VUV photodissociation of cationic alkylated PAHs and water-PAH complexes and formation of pentagonal carbon rings

A. Marciniak[1,2], S. Zamith[2], G. Mulas[3], H. Leboucher[4], A. Simon[4], S. Rodriguez Castillo[1,5], A. Giuliani[6,7], L. Nahon[6] A. Bonnamy[1] and C. Joblin[1]

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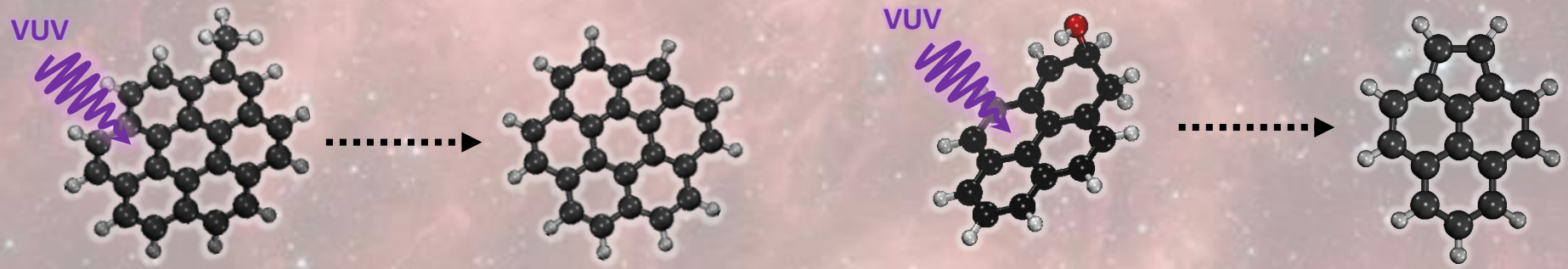
[2]LCAR/FERMI, Université de Toulouse, CNRS, France
[3]INAF Osservatorio Astronomico di Cagliari, I-09047 Selargius (CA), Italy
[4]LCPQ/FERMI, Université de Toulouse, CNRS, France
[5]European Space Research & Technology Centre, Postbus, 299 2200 AG Noordwijk, The Netherlands
[6]Synchrotron SOLEIL, L'Orme des Merisiers, 91192 Saint Aubin, Gif-sur-Yvette, France
[7]INRAE, UAR1008, Transform Department, Rue de la Géraudière, BP 71627, 44316 Nantes, France



nanoCOSMOS

European Research Council

cnrs

irap
astrophysique & planétologie

LCAR
Laboratoire Collisions Agrégats Réactivité

LCPQ
Laboratoire de Chimie et Physique Quantiques

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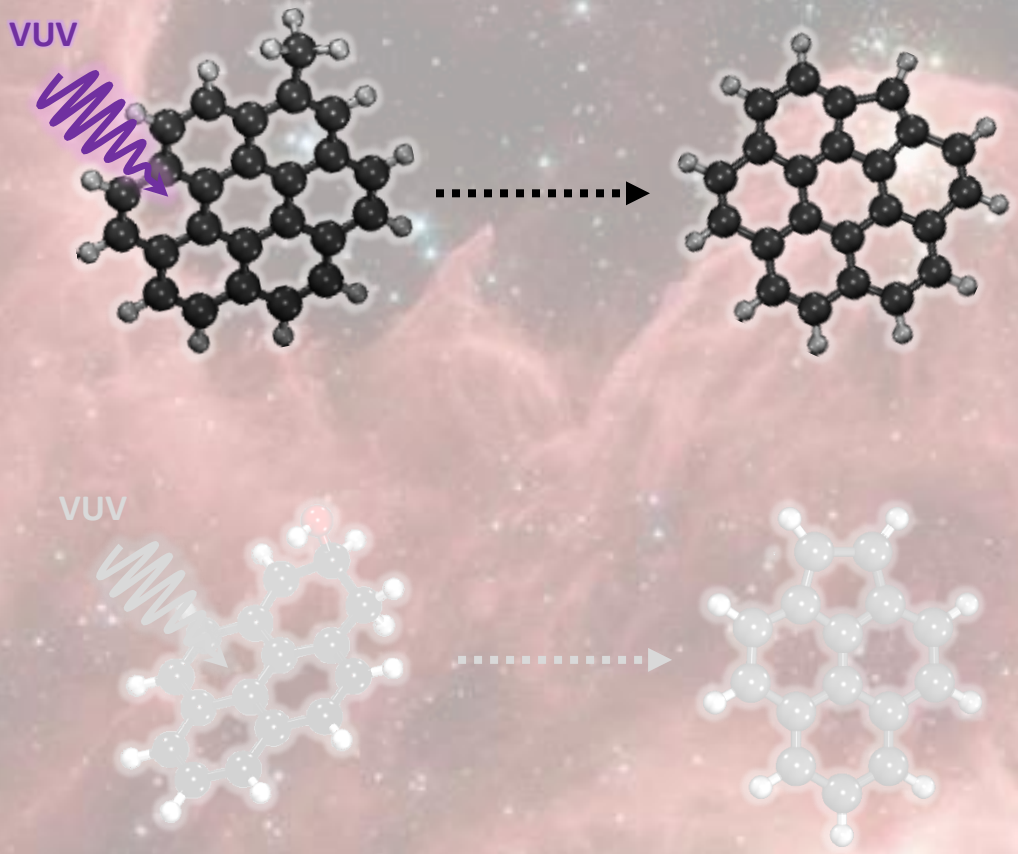
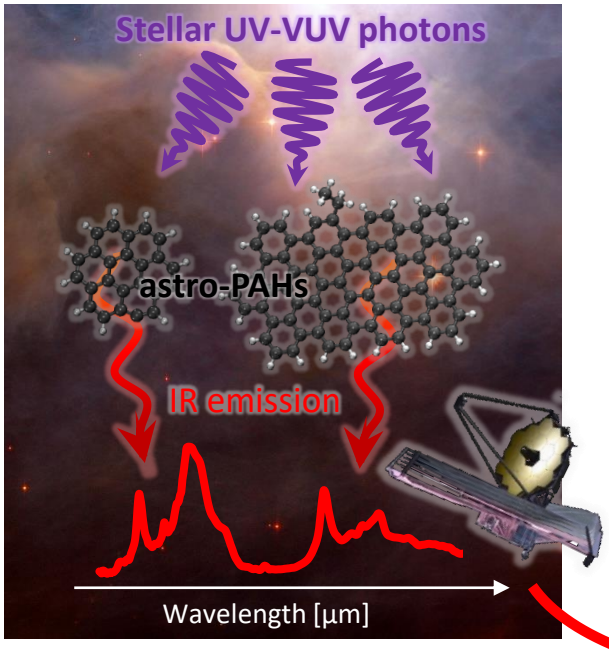
Université de Toulouse

VUV photodissociation of cationic alkylated PAHs

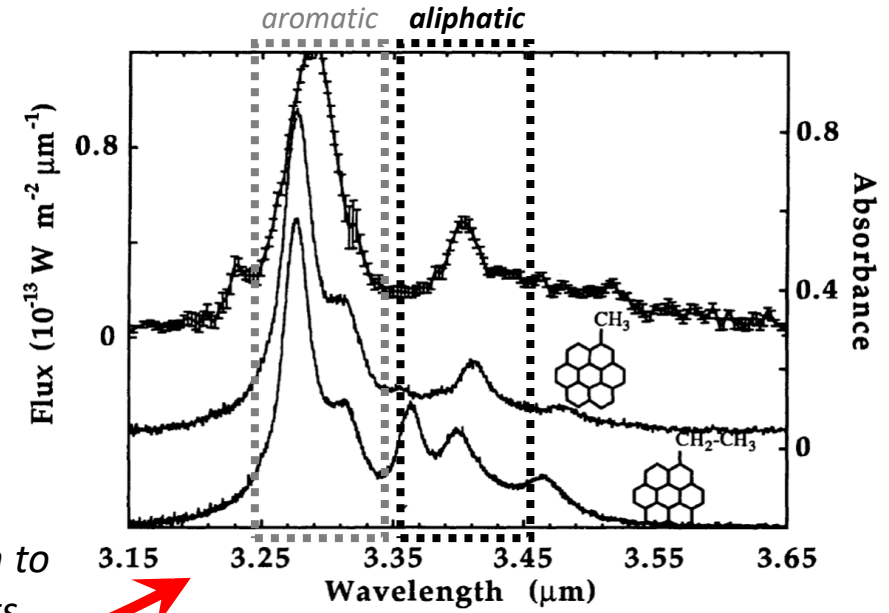


Signature of aliphatic PAHs in photodissociation regions



NGC 7023 ESA/Hubble – IR spectrum from Spitzer

Comparison to lab. results



C. Joblin et al. ApJ 458:610-620 (1996)

Good candidates for the 3.4 μm band:

- **Alkylated PAHs** : methy-, ethyl-PAH,… (e.g. methylCoronene)

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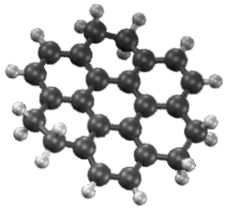
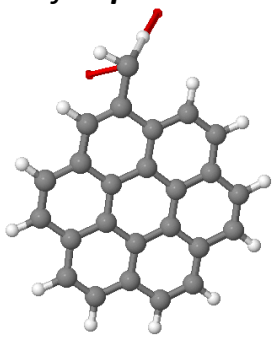
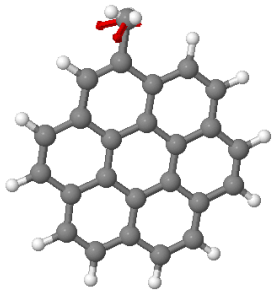


*Example of **aliphatic** C-H stretching modes in methyl-Cor*





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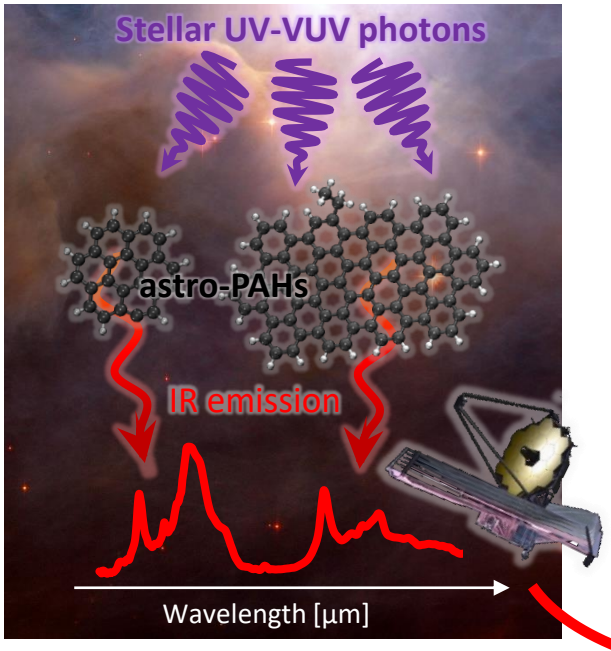

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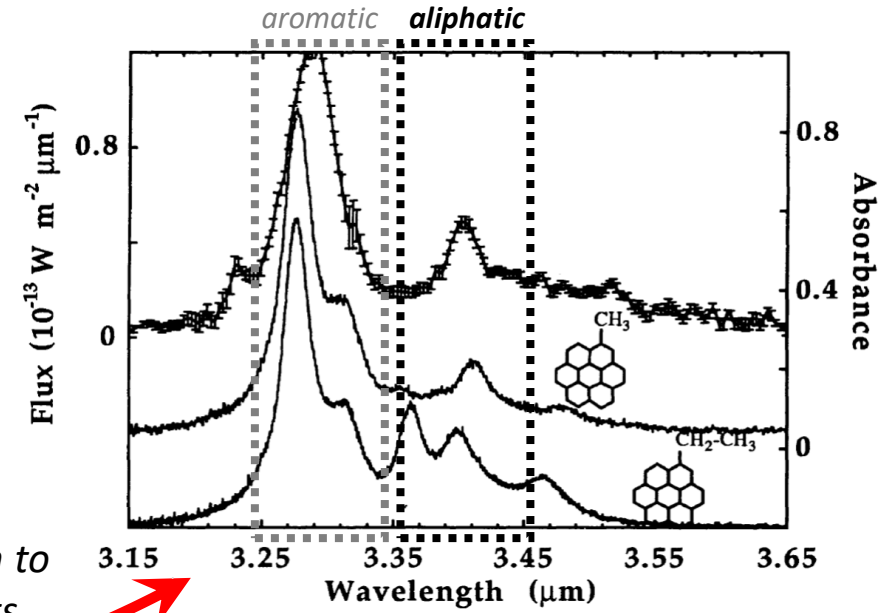

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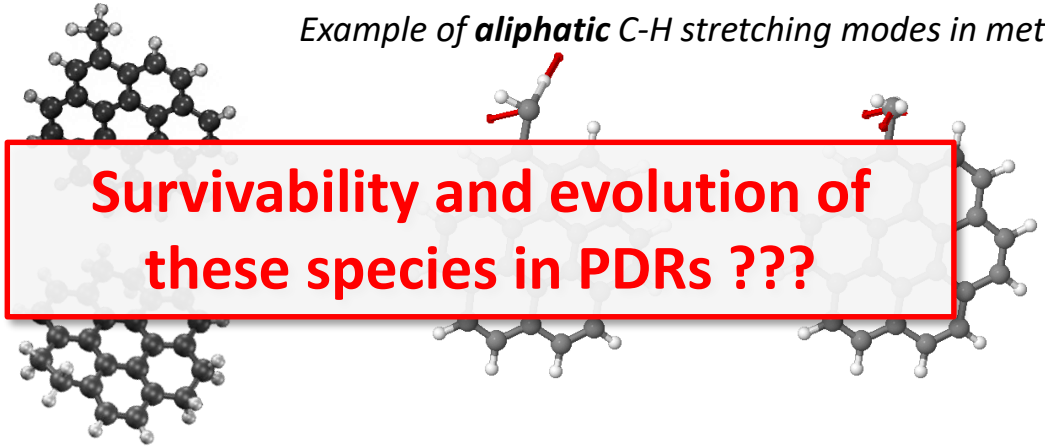
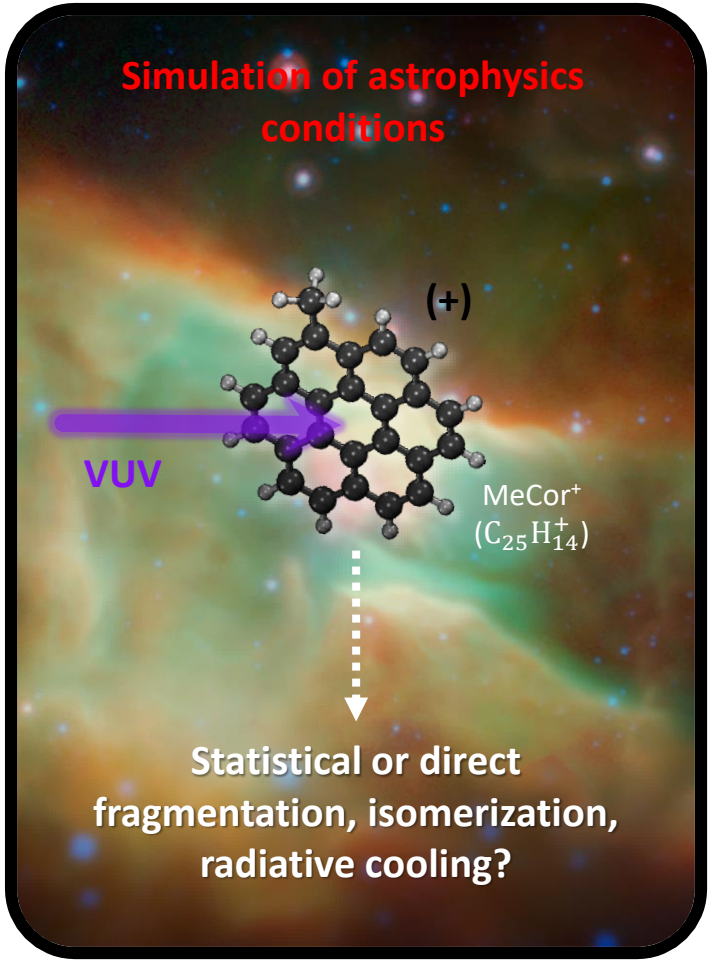


Survivability and evolution of these species in PDRs ???

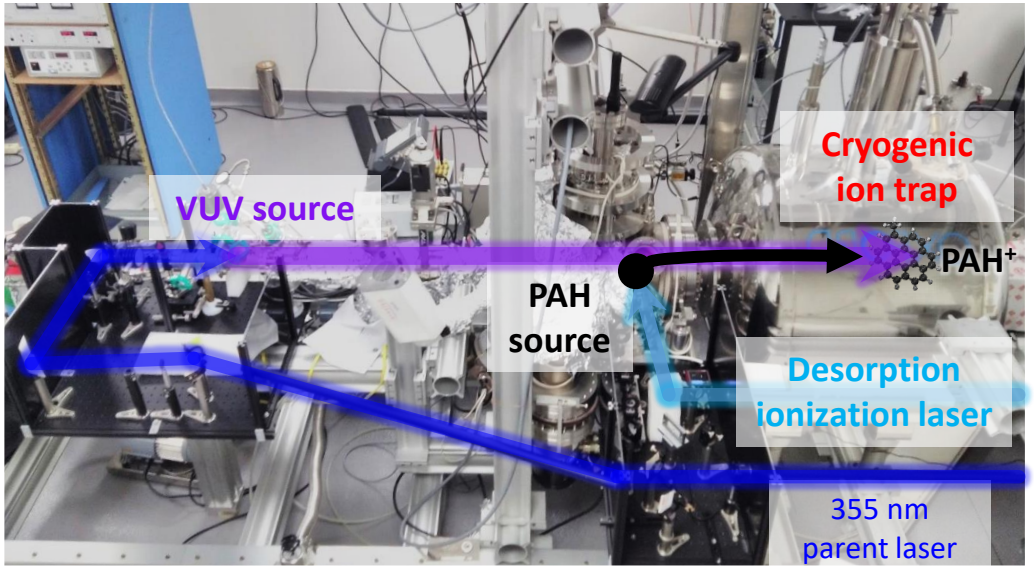
Principle of the study

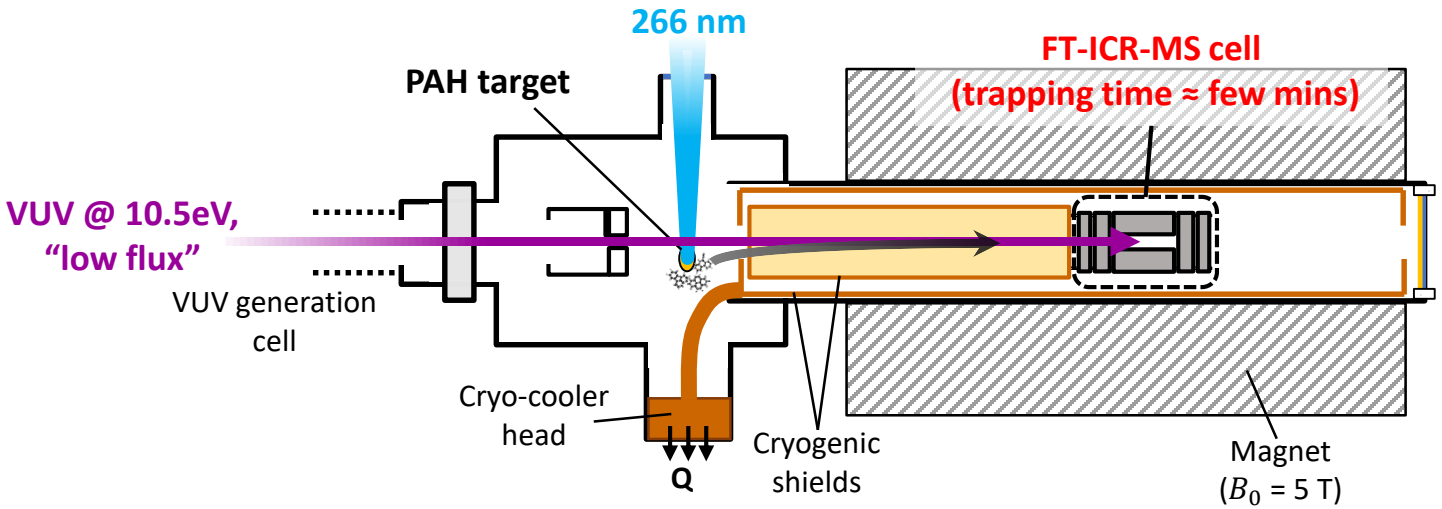


PIRENEA

(**P**iège à **I**ons pour la **R**echerche et l'**E**tude de **N**ouvelles **E**spèces **A**strochimiques)

Collisionless and cold environment: 10^{-11} mbar, 30 K





Studied PAH^+ and PAH^+ derivatives

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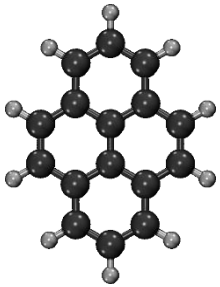	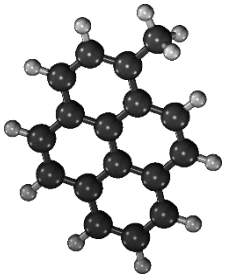	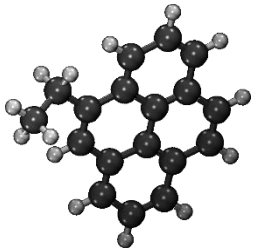	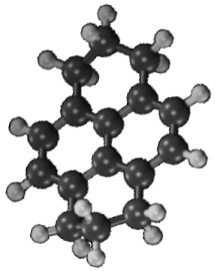	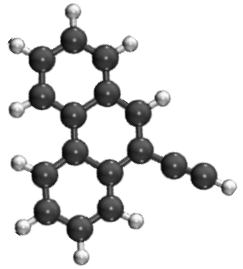	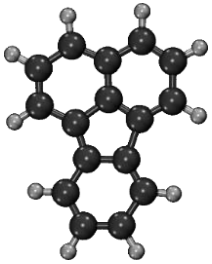
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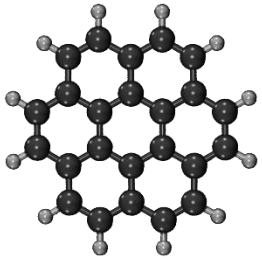
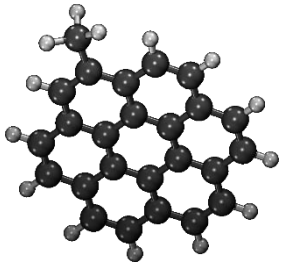
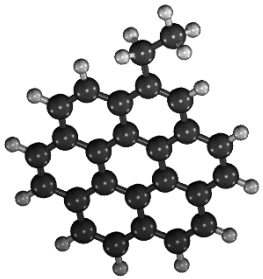
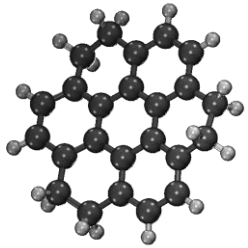
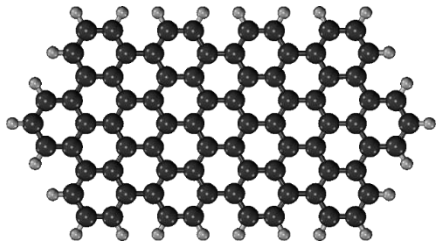
				**Large PAH^+** 	
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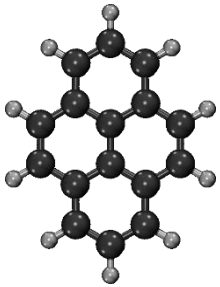	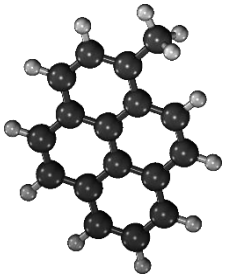	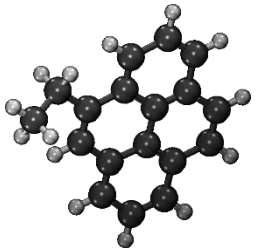			
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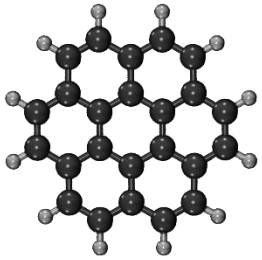	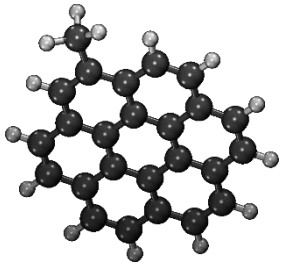	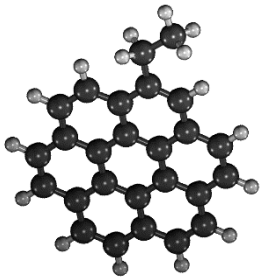	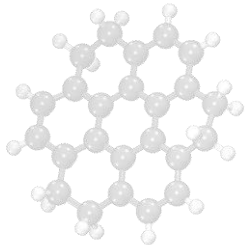	Large PAH^+	
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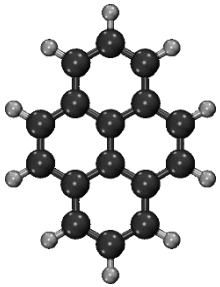	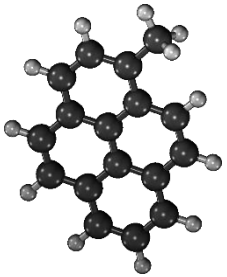	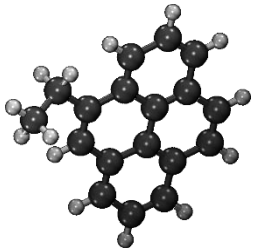			
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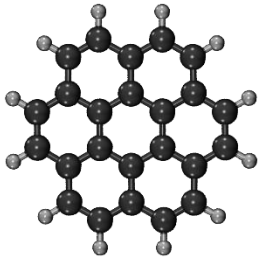	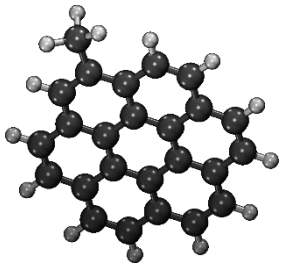	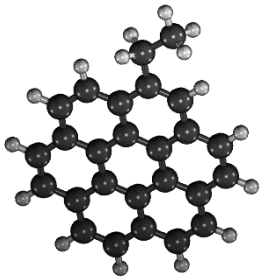	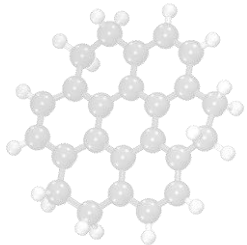	Large PAH$^+$	
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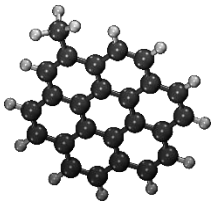

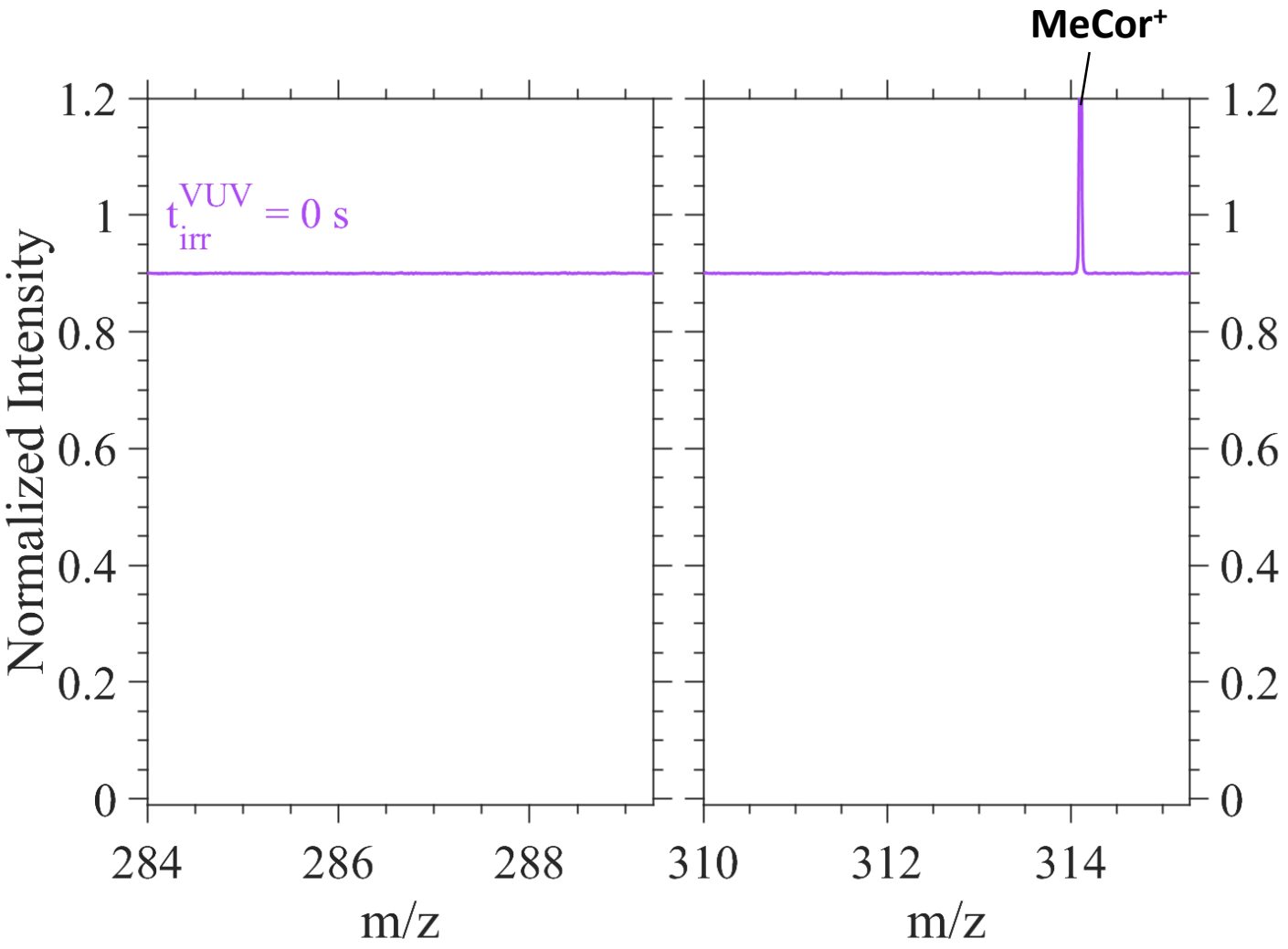

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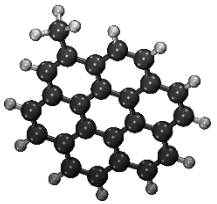

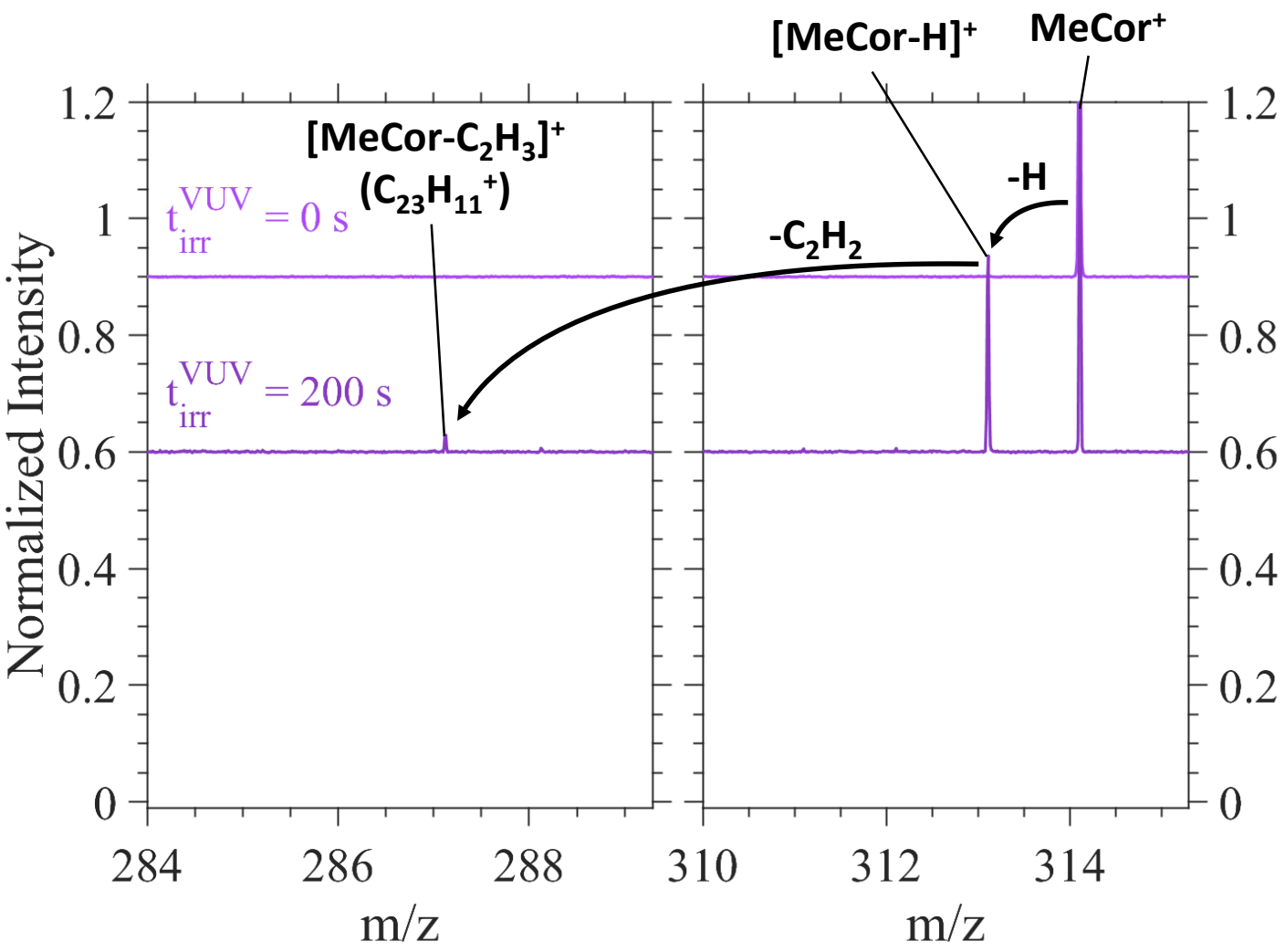

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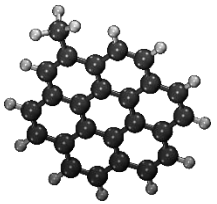
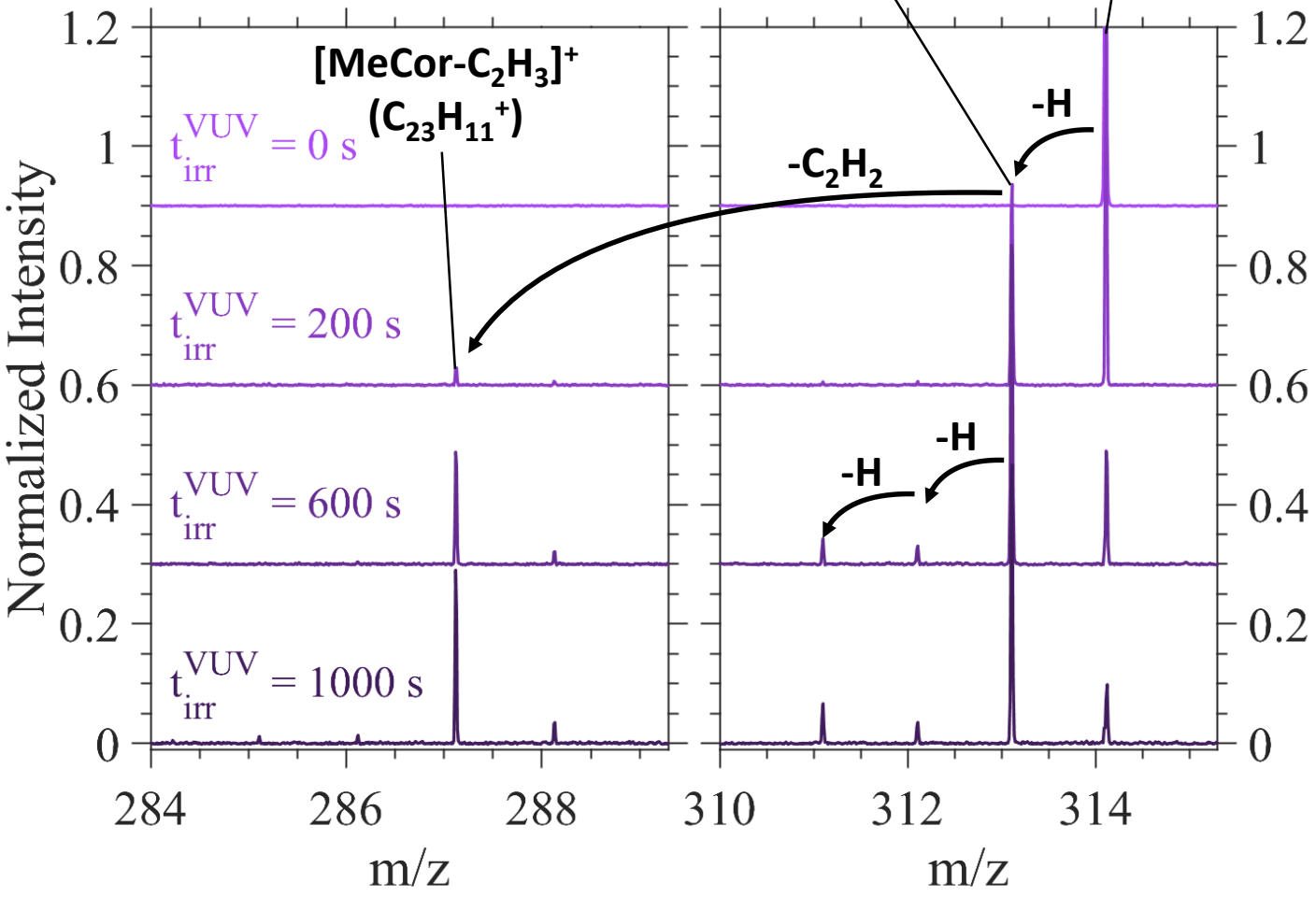
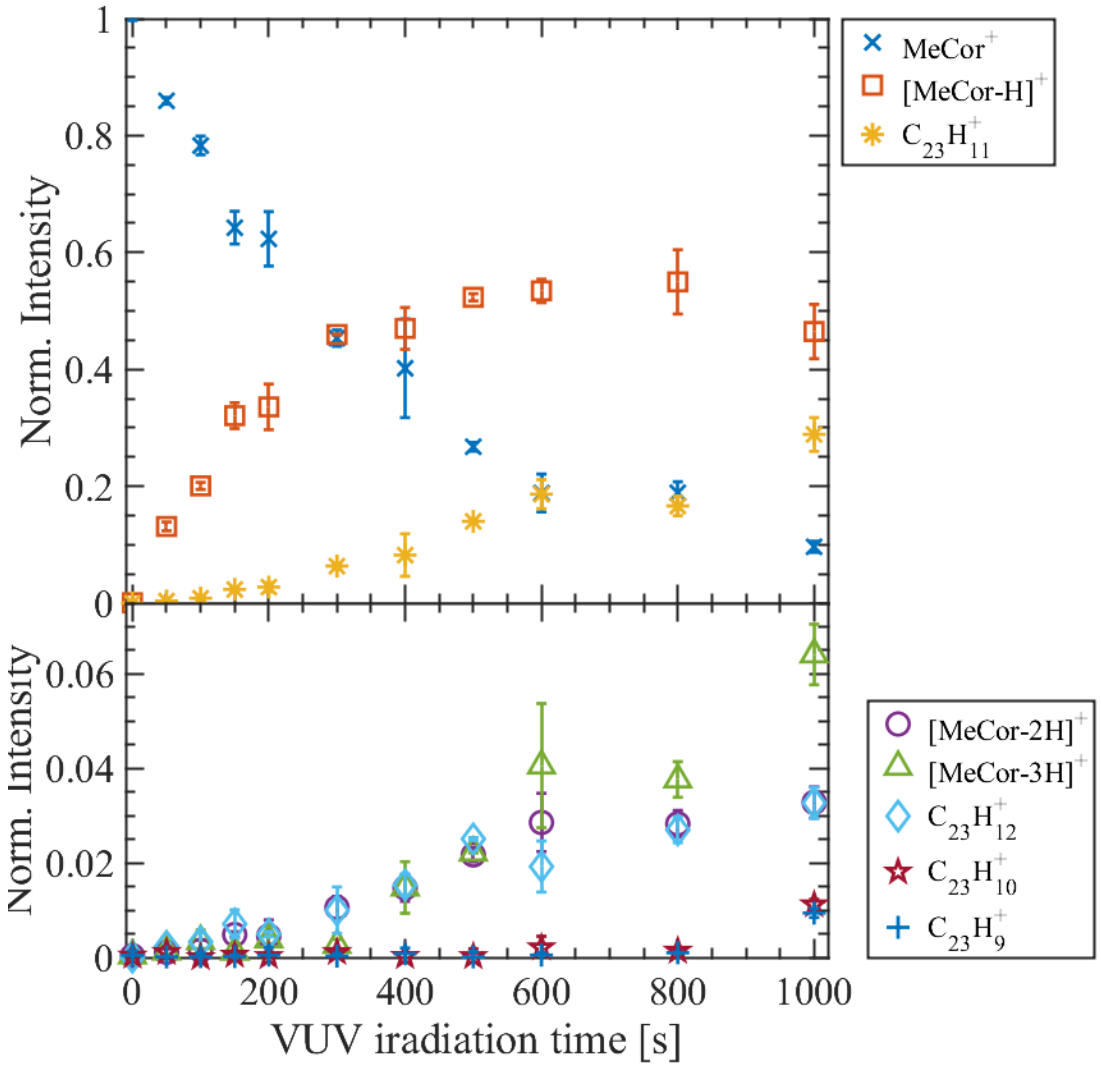


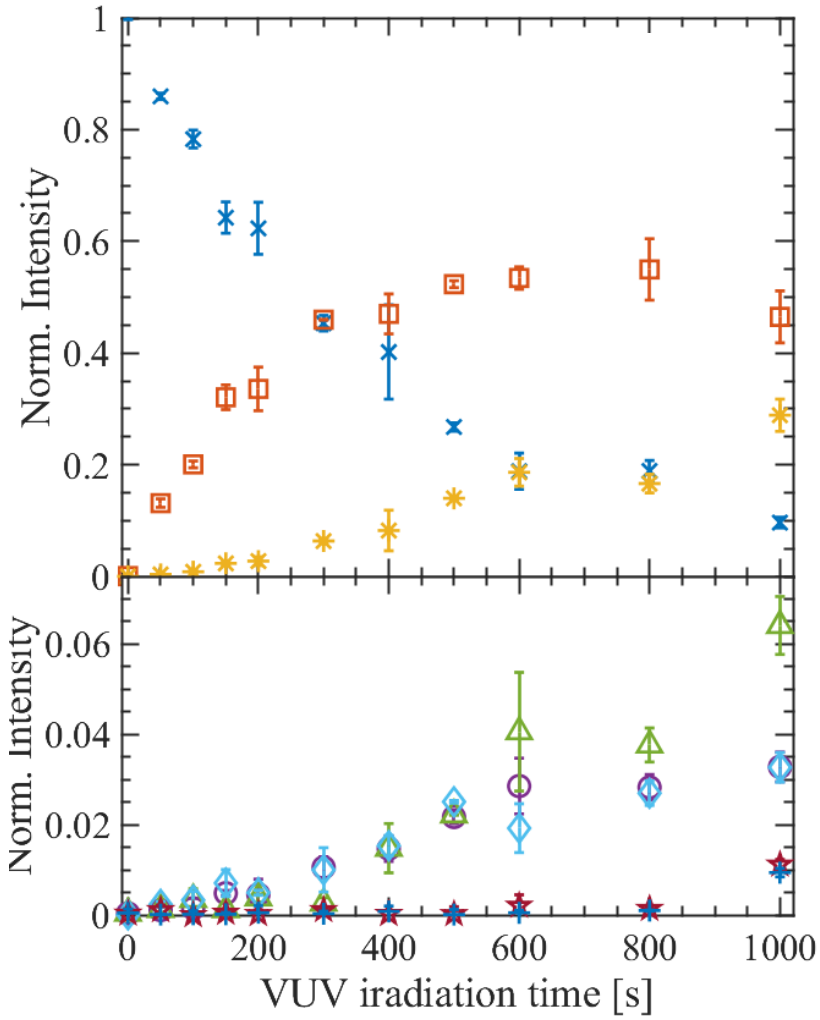


Kinetics results



Can we retrieve the dissociation pathway of the species ?

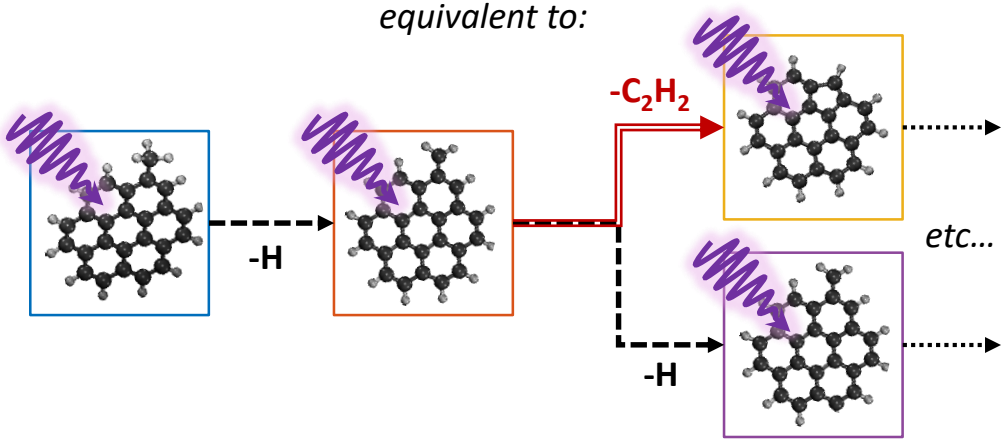
Fitting procedure



Master Equation with population and depopulation terms

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

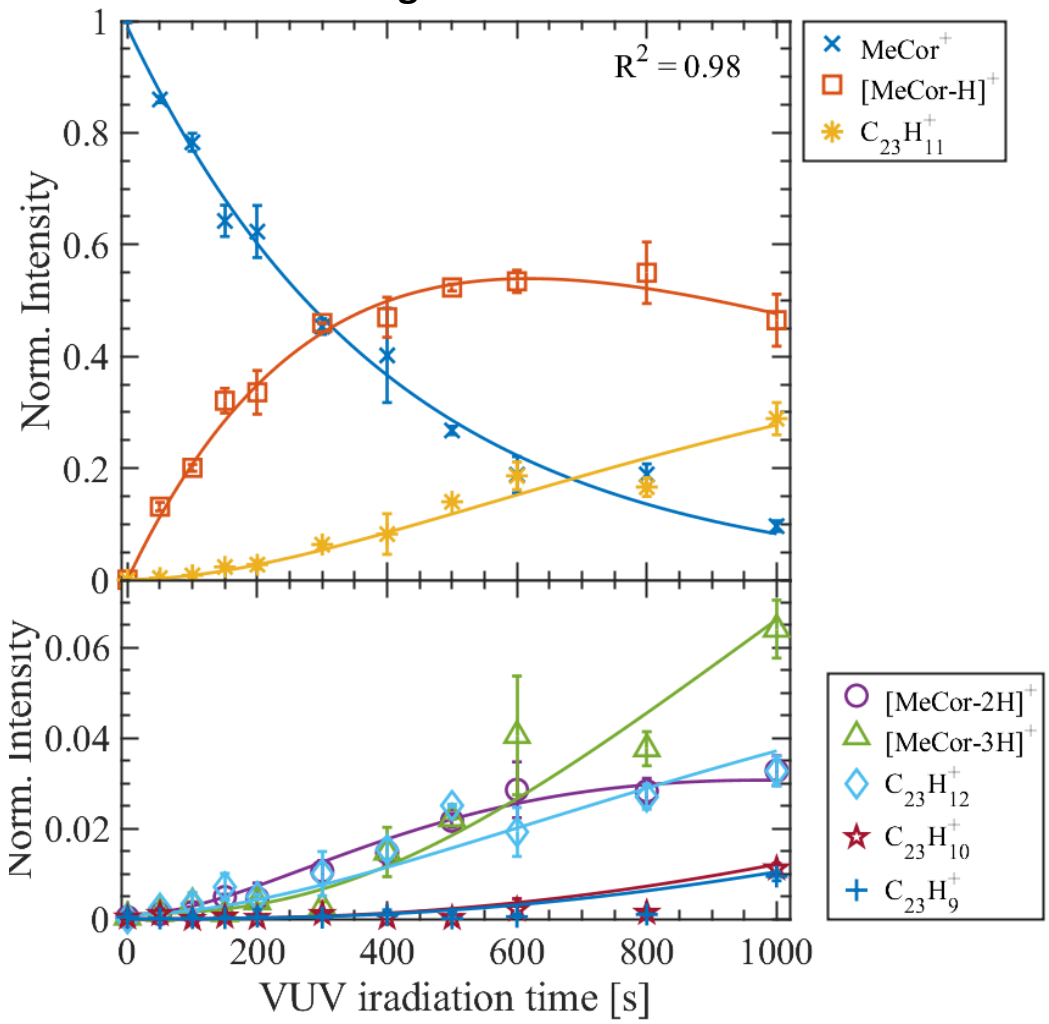
equivalent to:



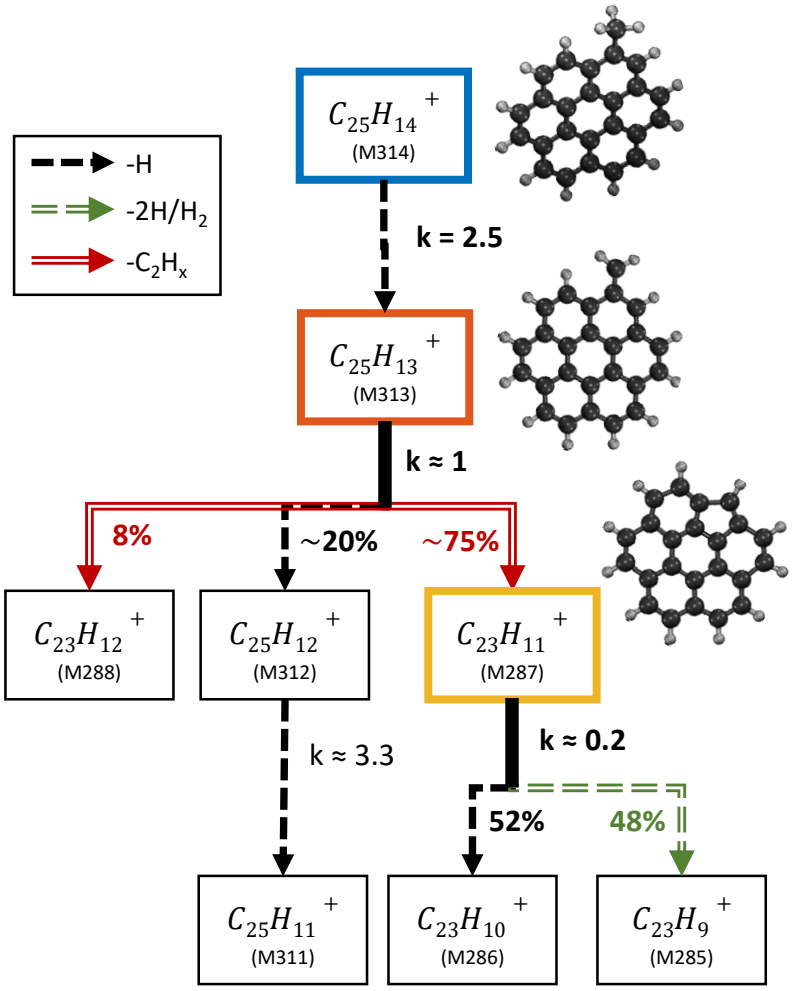
➔ **Only the $k_{frag}^{M_n\rightarrow M_i}$ are adjusted to fit the data**

Fitting procedure

Fitting results

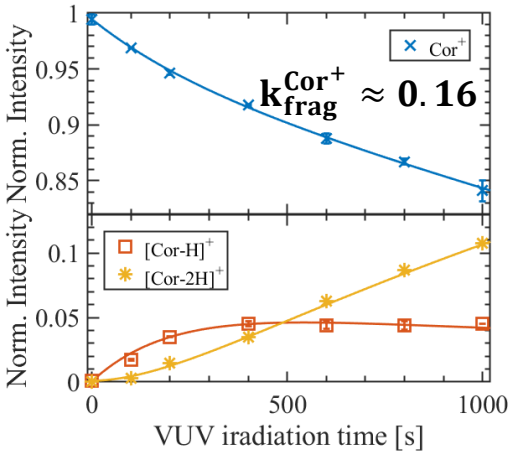


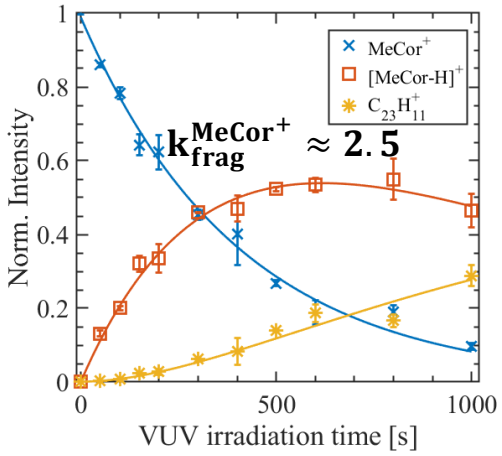
Fragmentation Map & Fragmentation Rates

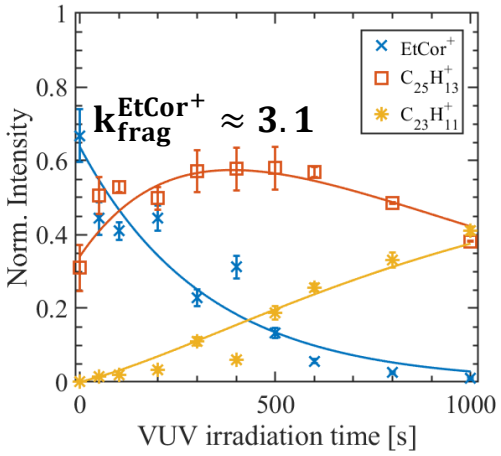


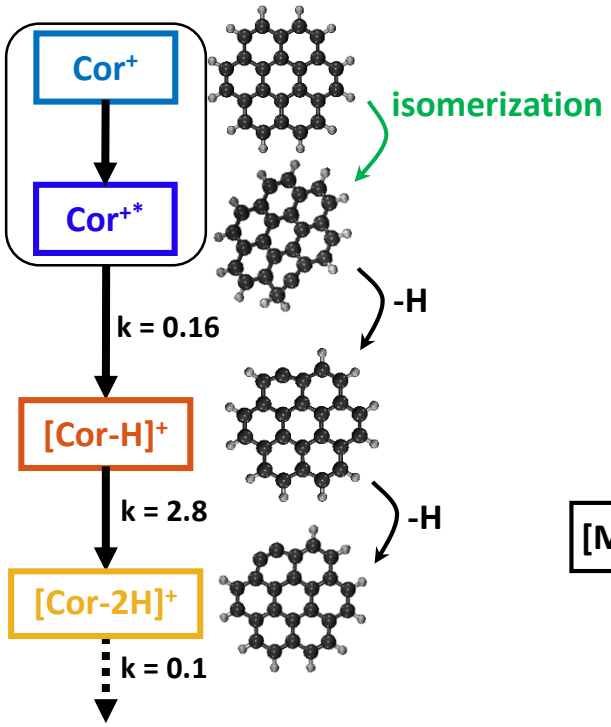
k are in $\times 10^{-3}$ s^{-1} (scalable with the VUV flux)

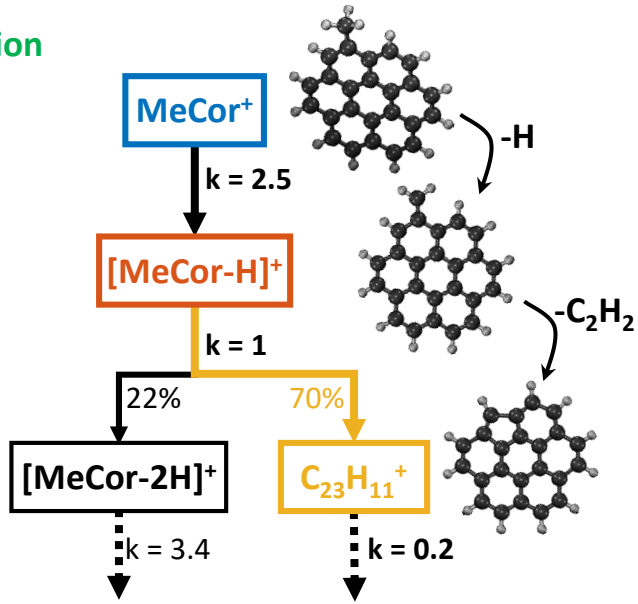
Simplified fragmentation paths : bare Cor⁺ vs. alkylated Cor⁺

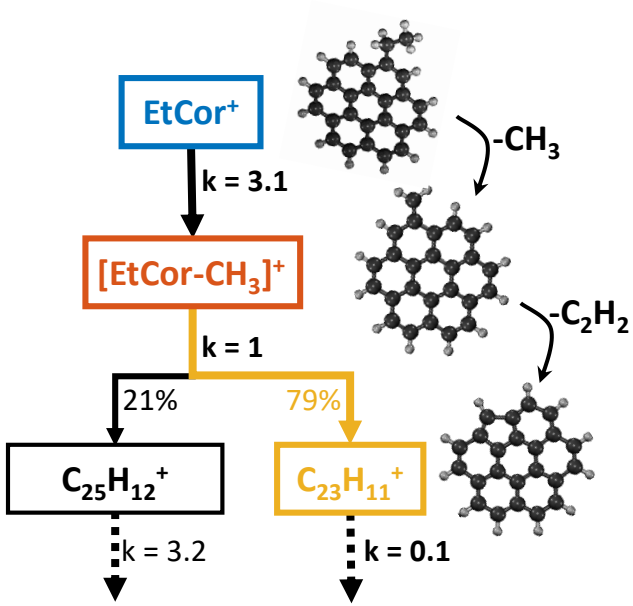






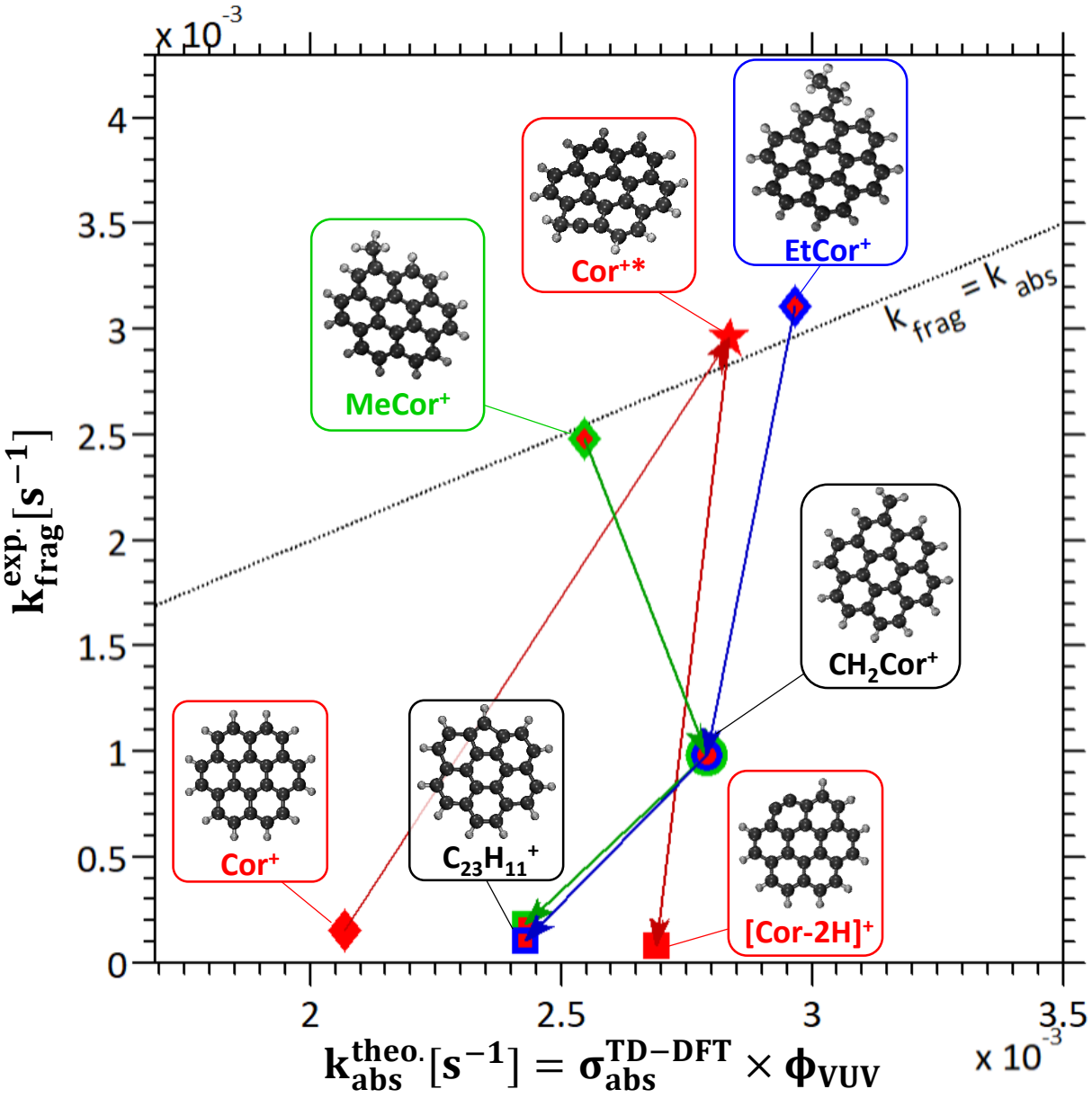






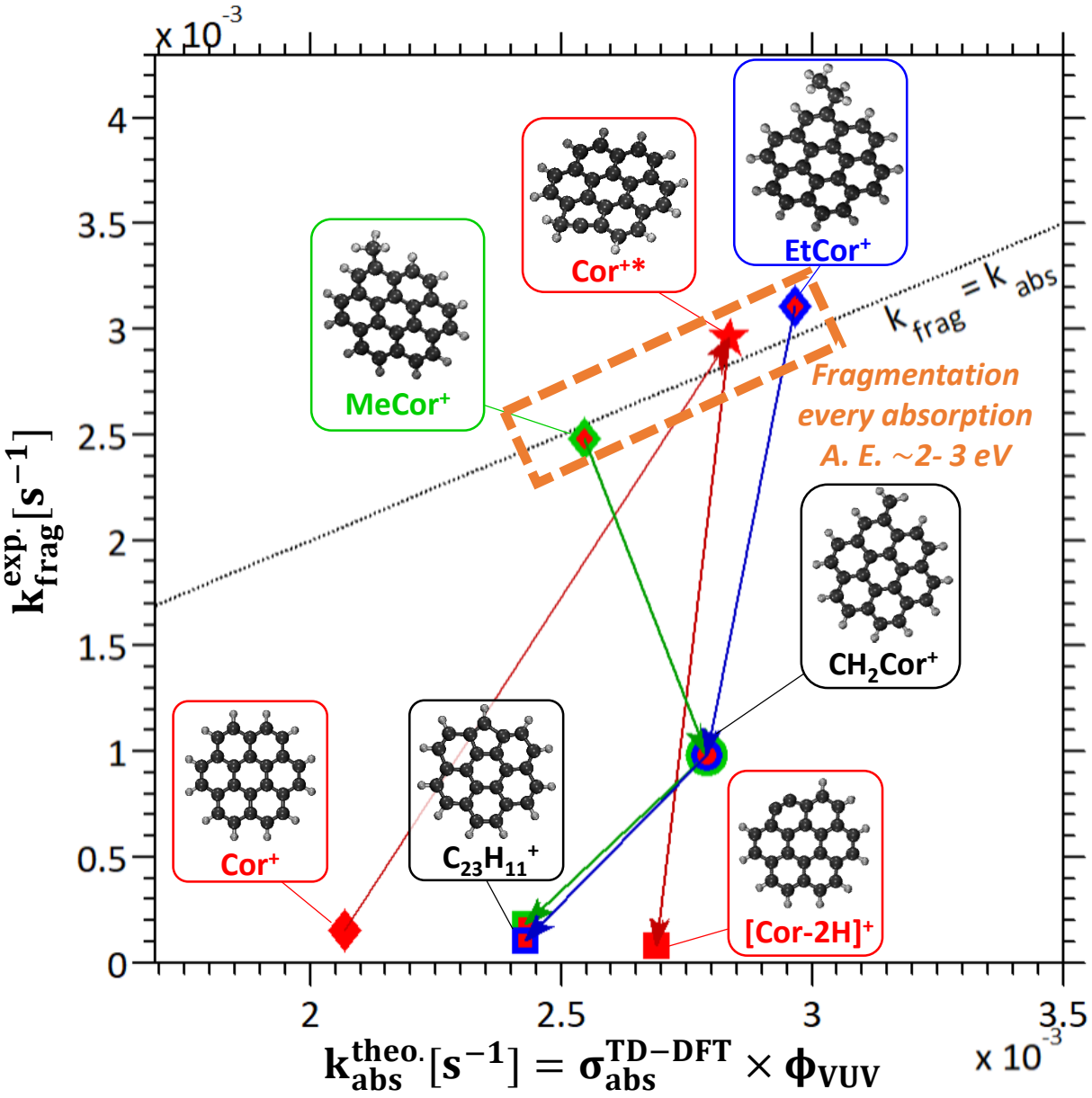
k are in ×10⁻³ s⁻¹ (scalable with the VUV flux)

PAH photostability all along the VUV irradiation



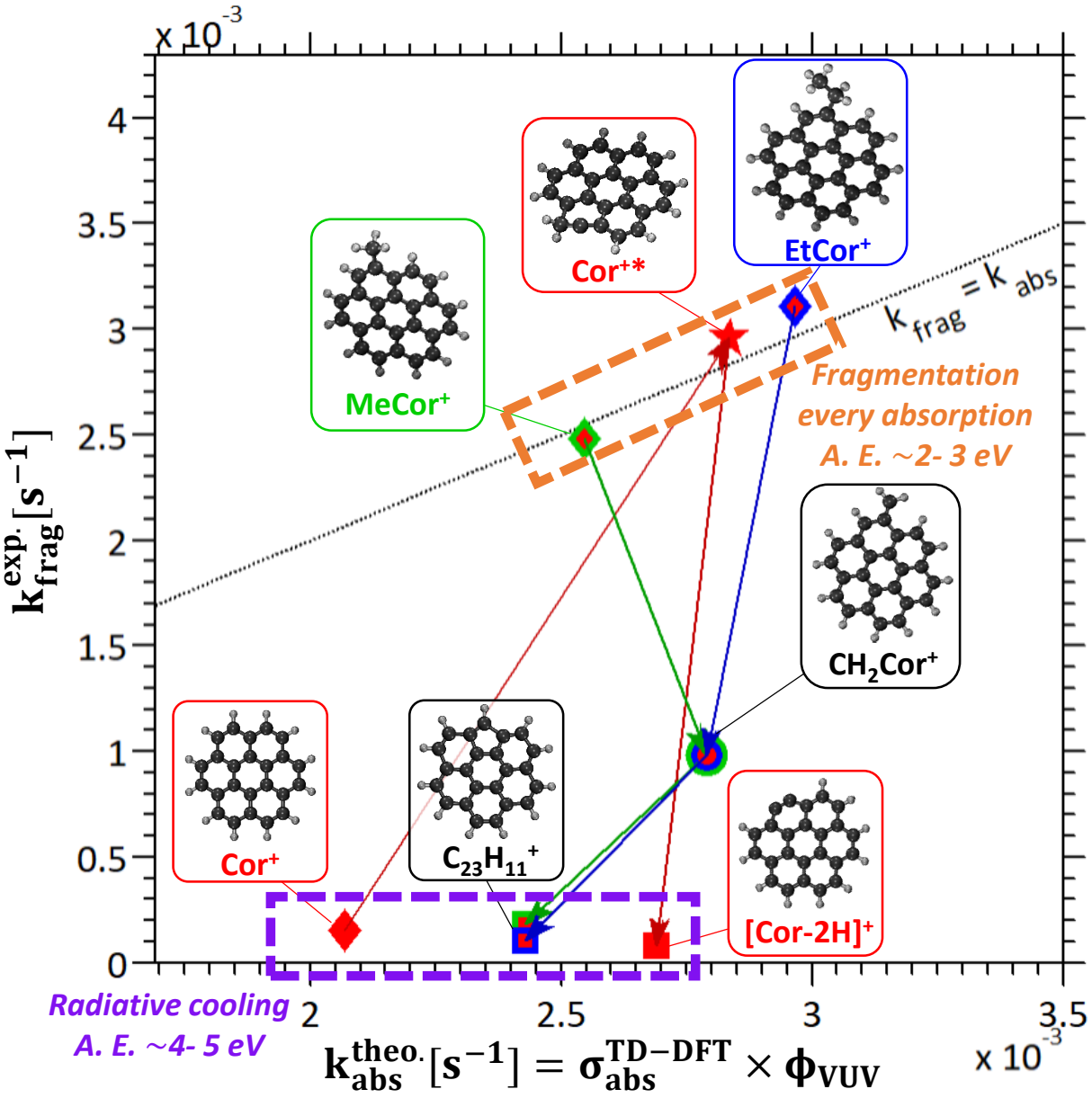
(coll. G. Mulas)

PAH photostability all along the VUV irradiation



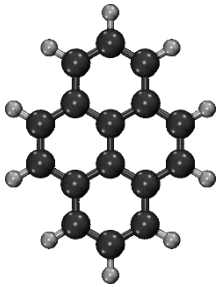
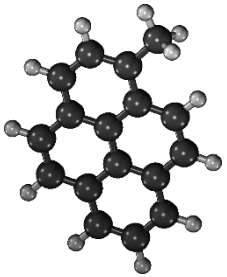
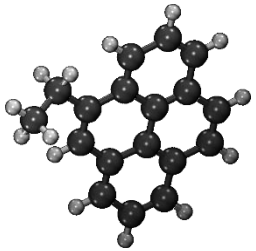
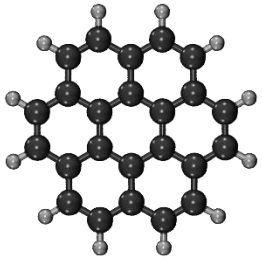
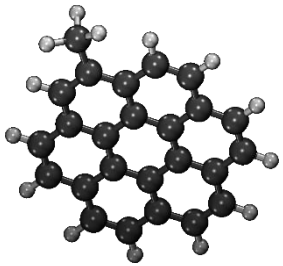
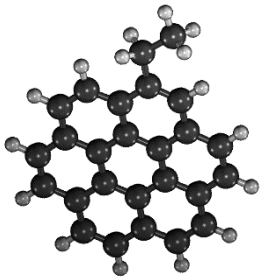
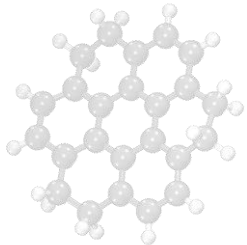
(coll. G. Mulas)

PAH photostability all along the VUV irradiation



(coll. G. Mulas)

Alkylated Pyrene$^+$

Bare PAH$^+$	Alkylated PAH$^+$		H_n-PAH$^+$	Pyrene ($C_{16}H_{10}^+$) Isomers	
					
pyrene	*1-methylpyrene*	*4-ethylpyrene*	*hexahydropyrene*	*9-ethynylphenanthrene*	*fluoranthene*
				Large PAH$^+$	
coronene	*methylcoronene*	*ethylcoronene*	*hexahydrocoronene*	$C_{78}H_{26}^+$	

Alkylated PAH → *A. Marciniak, et al. A&A 642, A42 (2021)*

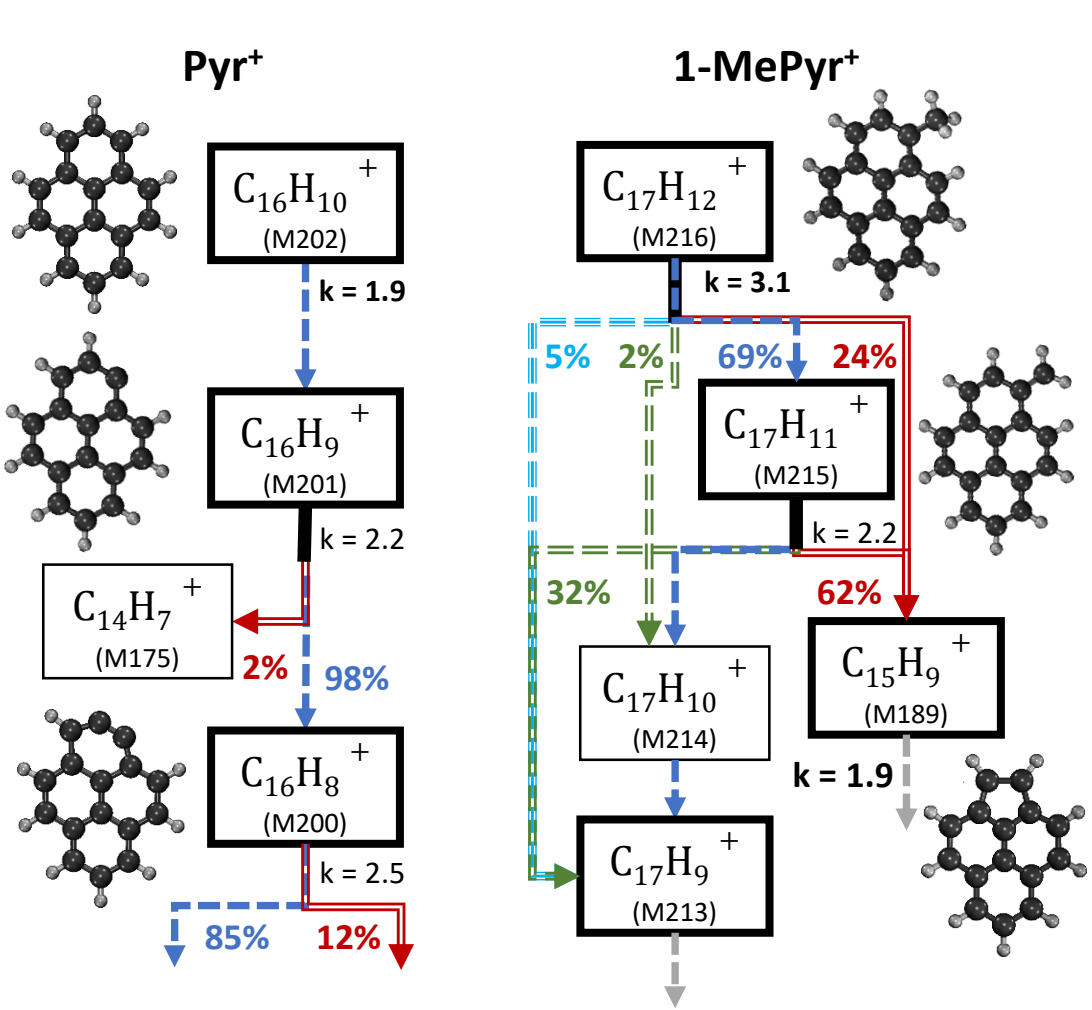
Pyrene isomers → *V. Meloottayil, et al., J. Chem. Phys. A, 126, p.5632 (2022)*

Super-hydrogenated coronene → *A. Marciniak, et al. in prep.*

Simplified fragmentation maps : bare Pyr^+ vs. alkylated Pyr^+

Mainly H loss

Simplified fragmentation maps : bare Pyr^+ vs. alkylated Pyr^+

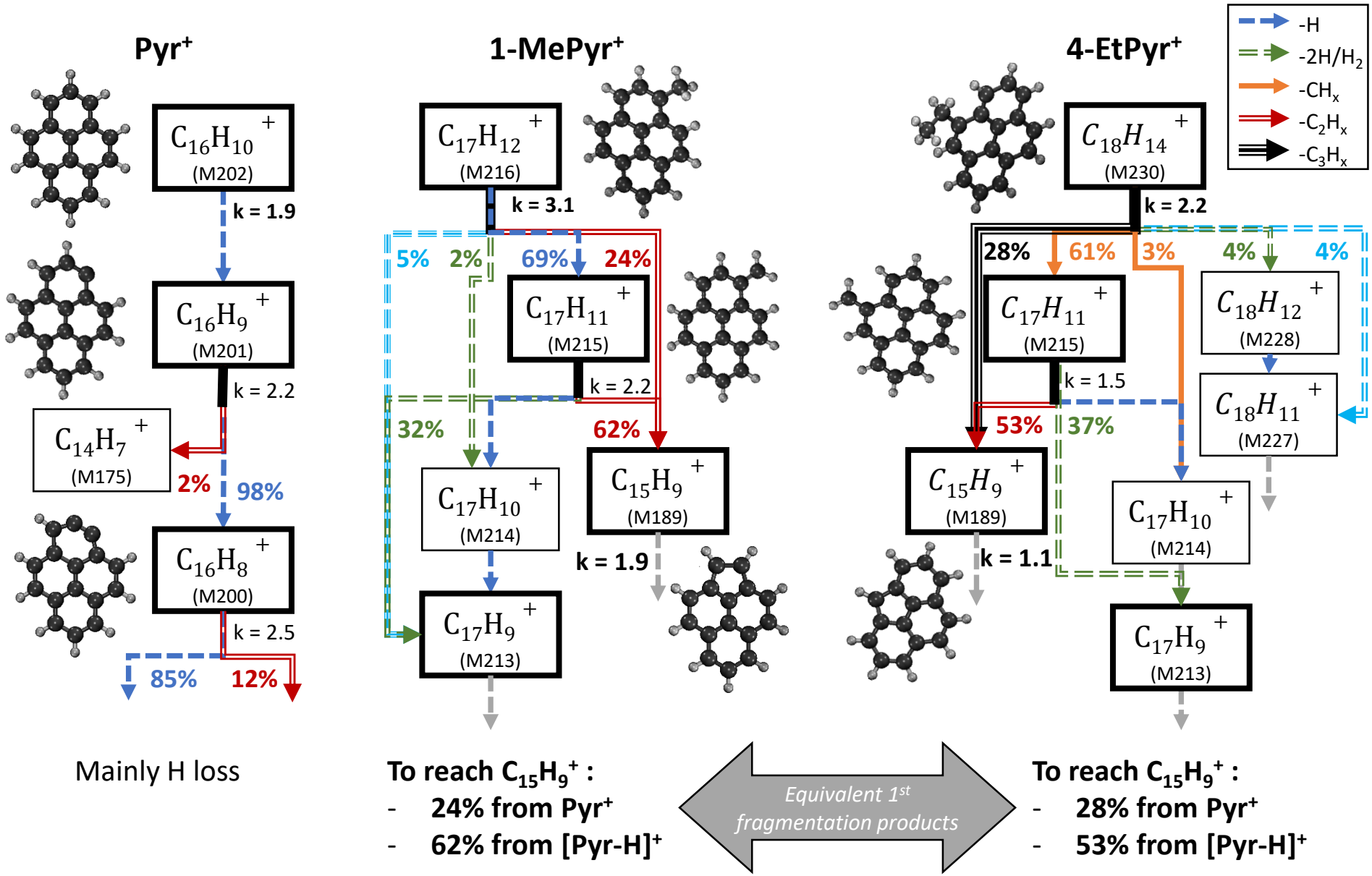


Mainly H loss

To reach $C_{15}H_9^+$:

- **24% from Pyr^+**
- **62% from $[Pyr-H]^+$**

Simplified fragmentation maps : bare Pyr⁺ vs. alkylated Pyr⁺



Mainly H loss

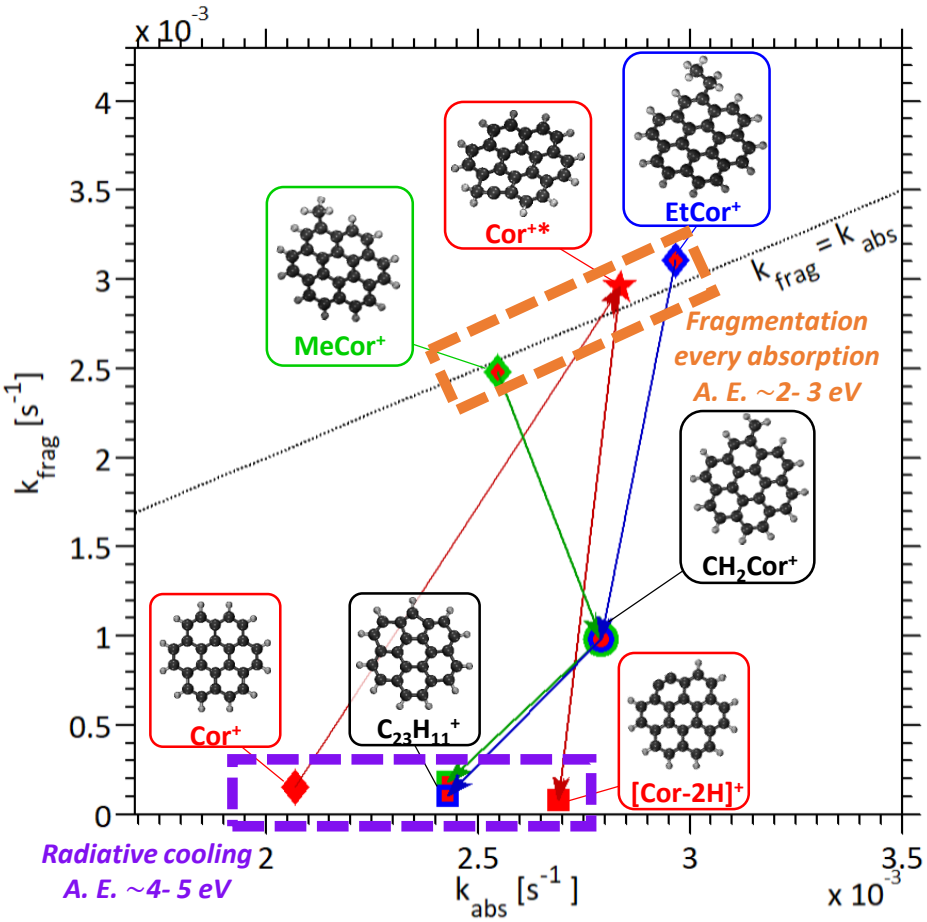
To reach $C_{15}H_9^+$:
- **24% from Pyr⁺**
- **62% from [Pyr-H]⁺**

Equivalent 1st fragmentation products

To reach $C_{15}H_9^+$:
- **28% from Pyr⁺**
- **53% from [Pyr-H]⁺**

VUV photostability of alkylated PAHs - Take home messages

- ✓ Carriers of the 3.4 µm band (alkylated or H-shifted PAHs) **photofragments efficiently**
- ✓ **Common species** are produced during the VUV photo-processing of alkylated PAHs
- ✓ **Pentagonal ring** formation stabilizes the structure as much (and even more) than the bare cationic PAH



A. Marciniak, et al. A&A 642, A42 (2021)

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Laboratoire Collisions Agrégats Réactivité

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OAC

G. Mulas

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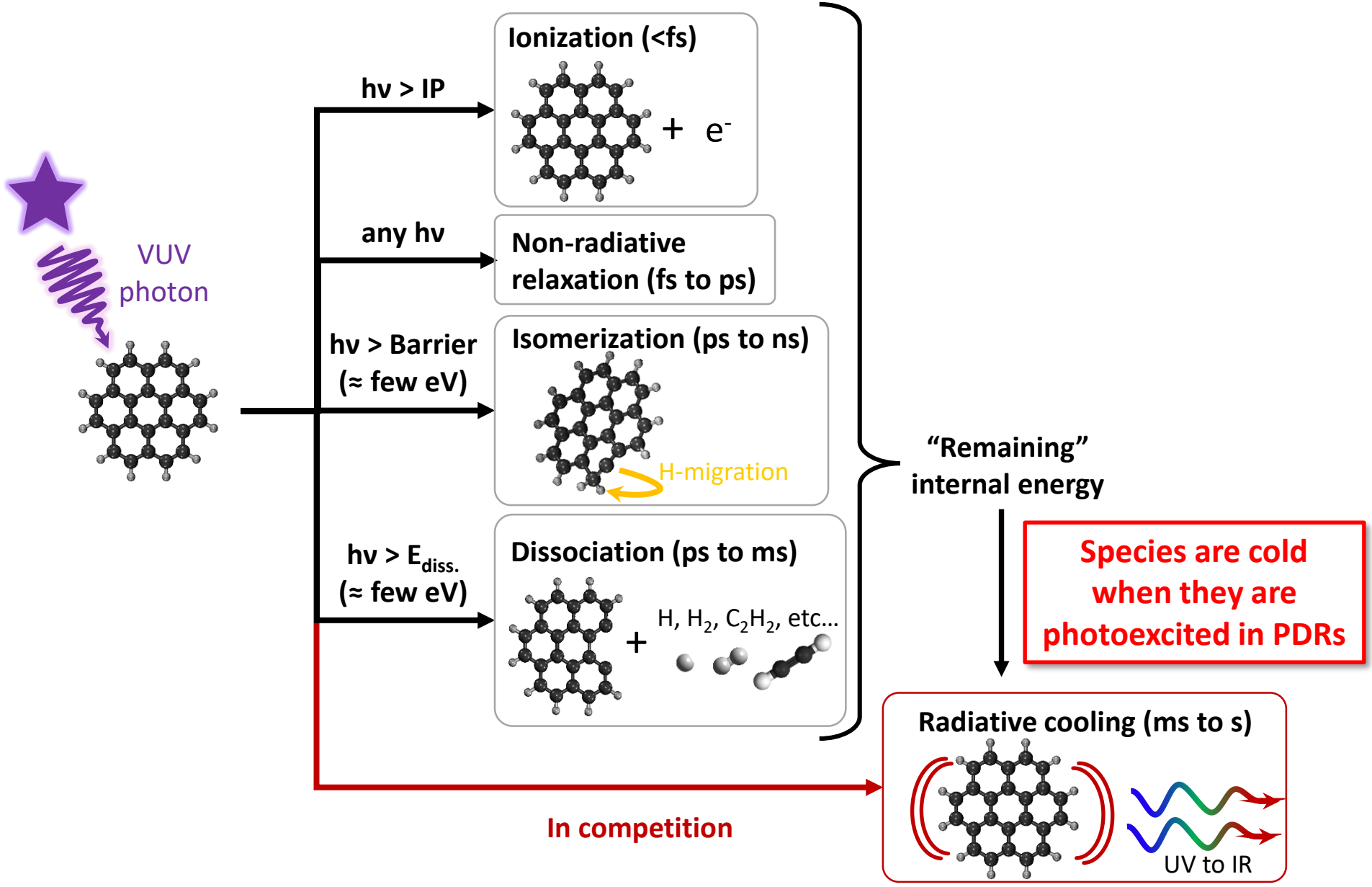
Université de Toulouse

Thanks for your attention !

Annexes

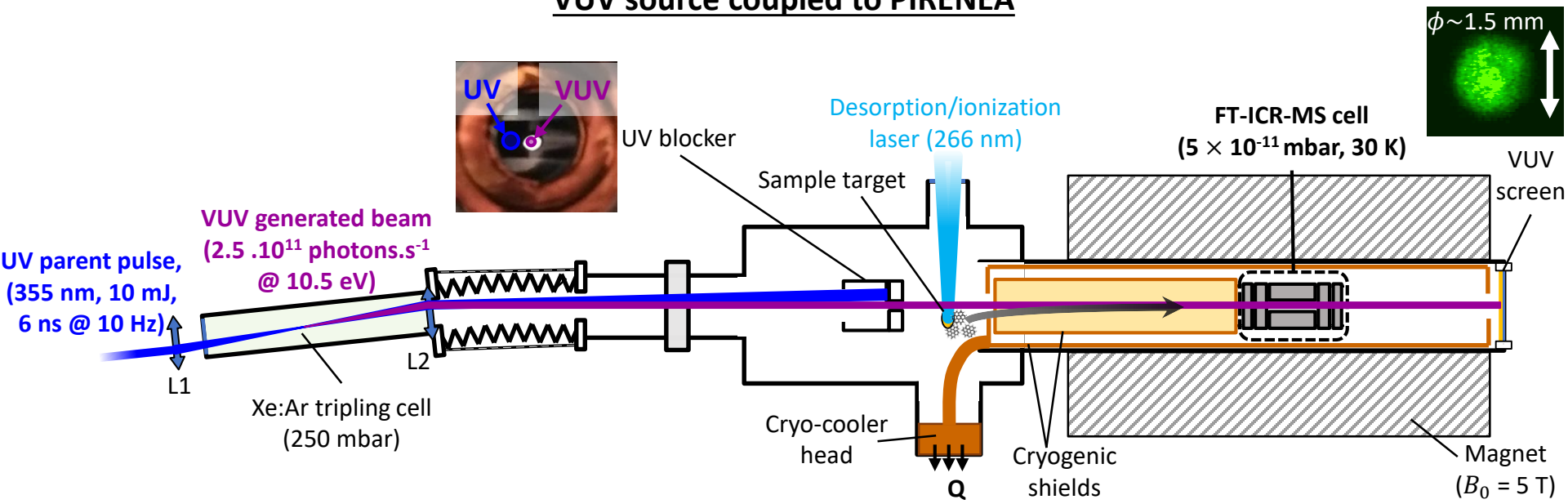
Relaxation of a photoexcited PAH in PDRs



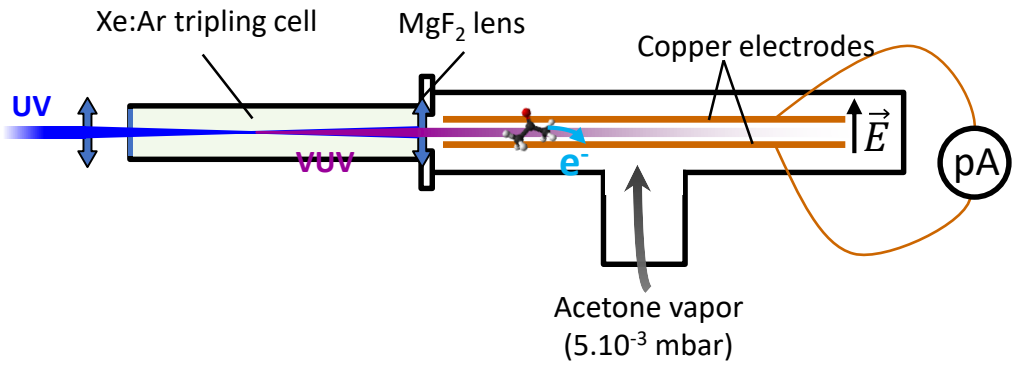
PIRENEA (details + calibration)

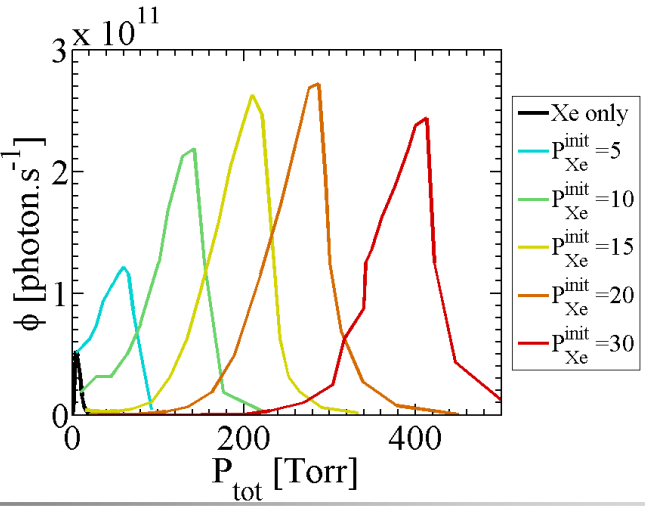
(**P**iège à **I**ons pour la **R**echerche et l'**E**tude de **N**ouvelles **E**spèces **A**strochimiques)

VUV source coupled to PIRENEA

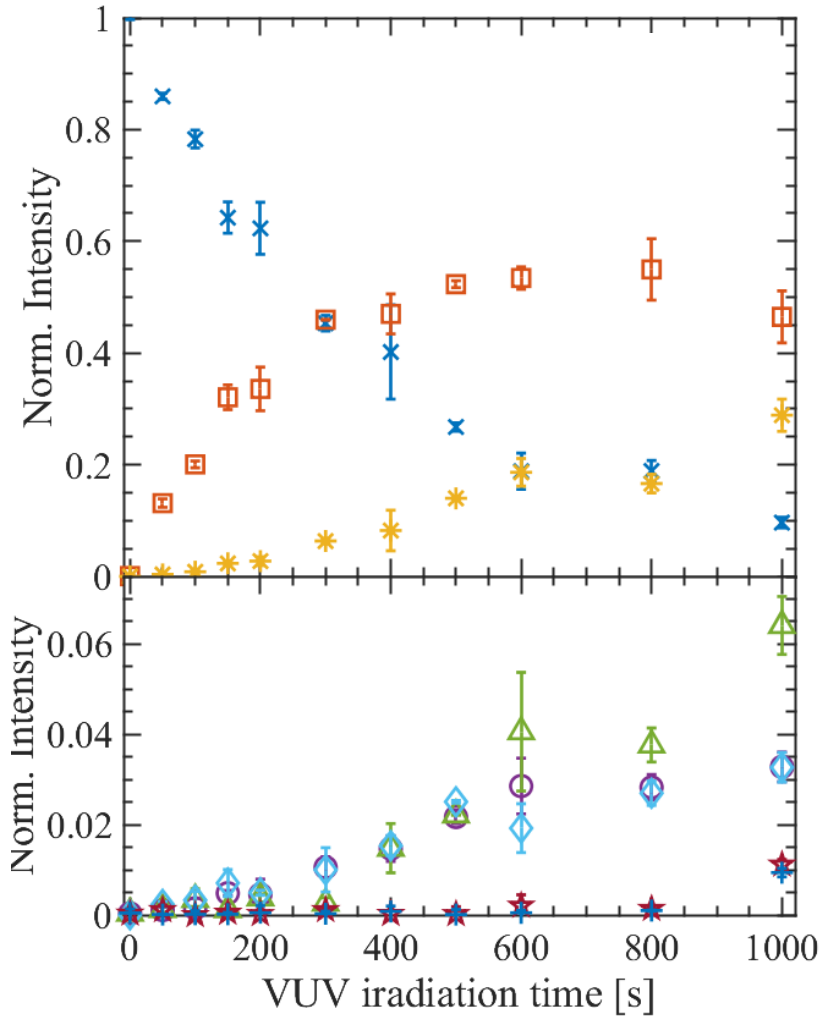


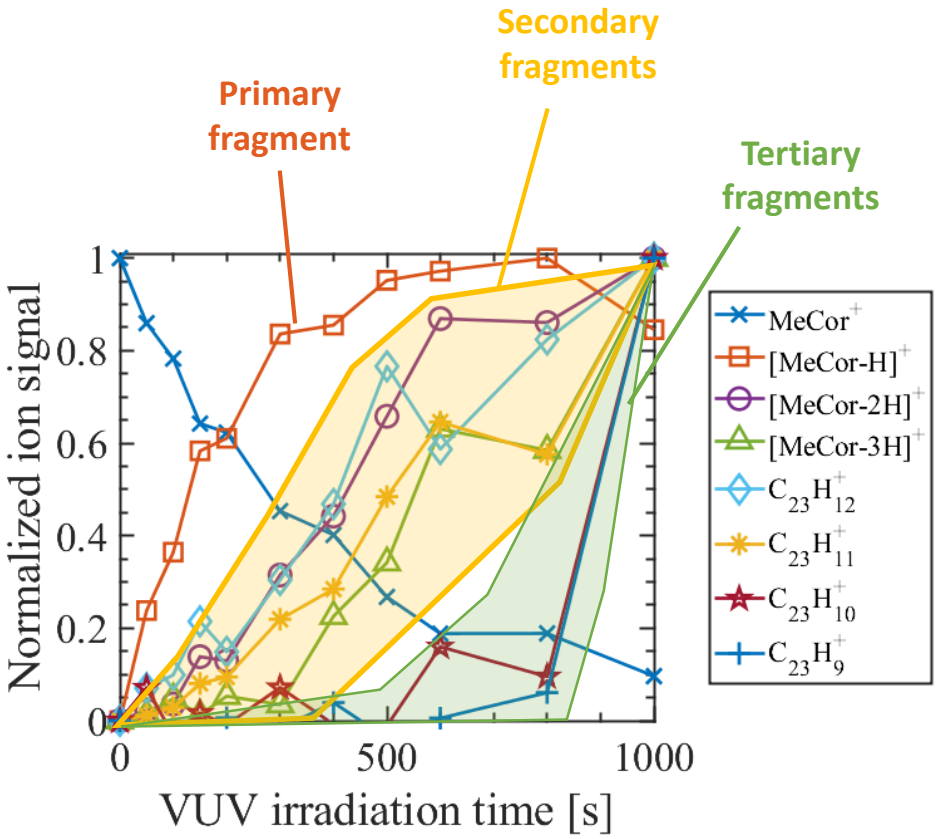
Calibration Procedure





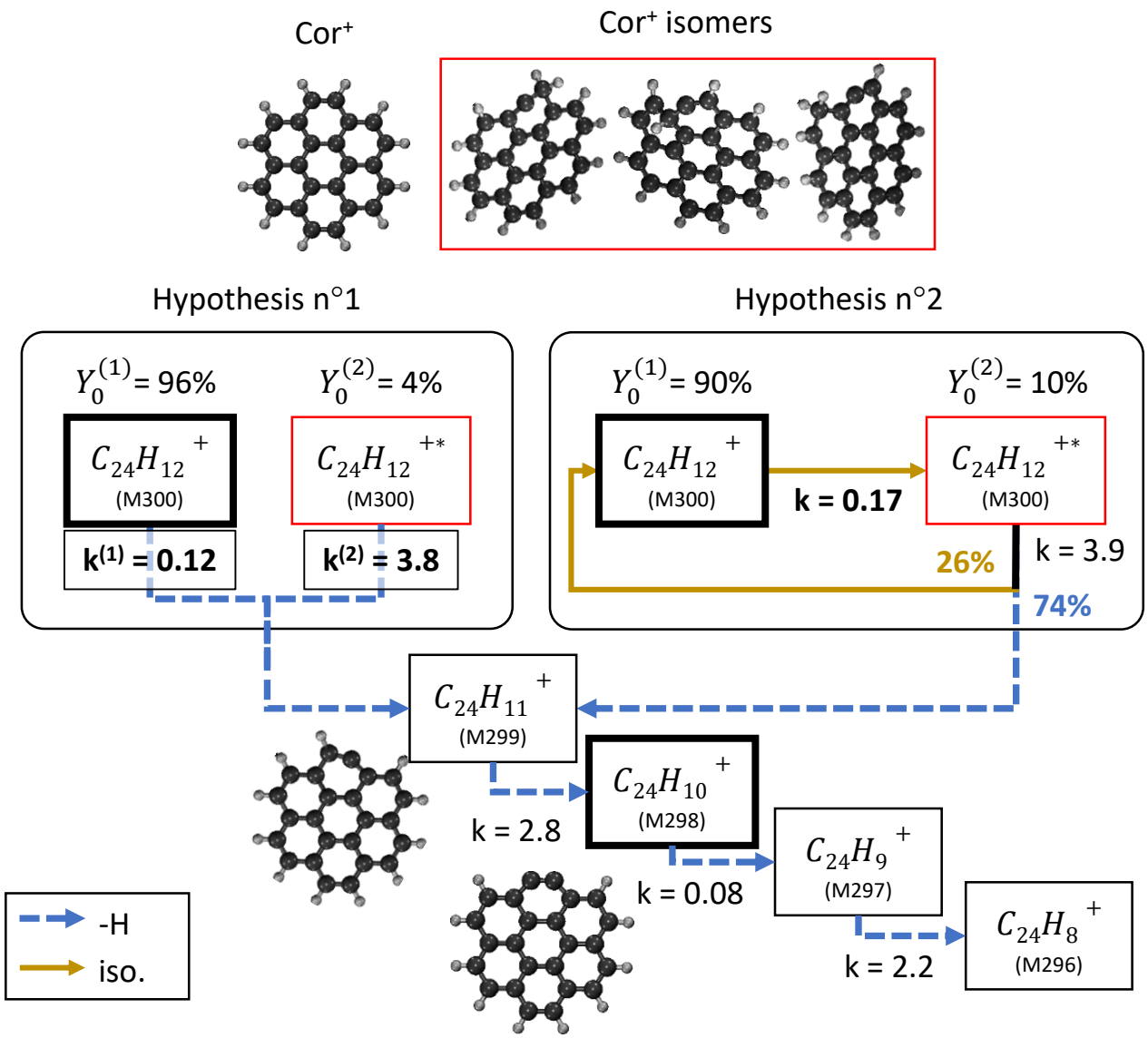
Fitting procedure



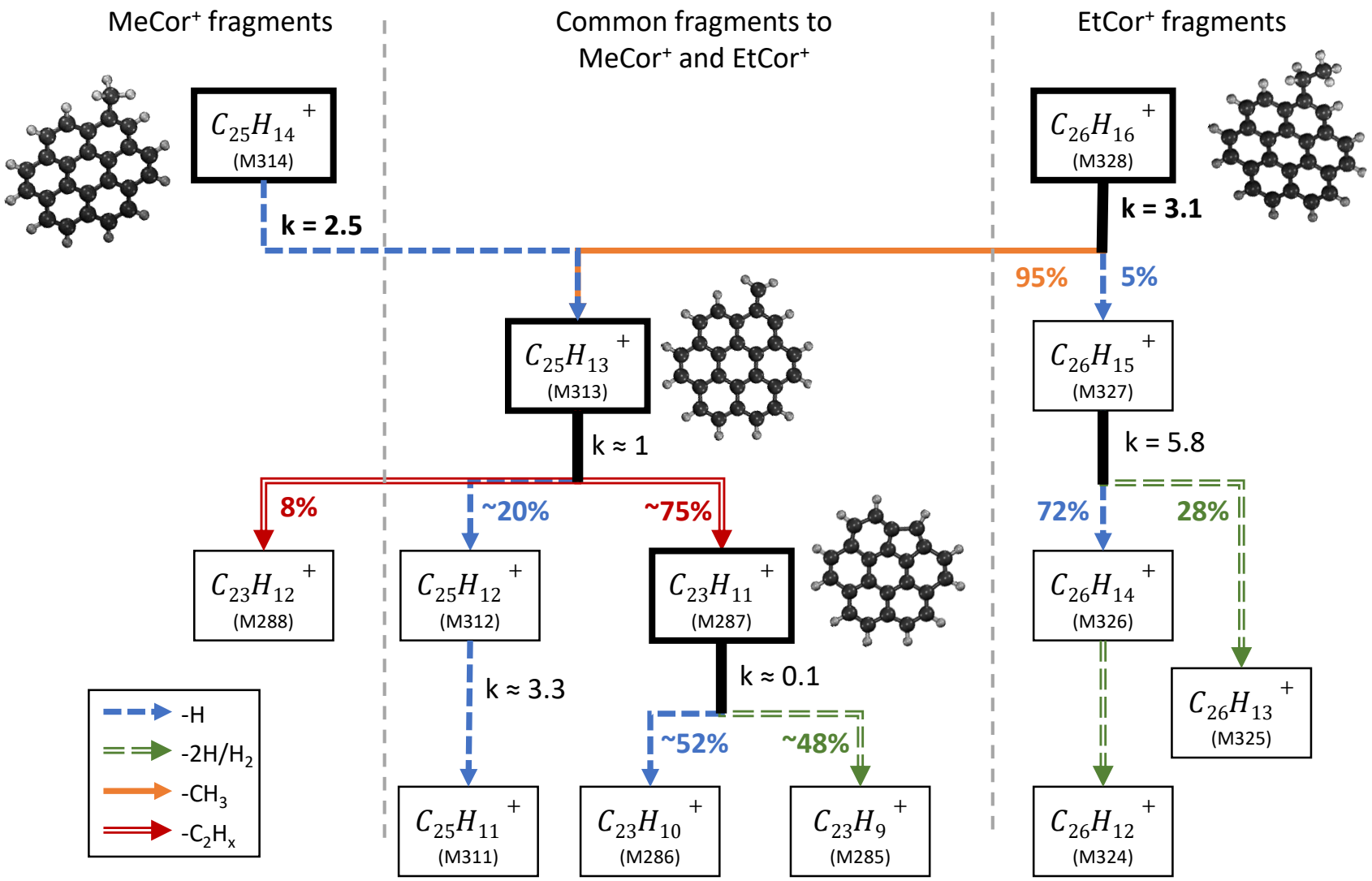


➔ **Parent-daughter relation between fragments**

Full fragmentation map of Coronene



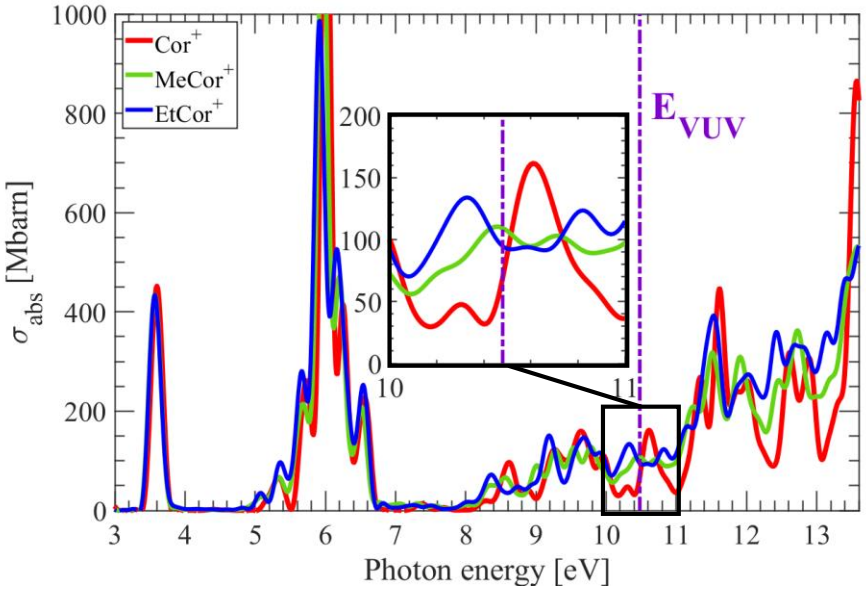
Full fragmentation map of methyl- and ethyl- coronene



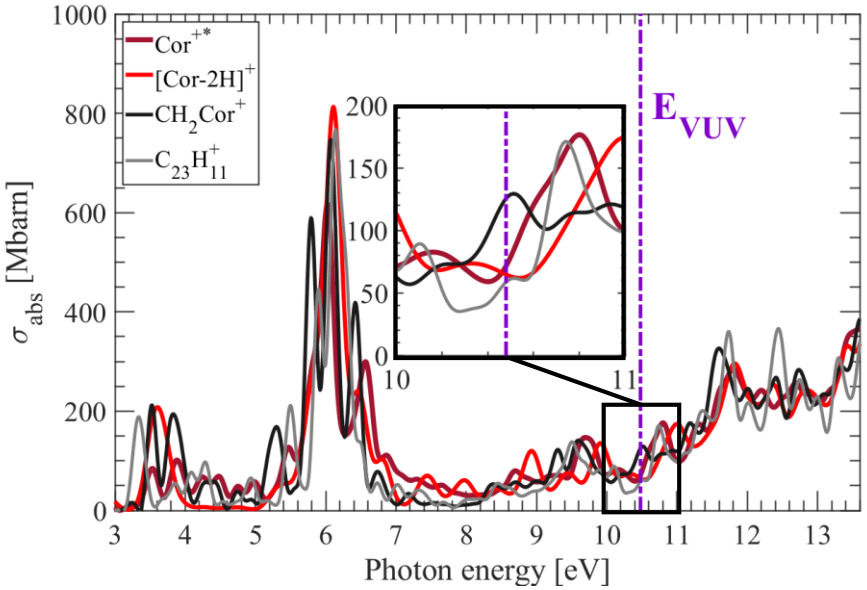
Theoretical absorption rates

TD-DFT calculations of the photoabsorption cross sections (G. Mulas)

Parents

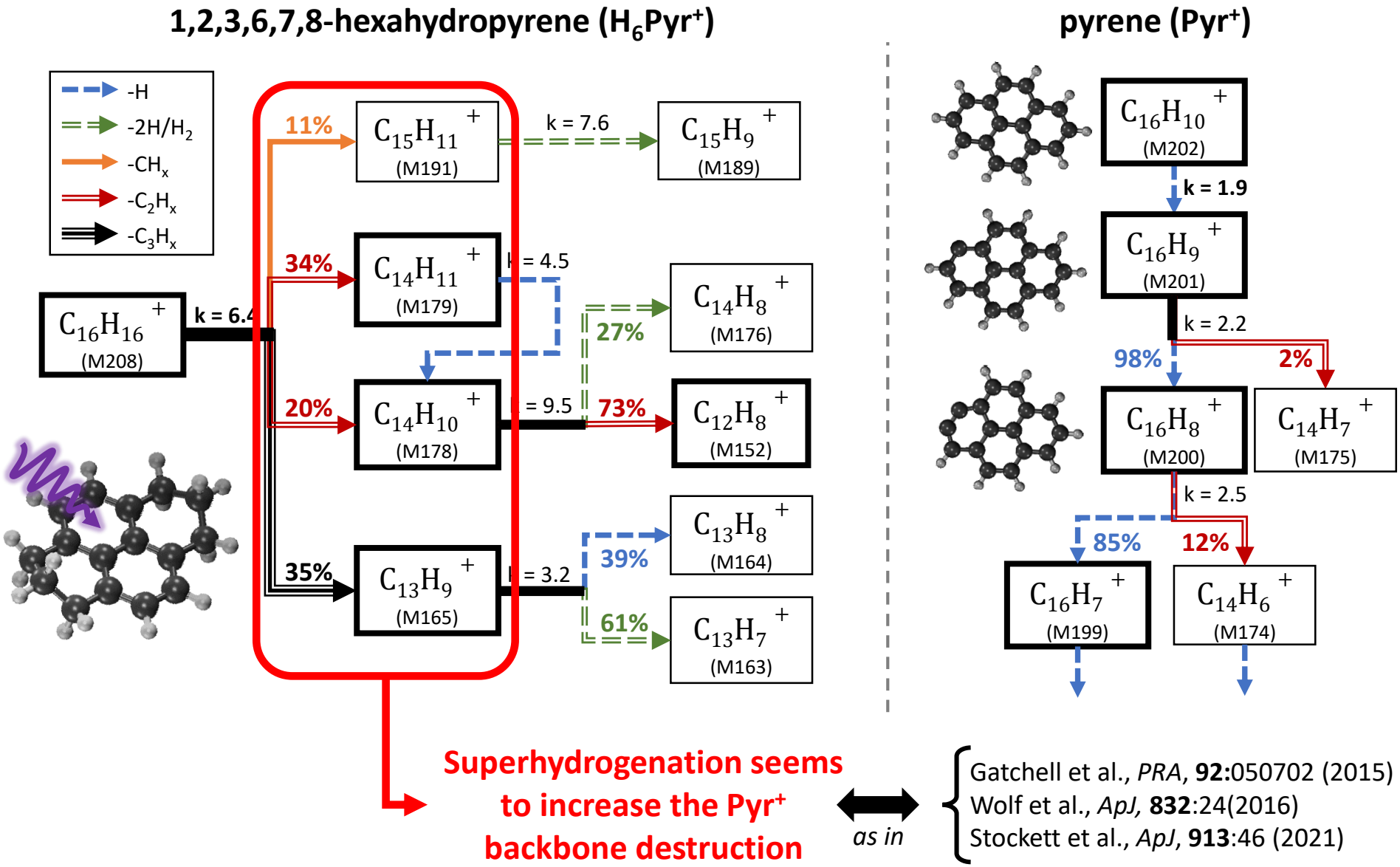


Main photoproducts



$$\overline{k_{abs}} = \overline{\sigma_{abs}(10.5\ \mathrm{eV})} \times (VUV\ Flux)$$

What about the VUV stability of H_n-PAH$^+$?



Superhydrogenation seems to increase the Pyr^+ backbone destruction

as in

- Gatchell et al., *PRA*, **92**:050702 (2015)
- Wolf et al., *ApJ*, **832**:24(2016)
- Stockett et al., *ApJ*, **913**:46 (2021)

A. Marciniak, et al. A&A 642, A42 (2021)