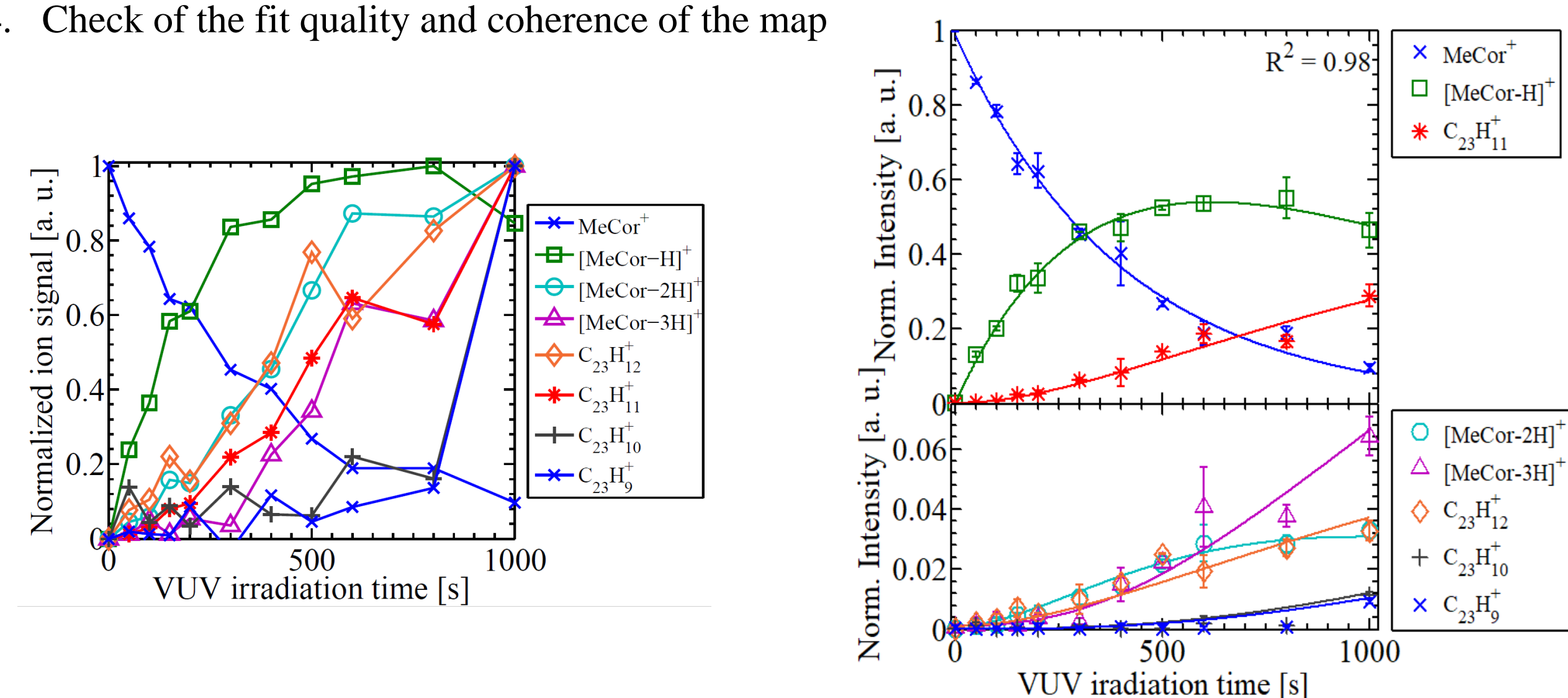


A kinetic model to extract rates and ratios

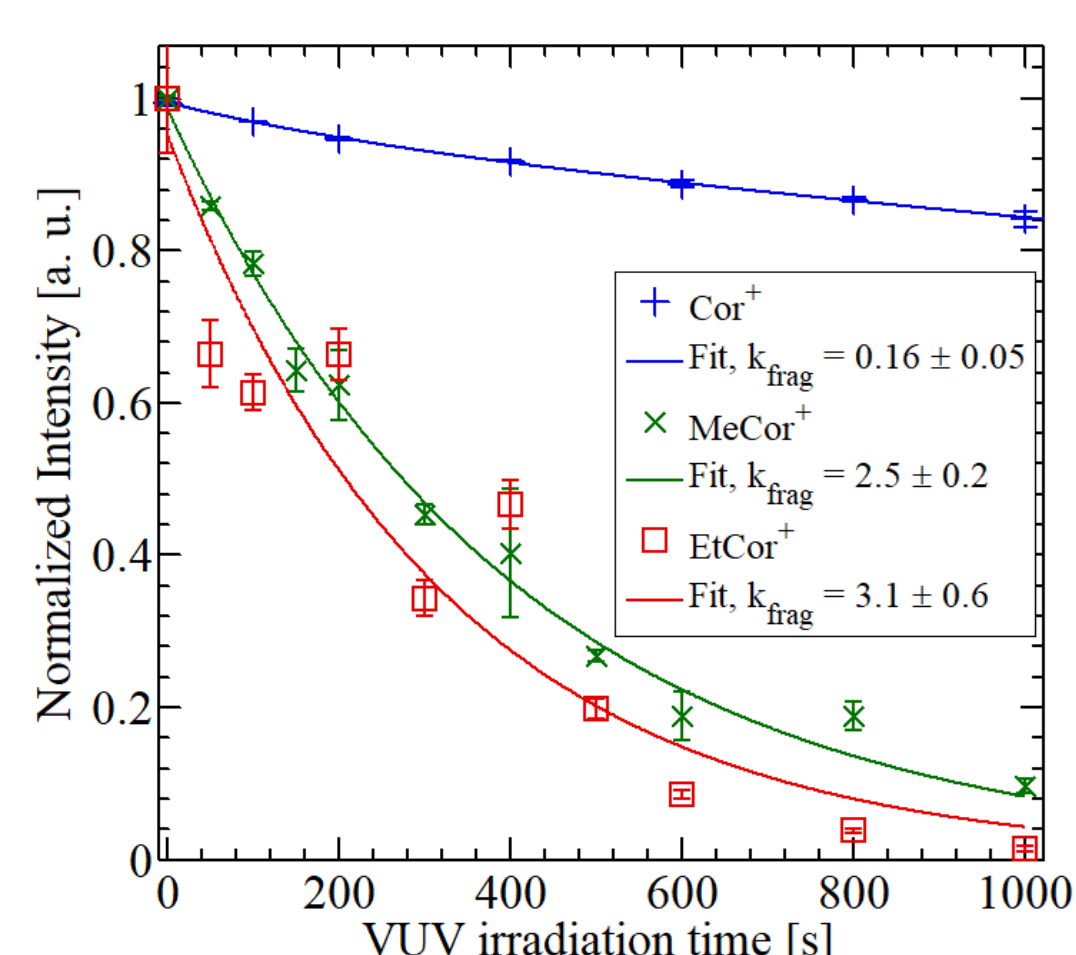
1. Search of parent-daughter relation between the observed fragments to determine the population and depopulation terms in the system of equations :

$$\begin{cases} (1^{st}) & \frac{dI_{M_{parent}}}{dt} = - \sum_{M_i < M_{parent}} k_{frag}^{M_{parent} \rightarrow M_i} I_{M_{parent}}(t) \\ \vdots & \\ (i^{th}) & \frac{dI_{M_i}}{dt} = \sum_{M_n > M_i} k_{frag}^{M_n \rightarrow M_i} I_{M_n}(t) - \sum_{M_j < M_i} k_{frag}^{M_i \rightarrow M_j} I_{M_i}(t) \end{cases}$$

2. Fit of the kinetics data points in order to extract the $k_{frag}^{M_i \rightarrow M_j}$
3. Feedback loop in order to remove or add population/depopulation terms with educated guesses
4. Check of the fit quality and coherence of the map



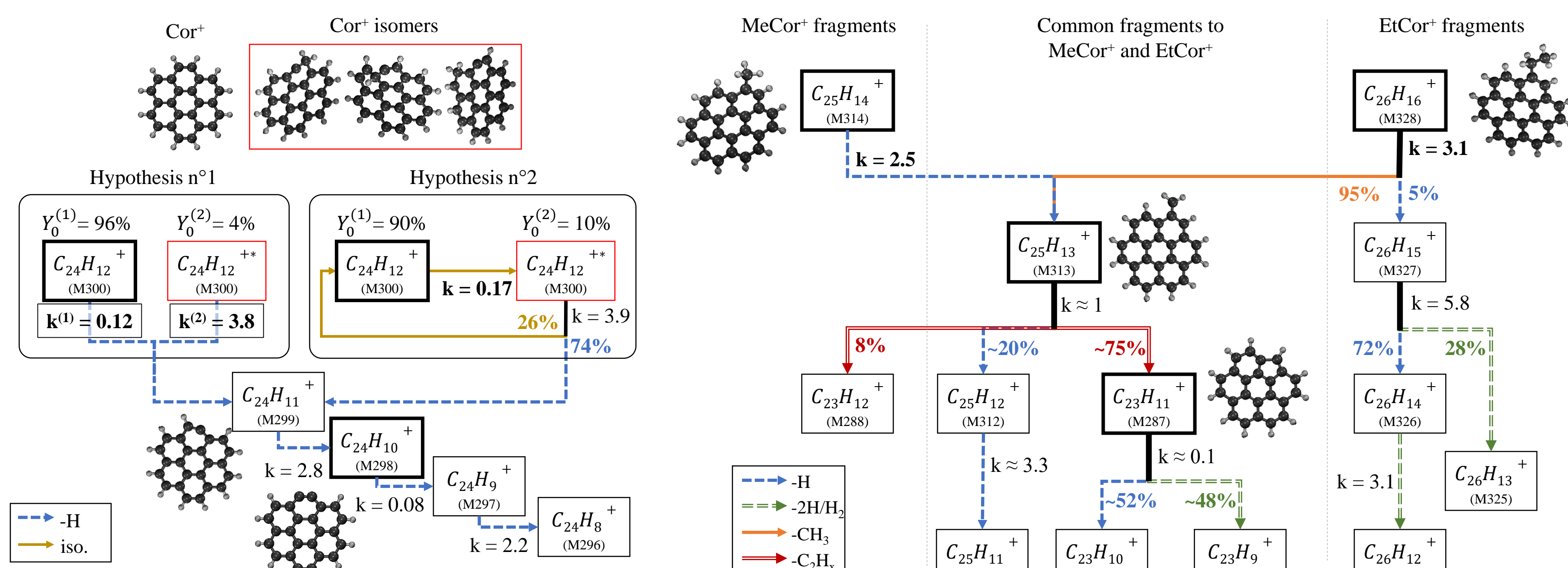
Retrieved fragmentation maps of the studied species



- Sequential loss of H atoms with a global low rate ($k = 0.16 \times 10^{-3}$ s $^{-1}$)
- Need of an isomer population to fit the data (several hypotheses)
- Isomers can be formed by H-migration on the peripheral backbone
- [Cor-2H]⁺ is also a stable and highly populated species

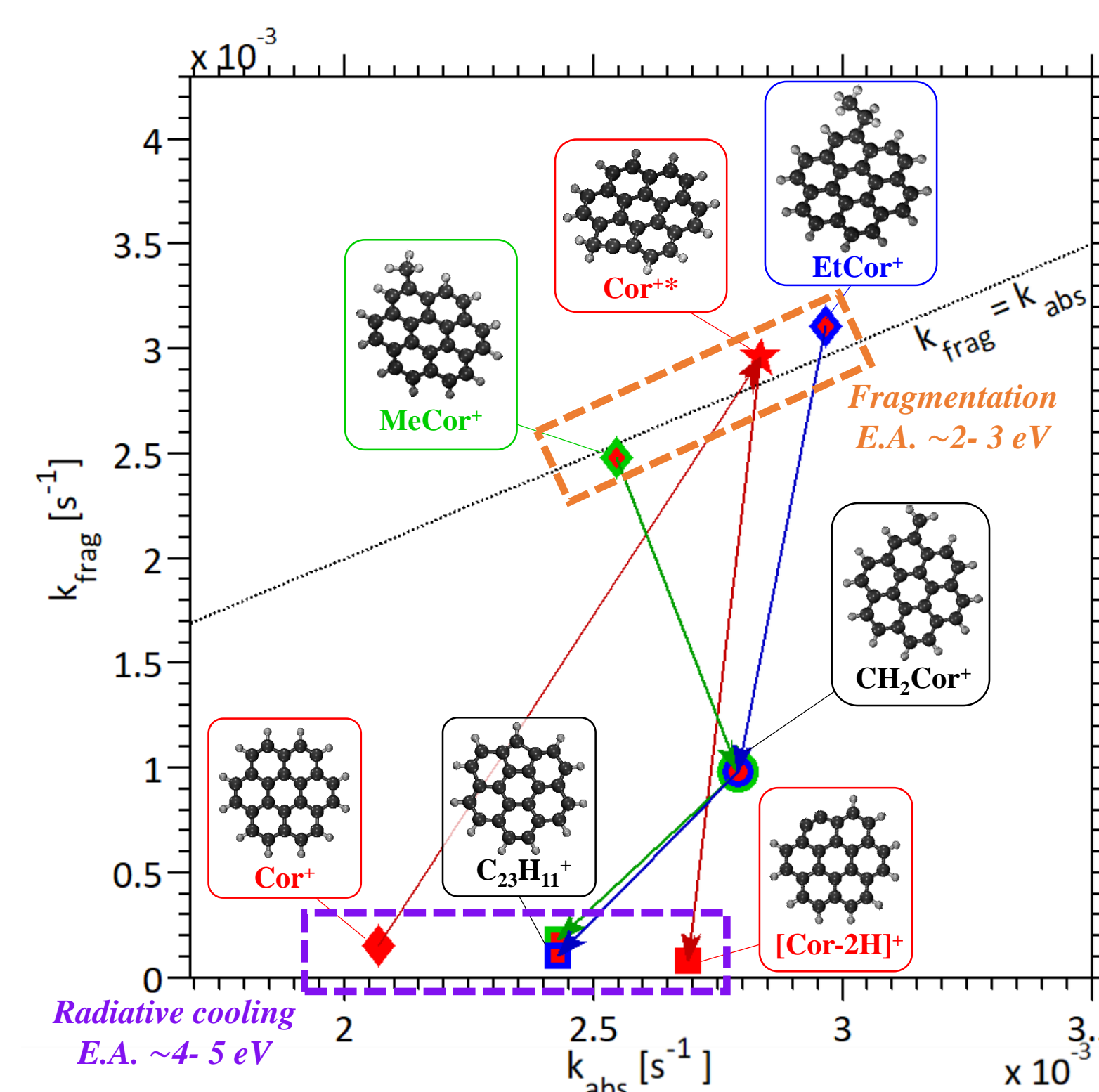
Methyl-coronene and Ethyl-coronene

- Strong fragmentation rate with respect to coronene ($\sim 2.8 \times 10^{-3}$ s $^{-1}$)
- First step mostly corresponds to production of the methylene-coronene
- Additional sequential H-loss path for ethyl-coronene leading to ethynyl-coronene
- $\text{C}_{23}\text{H}_{11}^+$ is a stable and highly populated species



Competition of relaxation processes

Comparison of experimental fragmentation rates with photoabsorption rates from TD-DFT calculations



- Fragmentation for each absorbed photon for Cor⁺, MeCor⁺ and EtCor⁺
- Cooling fraction is predominant in Cor⁺, [Cor-2H]⁺ and $\text{C}_{23}\text{H}_{11}^+$
- The fragmentation cascade of alkylated species leads to stable fragments containing a pentagonal ring

Take-home messages and Perspectives

- ✓ Isomerization of Coronene is the first step before dissociation at 10.5 eV
- ✓ Common species are produced during the VUV photo-processing of alkylated PAHs
- ✓ Pentagonal rings formation stabilizes the structure
- ✓ Two carriers for the 3.4 μm : methyl-PAHs and H-shifted PAHs

- VUV photo-processing to differentiate isomers
- Exploration of the fragmentation kinetics of larger alkylated or superhydrogenated PAHs

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