

From the VUV photoprocessing of super-hydrogenated PAHs in astro-relevant conditions to the study of PAH-water interactions

A. Marciniak^{a,b}, S. Zamith^a, F. Baterdouk^a, A. M. Nair^a, H. Leboucher^c, V. Rao Mundlapati^b, A. Bonnamy^b, A. Simon^c, M. Rapacioli^c, G. Mulas^d, P. Moretto-Capelle^a, L. Nogues^b, O. Coeur-Joly^b, D. Murat^b, J. M. L'Hermite^a and C. Joblin^b

^a LCAR/FerMI, Université Toulouse III, CNRS, 118 Route de Narbonne, 31062 Toulouse, France

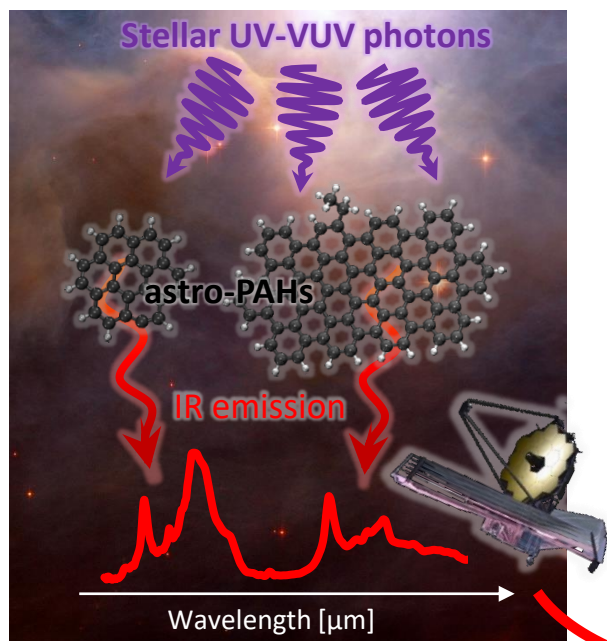
^b IRAP, Université Toulouse III, CNRS, CNES, 9 Av. du Col. Roche 31028 Toulouse Cdx 4, France

^c LCPQ/FerMI, Université Toulouse III, CNRS, 118 Route de Narbonne, 31062 Toulouse, France

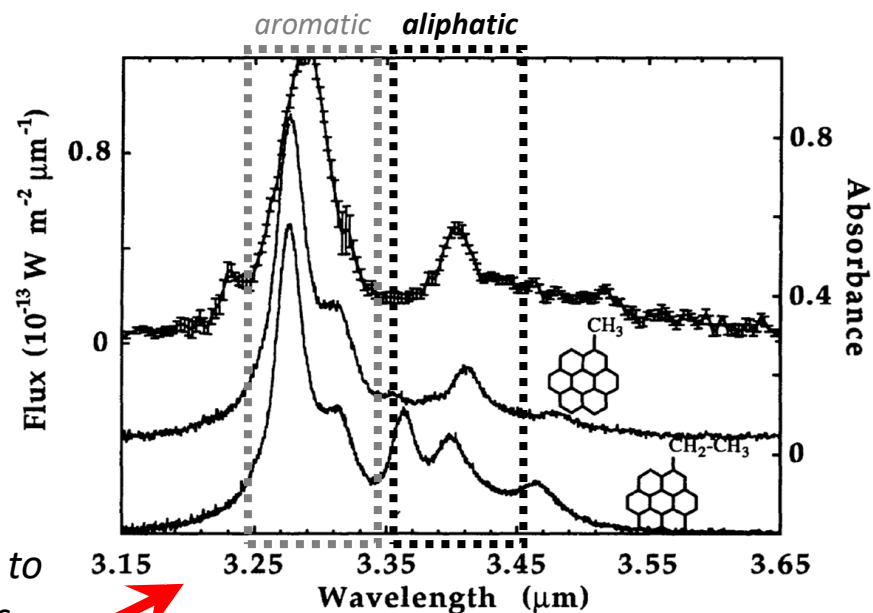
^d INAF - Osservatorio Astronomico di Cagliari, Via della Scienza 5, I-09047 Selargius (CA), Italy



Signature of aliphatic PAHs in photodissociation regions



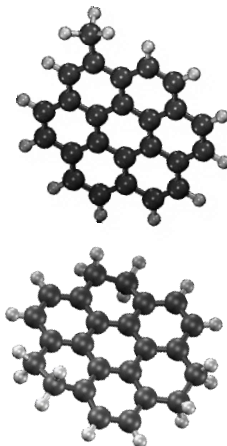
NGC 7023 ESA/Hubble – IR spectrum from Spitzer



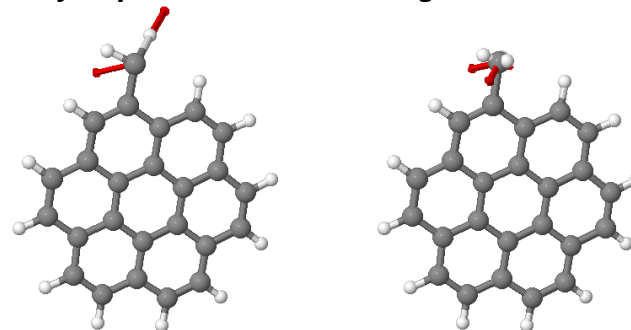
Comparison to lab. results

Good candidates for the 3.4 μm band:

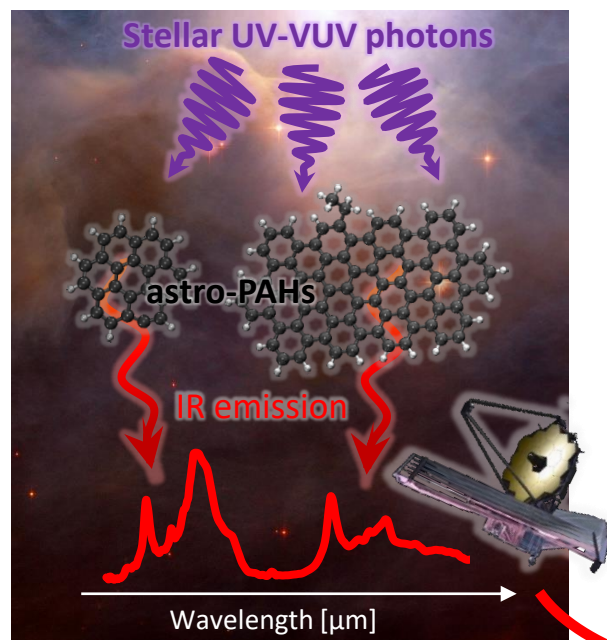
- **Alkylated PAHs** : methy-, ethyl-PAH,... (e.g. methylCoronene)
- **Superhydrogenated PAHs**: H_n -PAH (e.g. H_6 Coronene)



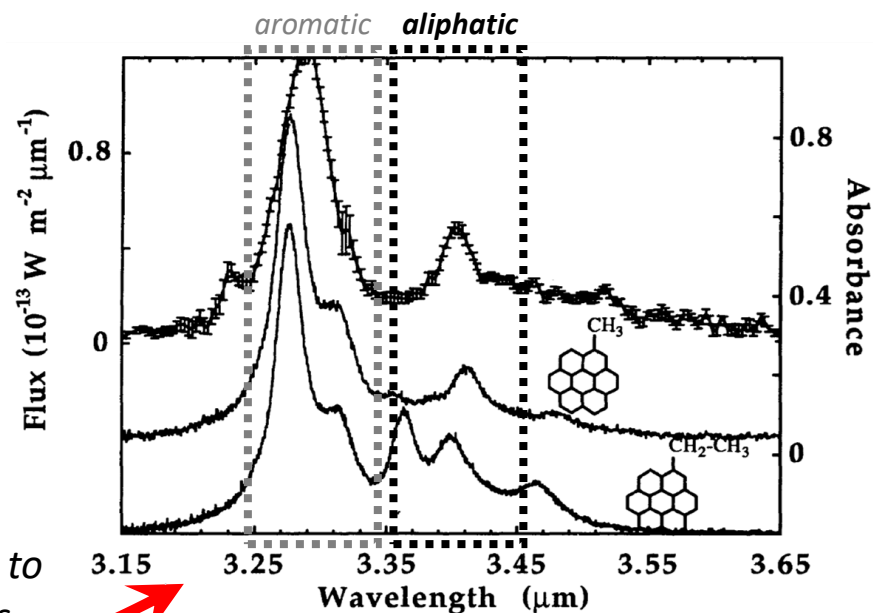
Example of **aliphatic** C-H stretching modes in methyl-Cor



Signature of aliphatic PAHs in photodissociation regions



NGC 7023 ESA/Hubble – IR spectrum from Spitzer



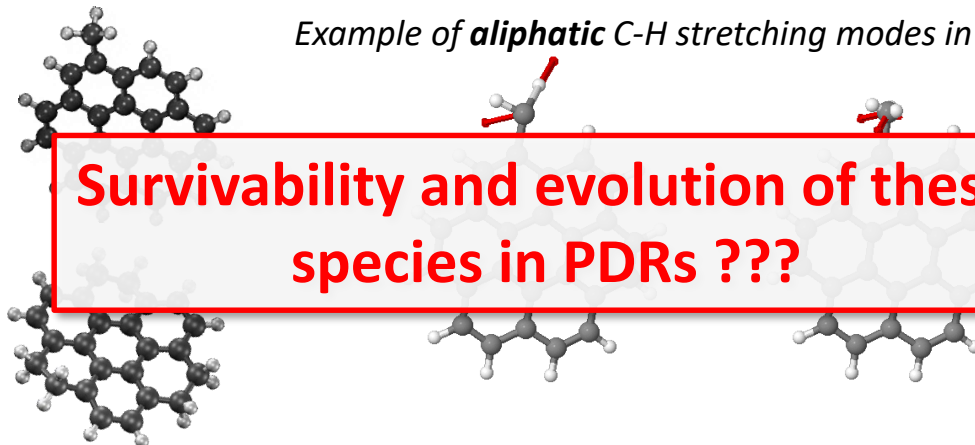
Comparison to lab. results

Good candidates for the 3.4 μm band:

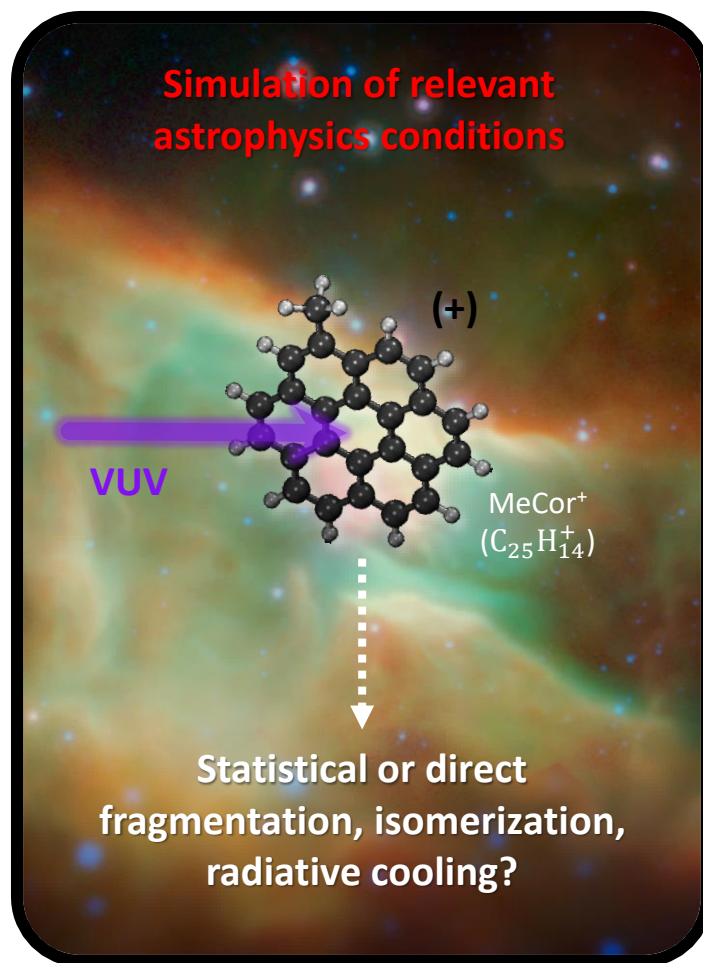
- Alkylated PAHs : methy-, ethyl-PAH,... (e.g. methylCoronene)
- Superhydrogenated PAHs: H_n -PAH (e.g. H_6 Coronene)

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

Survivability and evolution of these species in PDRs ???



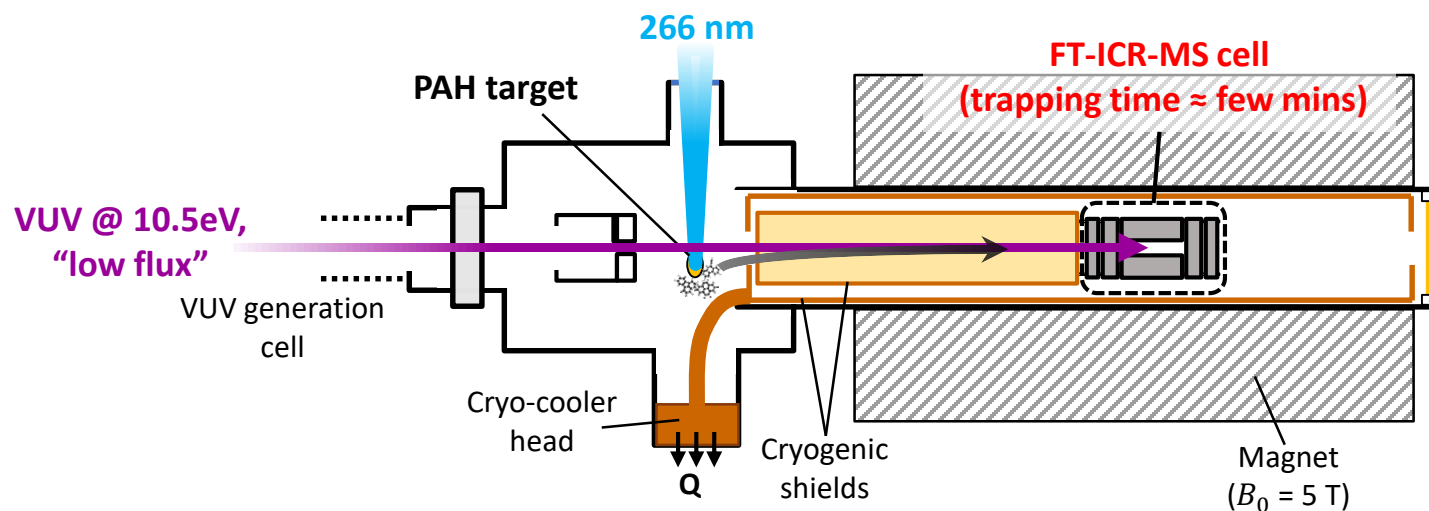
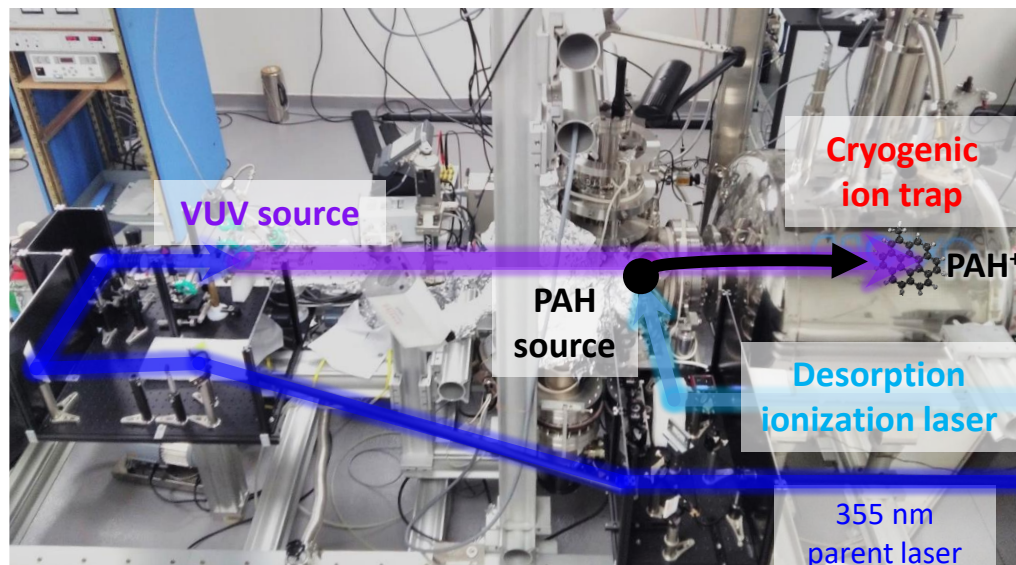
Studying the survivability and evolution of aliphatic PAH⁺ in principle



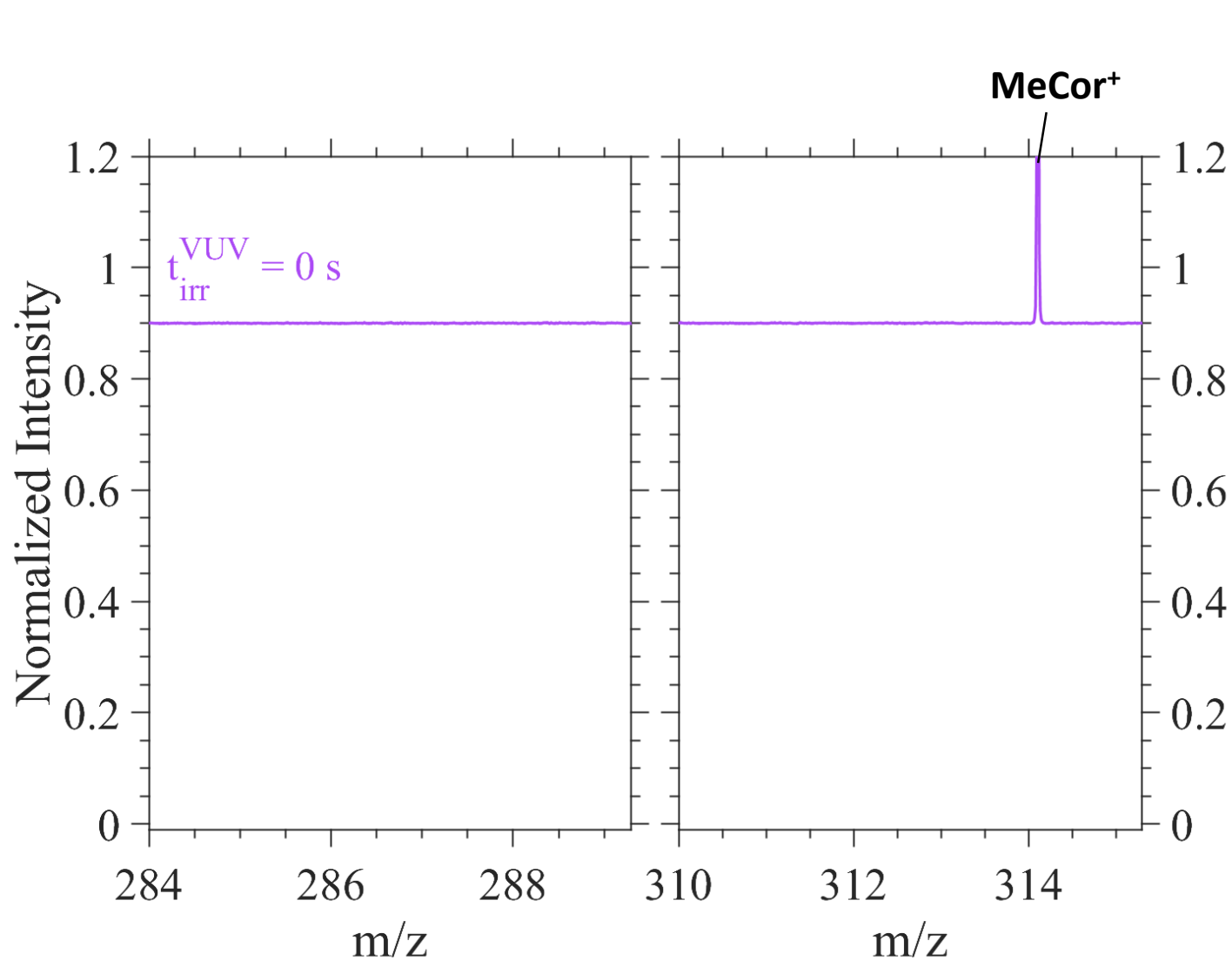
PIRENEA

(Piège à Ions pour la Recherche et l'Etude de Nouvelles Espèces Astrochimiques)

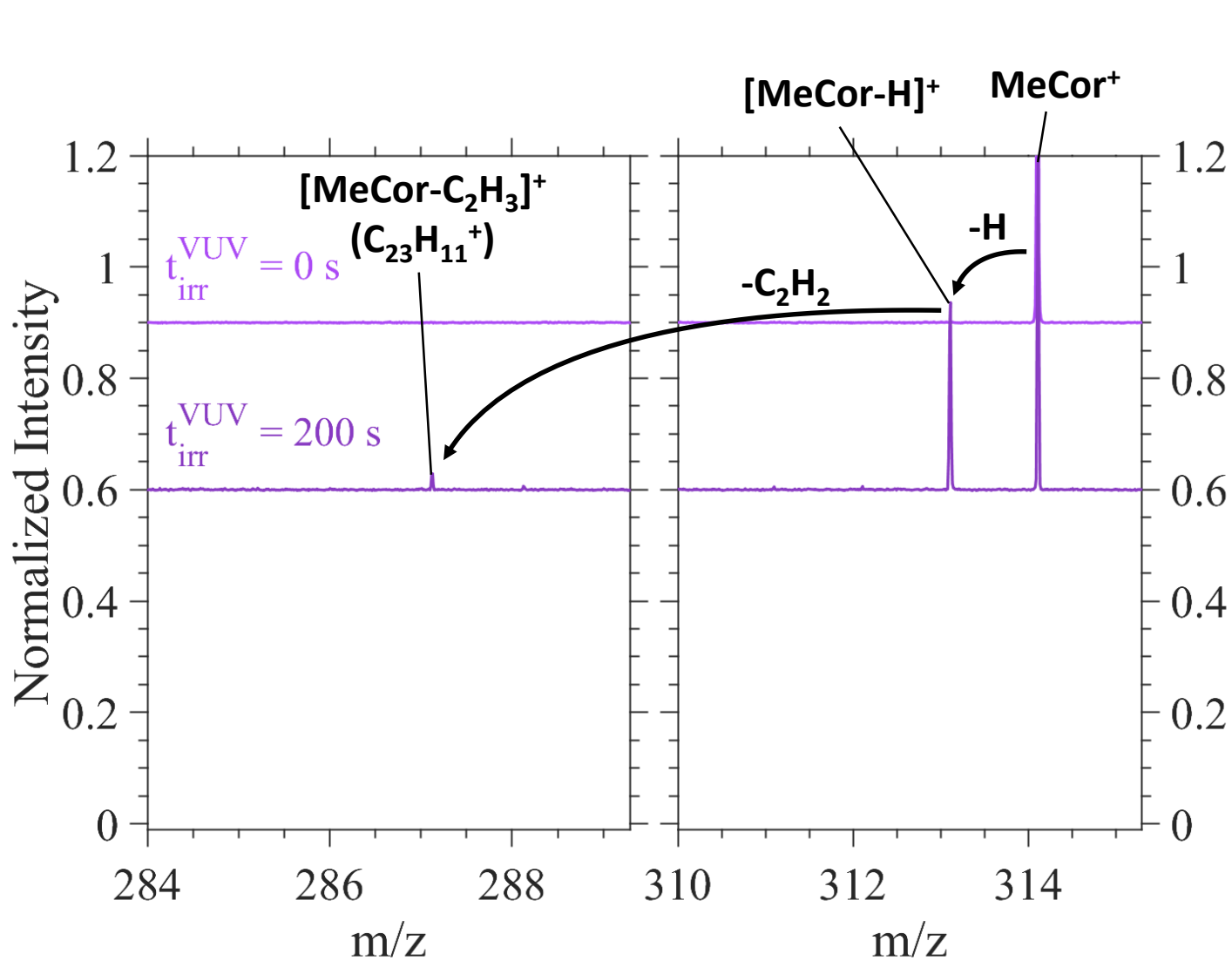
Collisionless and cold environment: 10^{-11} mbar, 30 K



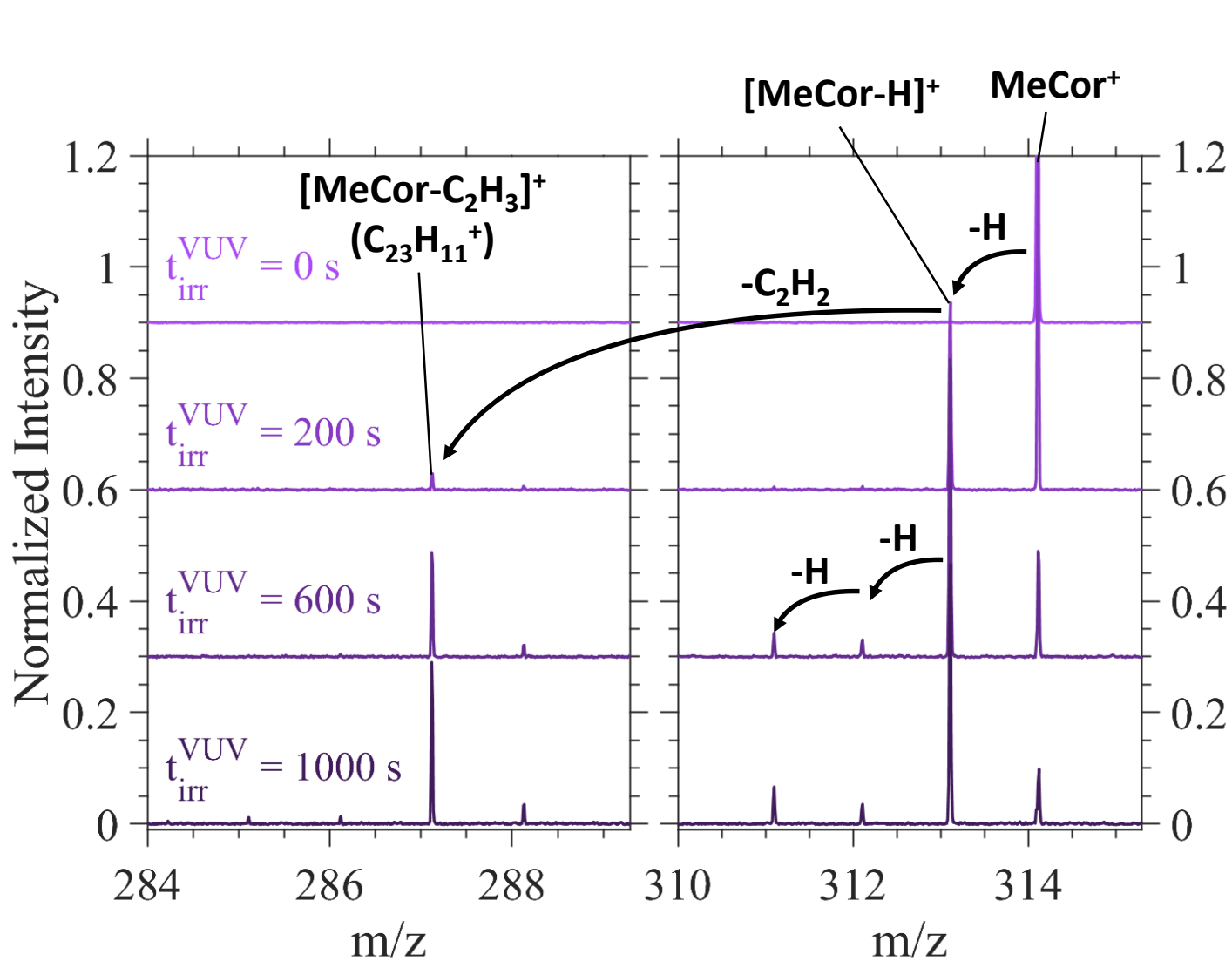
Mass Spectra as a function of the VUV Irradiation time



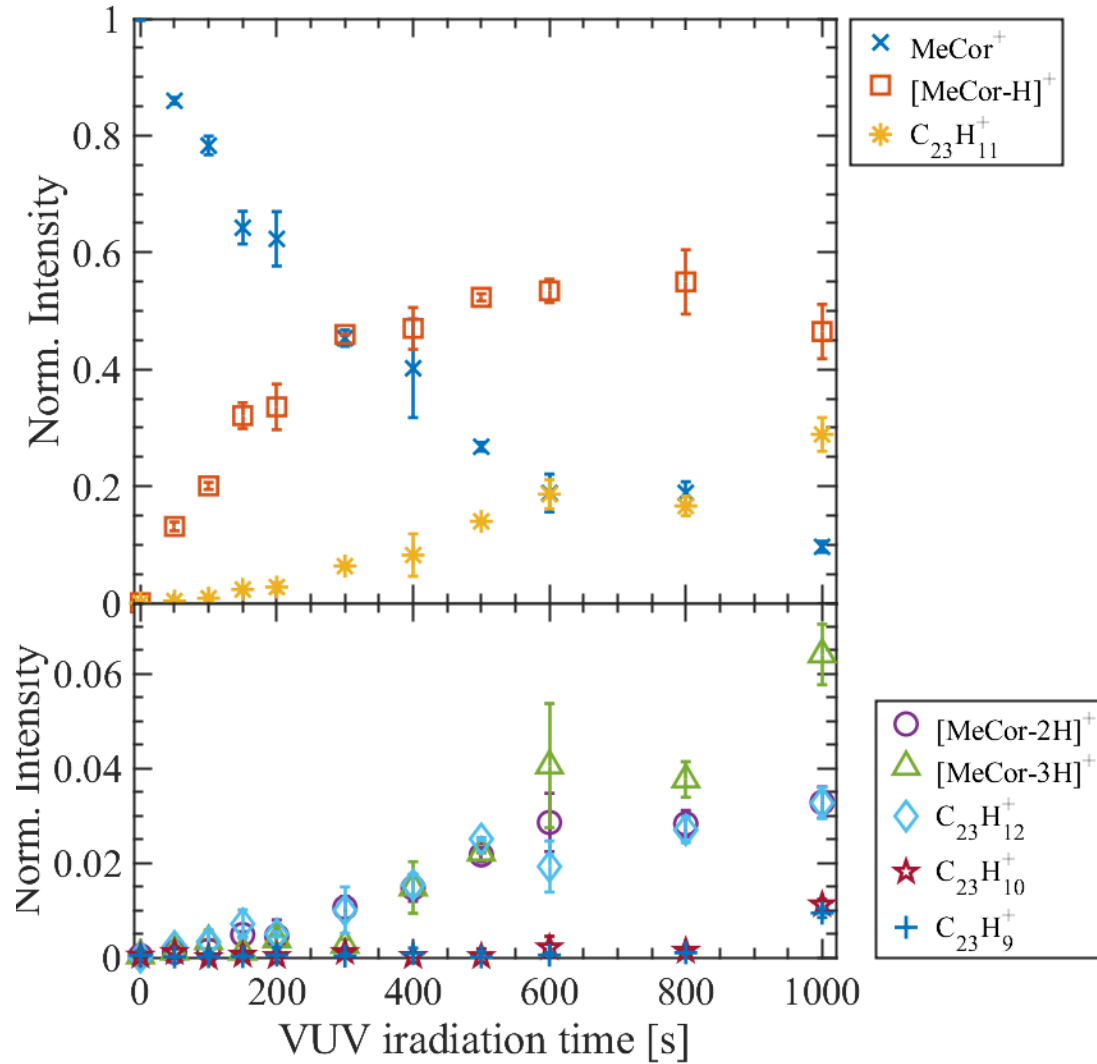
Mass Spectra as a function of the VUV Irradiation time



Mass Spectra as a function of the VUV Irradiation time

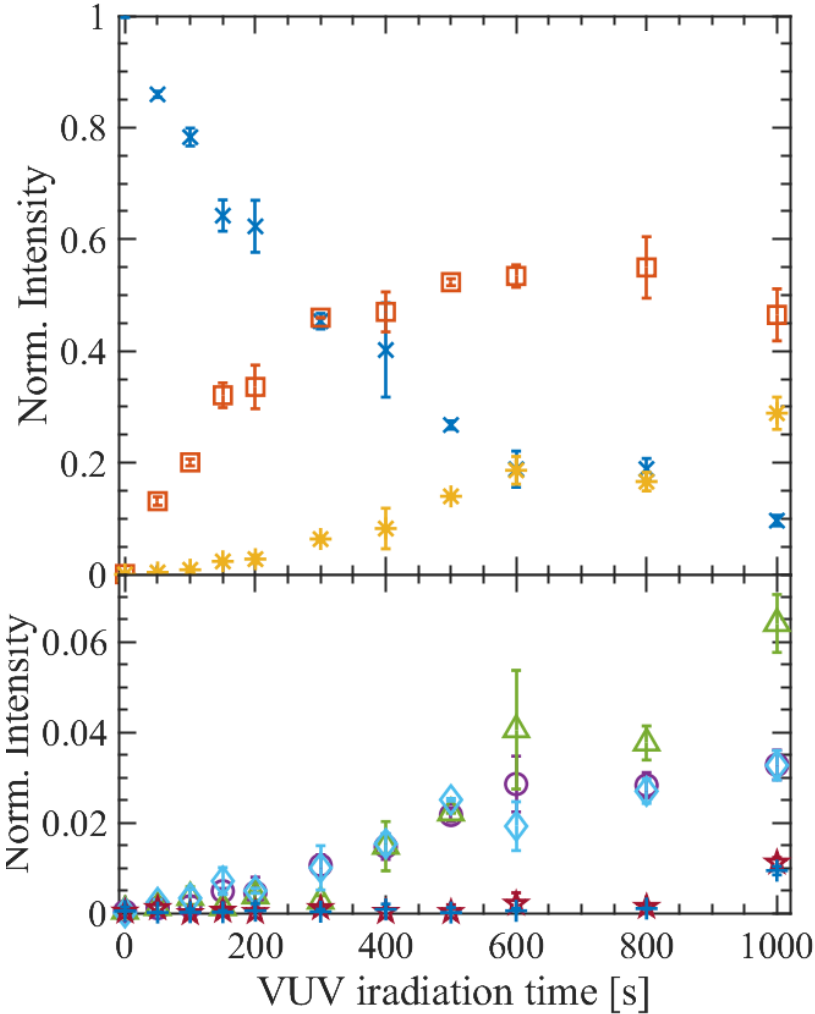


Kinetics results



How to retrieve the fragmentation map of each species ?

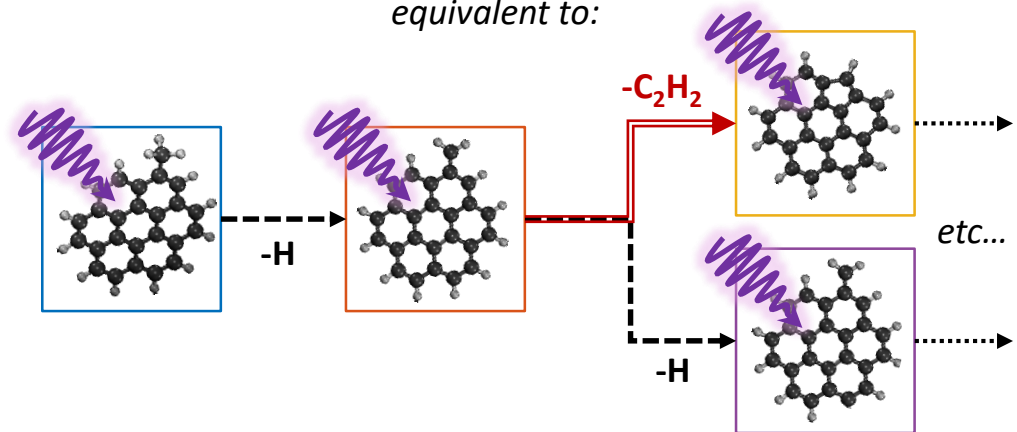
Fitting procedure to obtain a fragmentation map



Master Equation with population and depopulation terms

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

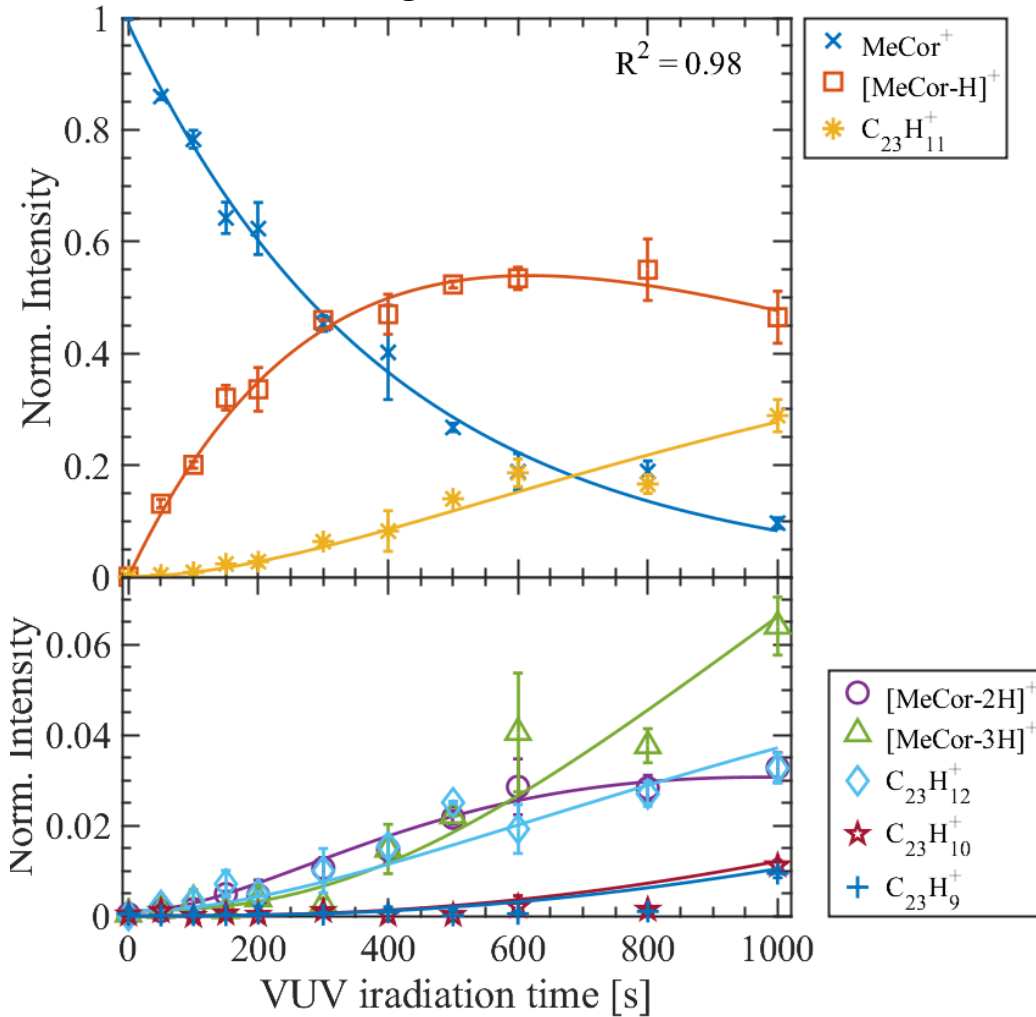
equivalent to:



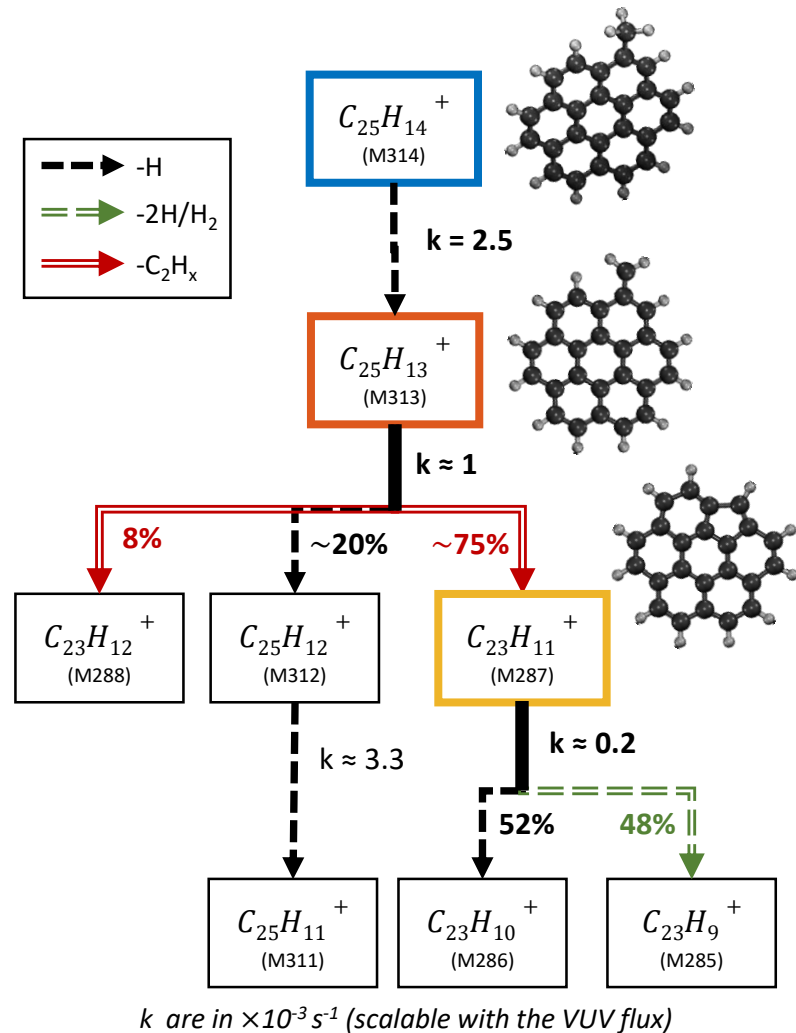
→ Only the $k_{frag}^{M_n \rightarrow M_i}$ are adjusted to fit the data

Fitting procedure to obtain a fragmentation map

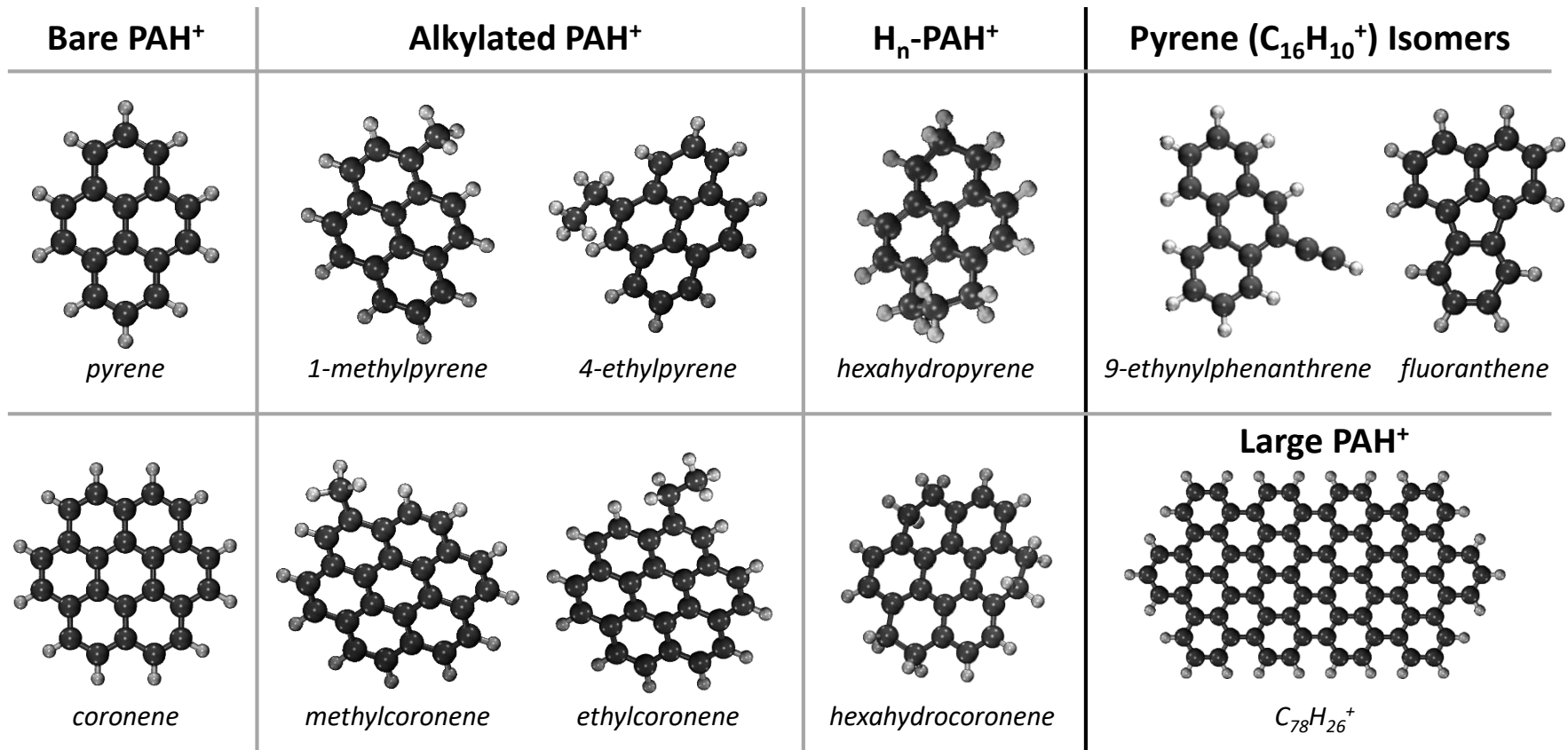
Fitting results



Fragmentation Map & Fragmentation Rates



Studied PAH⁺ and PAH⁺ derivatives

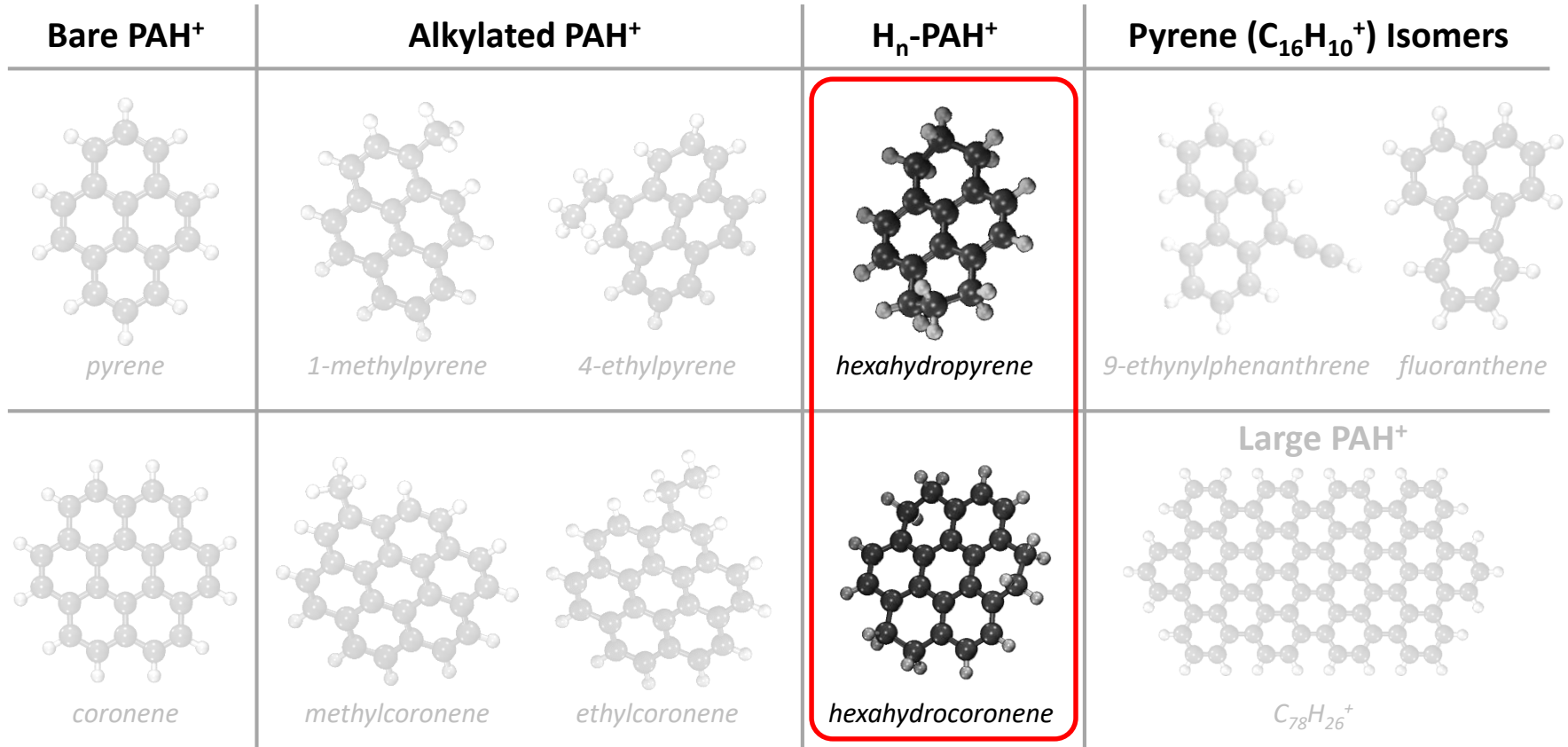


Alkylated PAH → A. Marciniak, et al. *A&A* 642, A42 (2021)

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

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

Super-hydrogenated PAH⁺



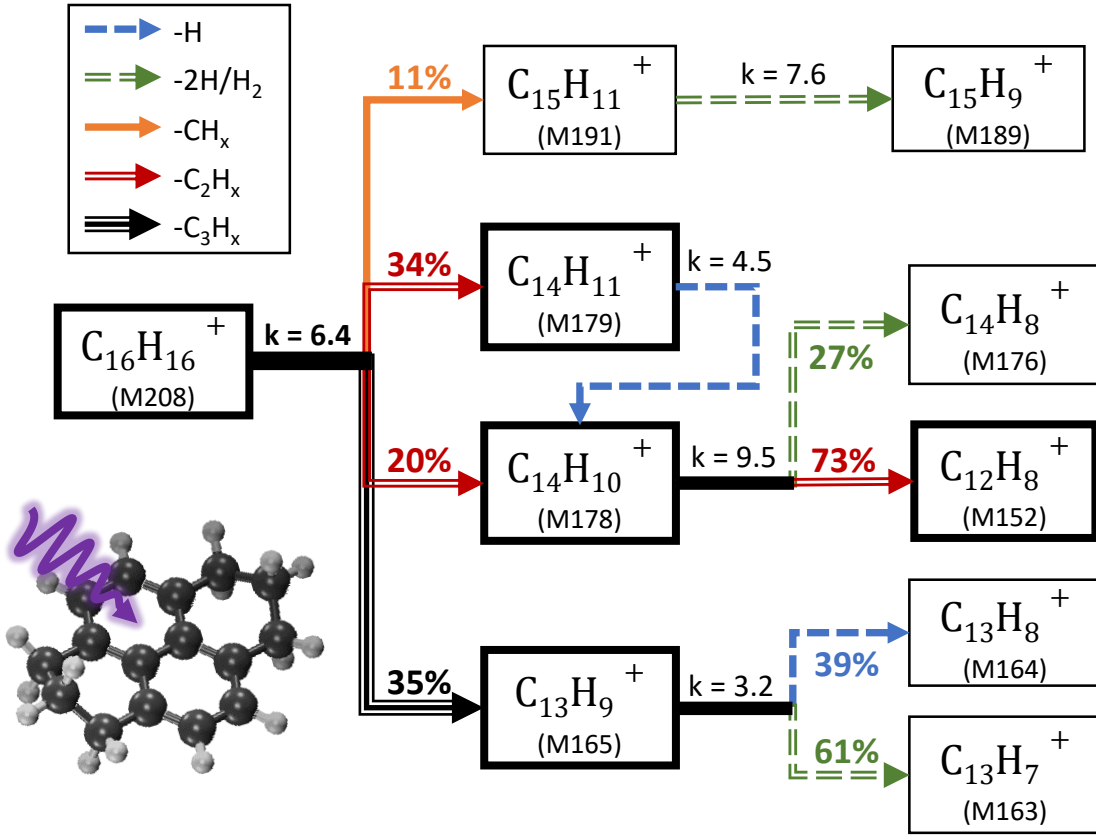
Alkylated PAH → A. Marciniak, et al. A&A 642, A42 (2021)

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

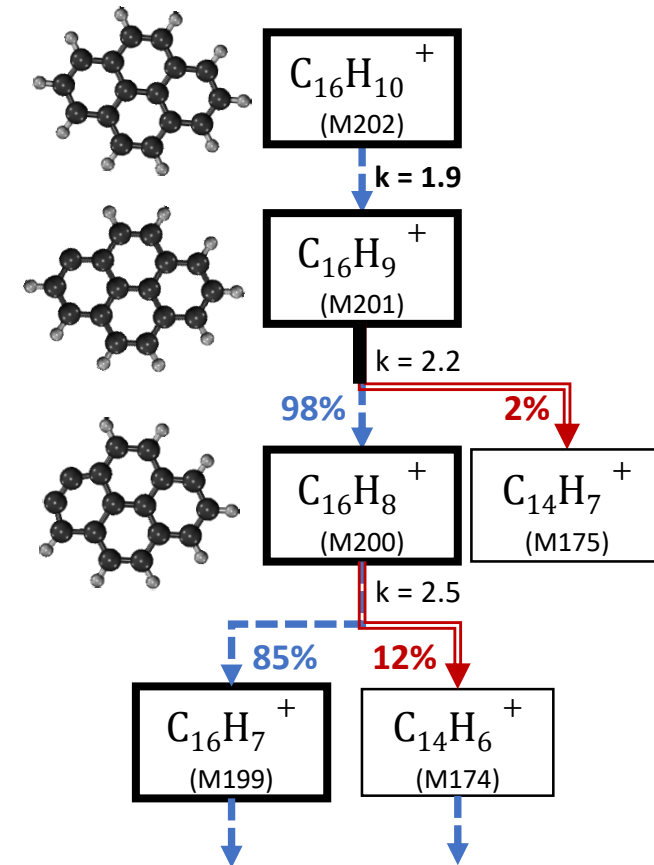
Super-hydrogenated coronene → A. Marciniak et al. in prep.

What about the VUV stability of H_n -Pyr⁺ ?

1,2,3,6,7,8-hexahydropyrene (H_6 Pyr⁺)



pyrene (Pyr⁺)

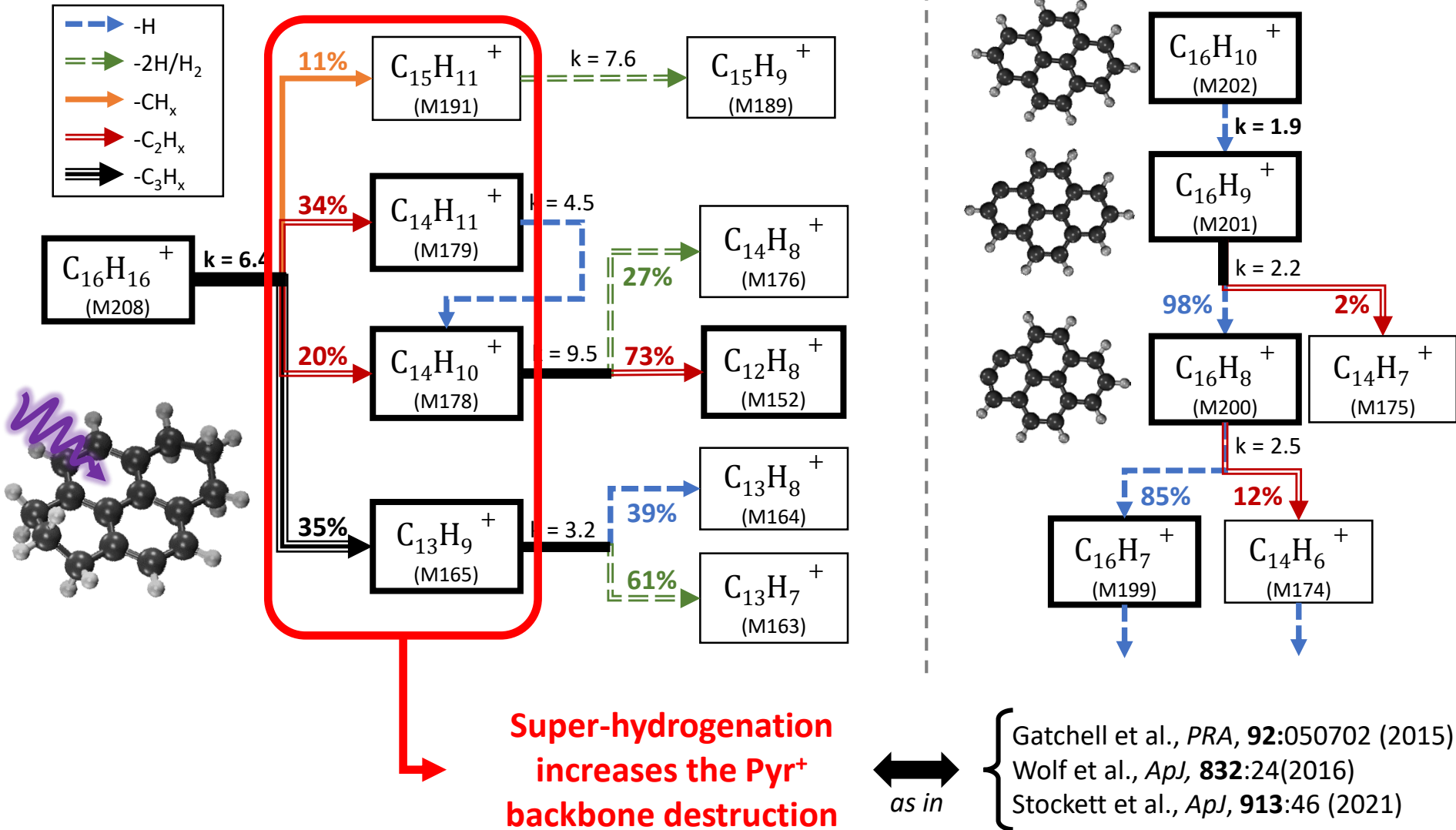


A. Marciniak, et al. A&A 642, A42 (2021)

What about the VUV stability of H_n -Pyr⁺ ?

1,2,3,6,7,8-hexahydropyrene (H_6 Pyr⁺)

pyrene (Pyr⁺)



What about the VUV stability of H_n -PAH⁺ ?

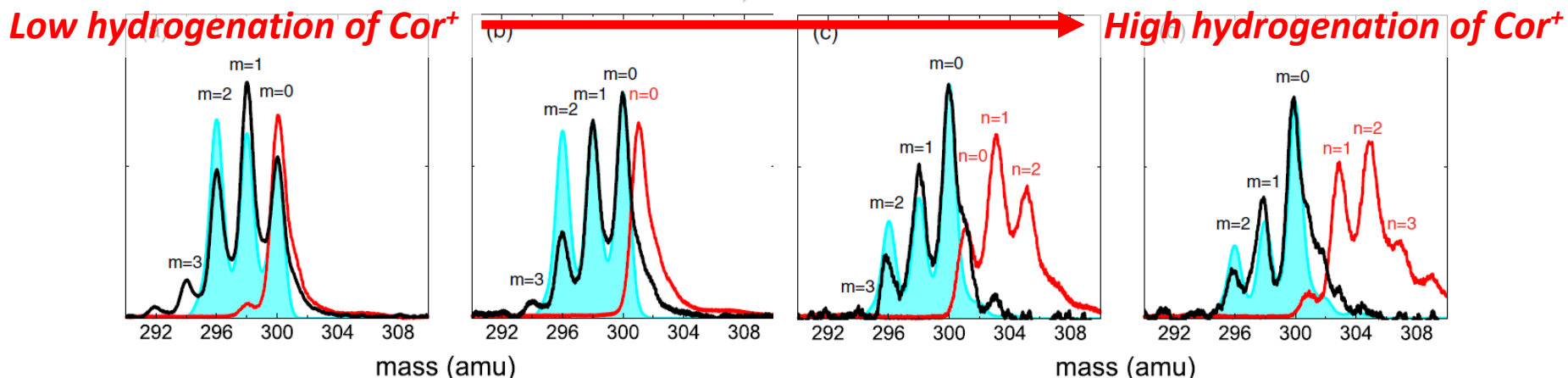
PRL 113, 053002 (2014)

PHYSICAL REVIEW LETTERS

week ending
1 AUGUST 2014

Deexcitation Dynamics of Superhydrogenated Polycyclic Aromatic Hydrocarbon Cations after Soft-x-Ray Absorption

G. Reitsma,^{1,*} L. Boschman,^{1,2} M. J. Deuzeman,¹ O. González-Magaña,¹ S. Hoekstra,³ S. Cazaux,²
R. Hoekstra,¹ and T. Schlathöler¹

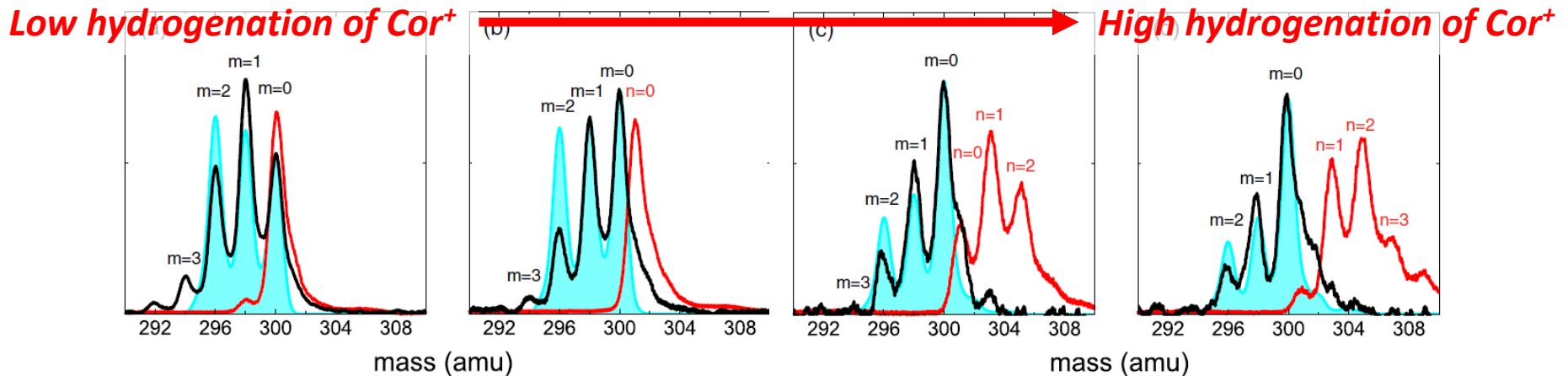


Despite this weakening, superhydrogenation clearly acts as a protection mechanism for PAH molecules.
(ii) Superhydrogenation may explain the existence of large amounts of PAHs in the interstellar medium, as deexcitation by H loss protects the C backbone from fragmentation.

What about the VUV stability of H_n -PAH⁺ ?

Deexcitation Dynamics of Superhydrogenated Polycyclic Aromatic Hydrocarbon Cations after Soft-x-Ray Absorption

G. Reitsma,^{1,*} L. Boschman,^{1,2} M. J. Deuzeman,¹ O. González-Magaña,¹ S. Hoekstra,³ S. Cazaux,²
R. Hoekstra,¹ and T. Schlathöler¹



Despite this weakening, superhydrogenation clearly acts as a protection mechanism for PAH molecules.
(ii) Superhydrogenation may explain the existence of large amounts of PAHs in the interstellar medium, as deexcitation by H loss protects the C backbone from fragmentation.

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)



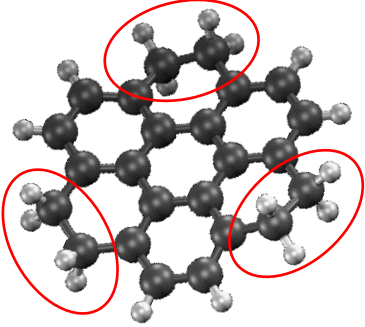
Super-hydrogenation of Cor⁺ seems to protect its backbone

VUV photoprocessing of $H_{n=1-6}Cor^+$



$(Cor^+ = C_{24}H_{12}^+)$

H_6Cor on the sample
target ($m/z \approx 306$)



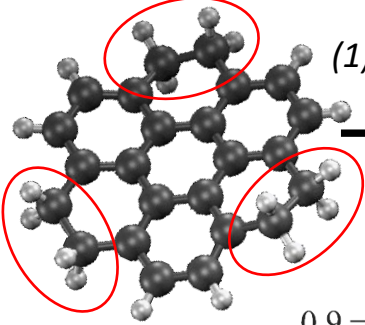
(Coll. D. Peña)

VUV photoprocessing of $H_{n=1-6}Cor^+$

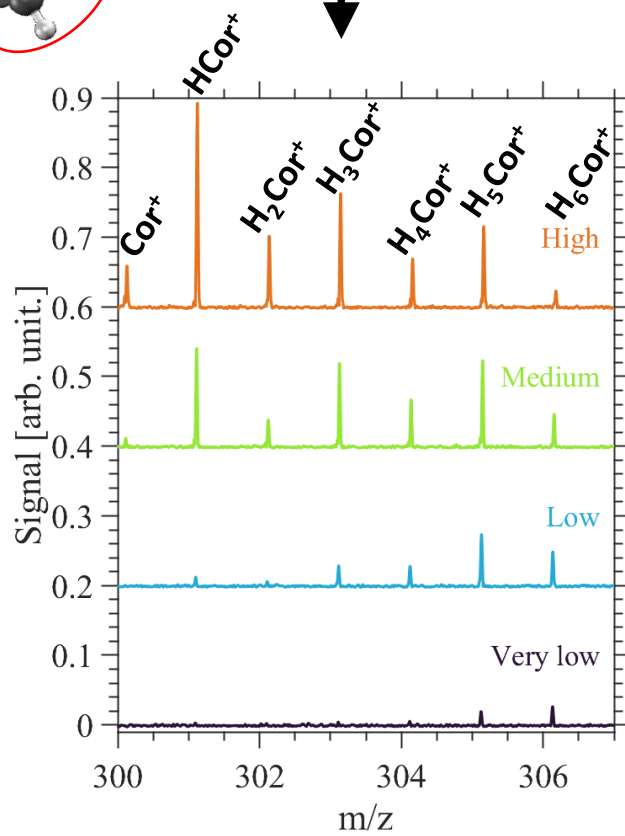


$(Cor^+ = C_{24}H_{12}^+)$

H_6Cor on the sample target ($m/z \approx 306$)



(1) Laser desorption ionization



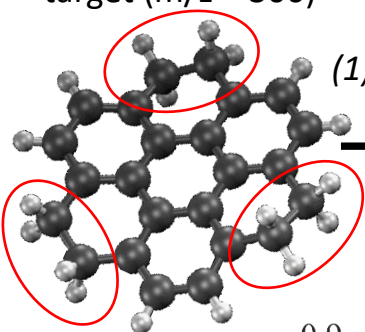
(Coll. D. Peña)

VUV photoprocessing of $H_{n=1-6}Cor^+$



$(Cor^+ = C_{24}H_{12}^+)$

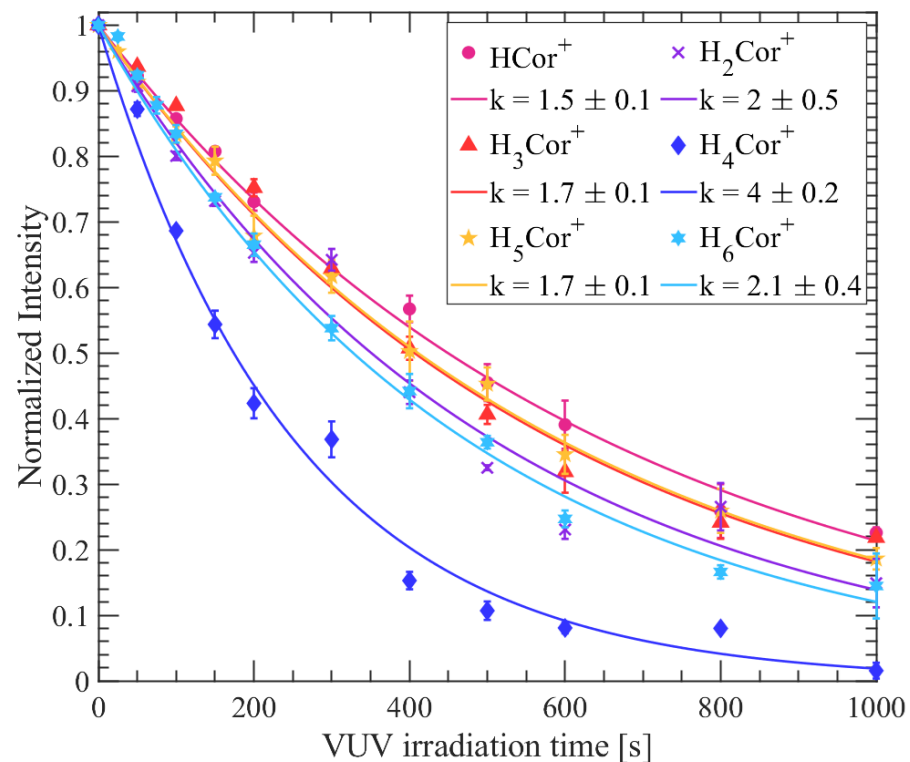
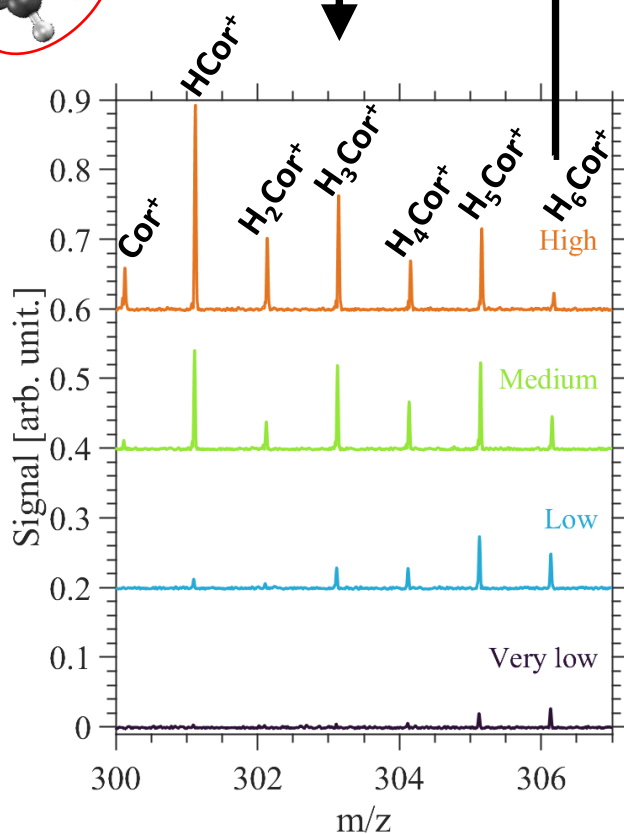
H_6Cor on the sample target ($m/z \approx 306$)



(1) Laser desorption ionization

(2) Isolation

(3) VUV irradiation

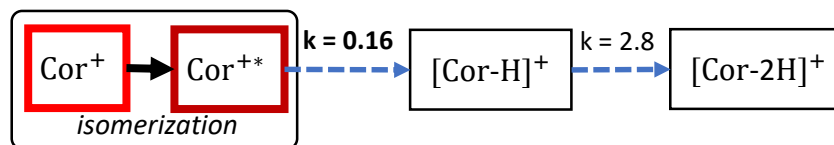


(Coll. D. Peña)

Fragmentation map of $H_{n=0,1-6}Cor^+$



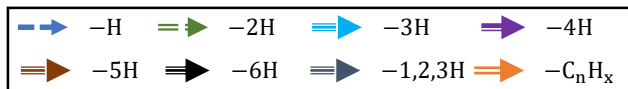
($Cor^+ = C_{24}H_{12}^+$)



Odd (n = 1; 3; 5)



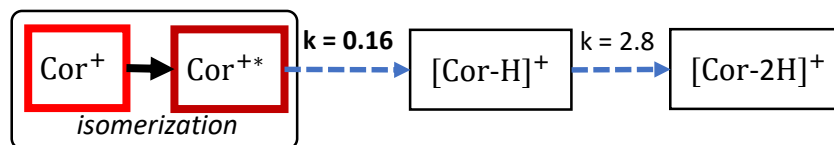
Even (n = 2; 4; 6)



Fragmentation map of $H_{n=0,1-6}Cor^+$



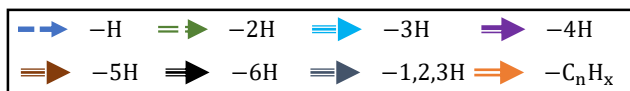
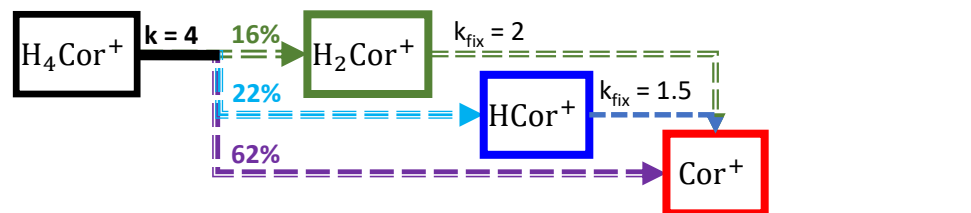
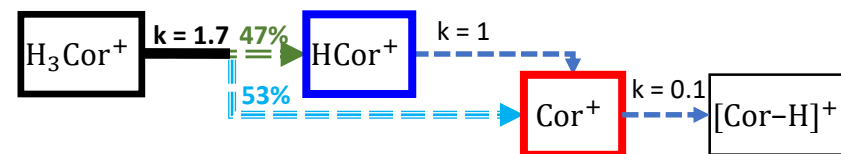
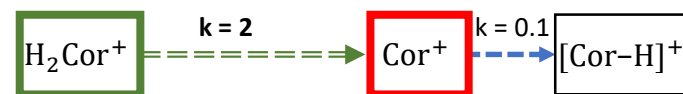
($Cor^+ = C_{24}H_{12}^+$)



Odd (n = 1; 3; 5)



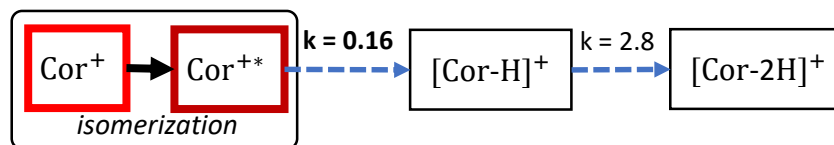
Even (n = 2; 4; 6)



Fragmentation map of $H_{n=0,1-6}Cor^+$



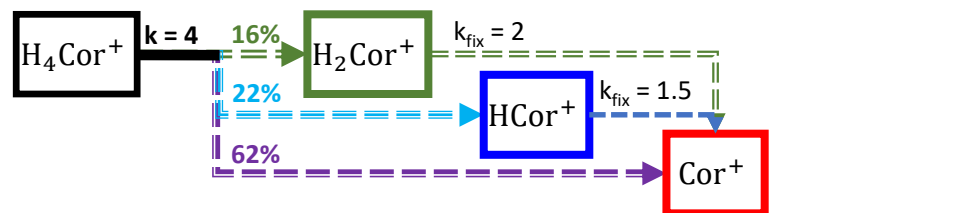
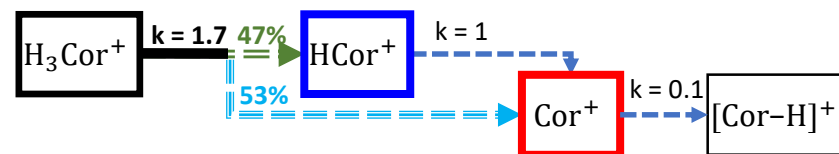
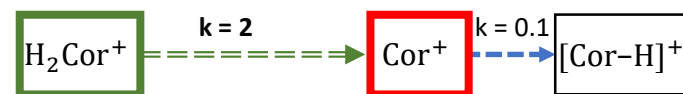
($Cor^+ = C_{24}H_{12}^+$)



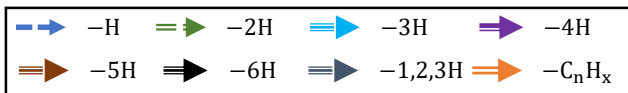
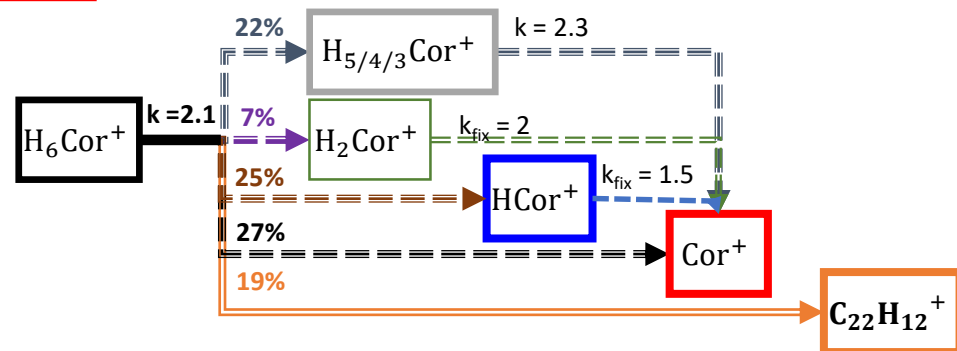
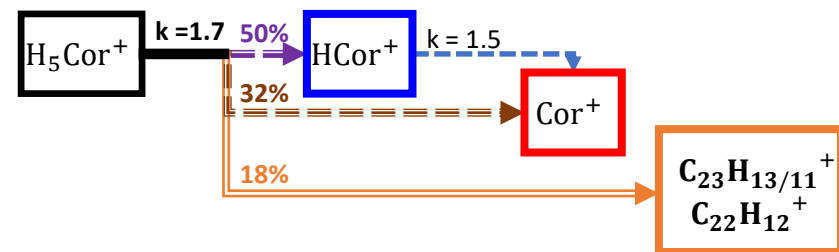
Odd ($n = 1; 3; 5$)



Even ($n = 2; 4; 6$)



C-loss limit

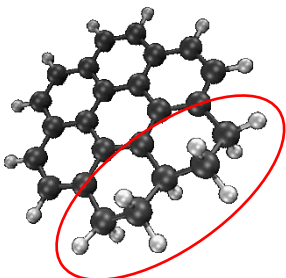


Fragmentation mechanisms of H_5Cor^+



SCC-DFTB + MD simulations at low internal energy (Coll. A. Simon)

H_5Cor^+



$$U_{int}^0 \approx 22.2 \text{ eV}$$

(4400 K)

Over 180 runs of 1 ns

deMon-Nano

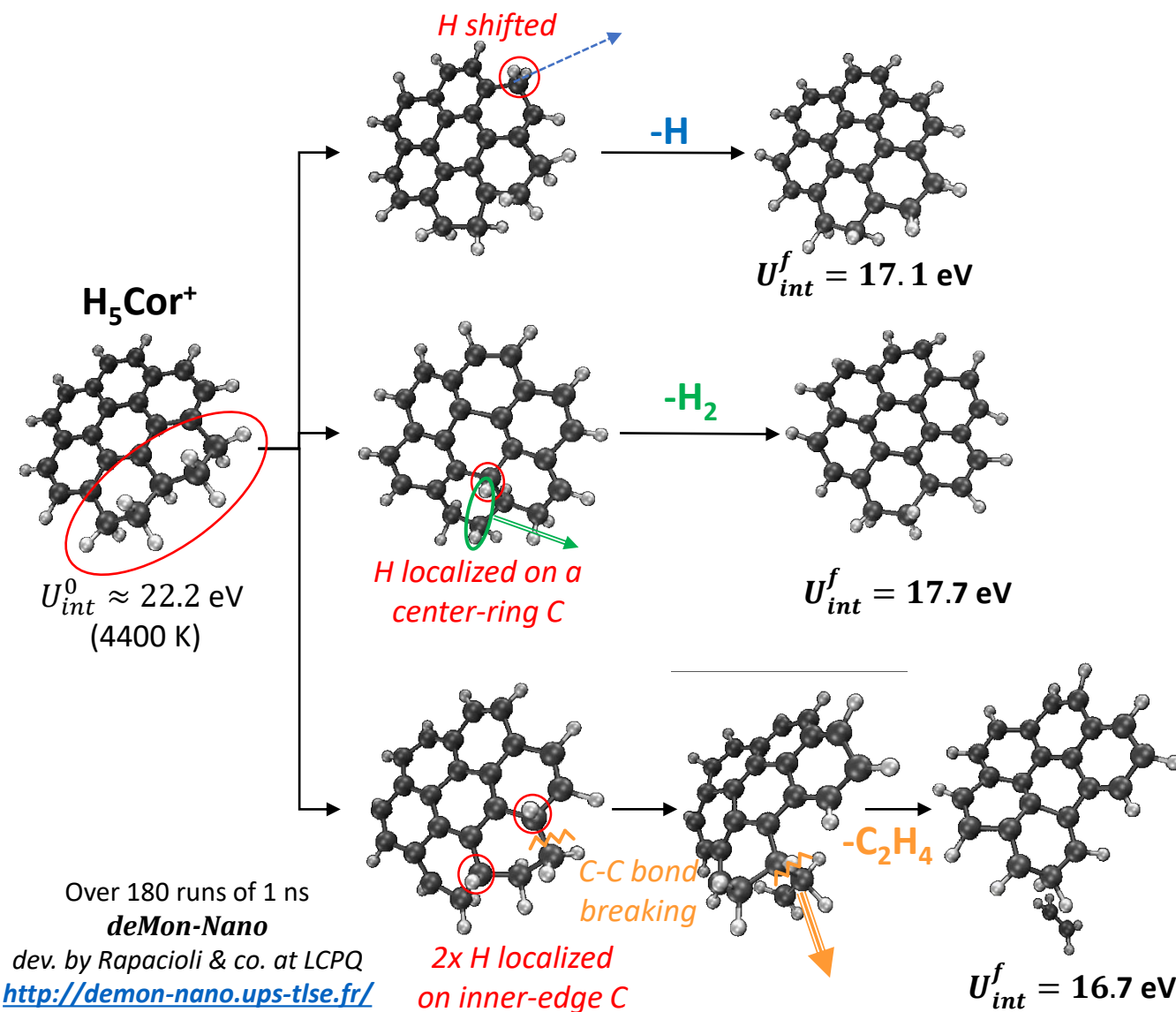
dev. by Rapacioli & co. at LCPQ

<http://demon-nano.ups-tlse.fr/>

Fragmentation mechanisms of H_5Cor^+



SCC-DFTB + MD simulations at low internal energy (Coll. A. Simon)



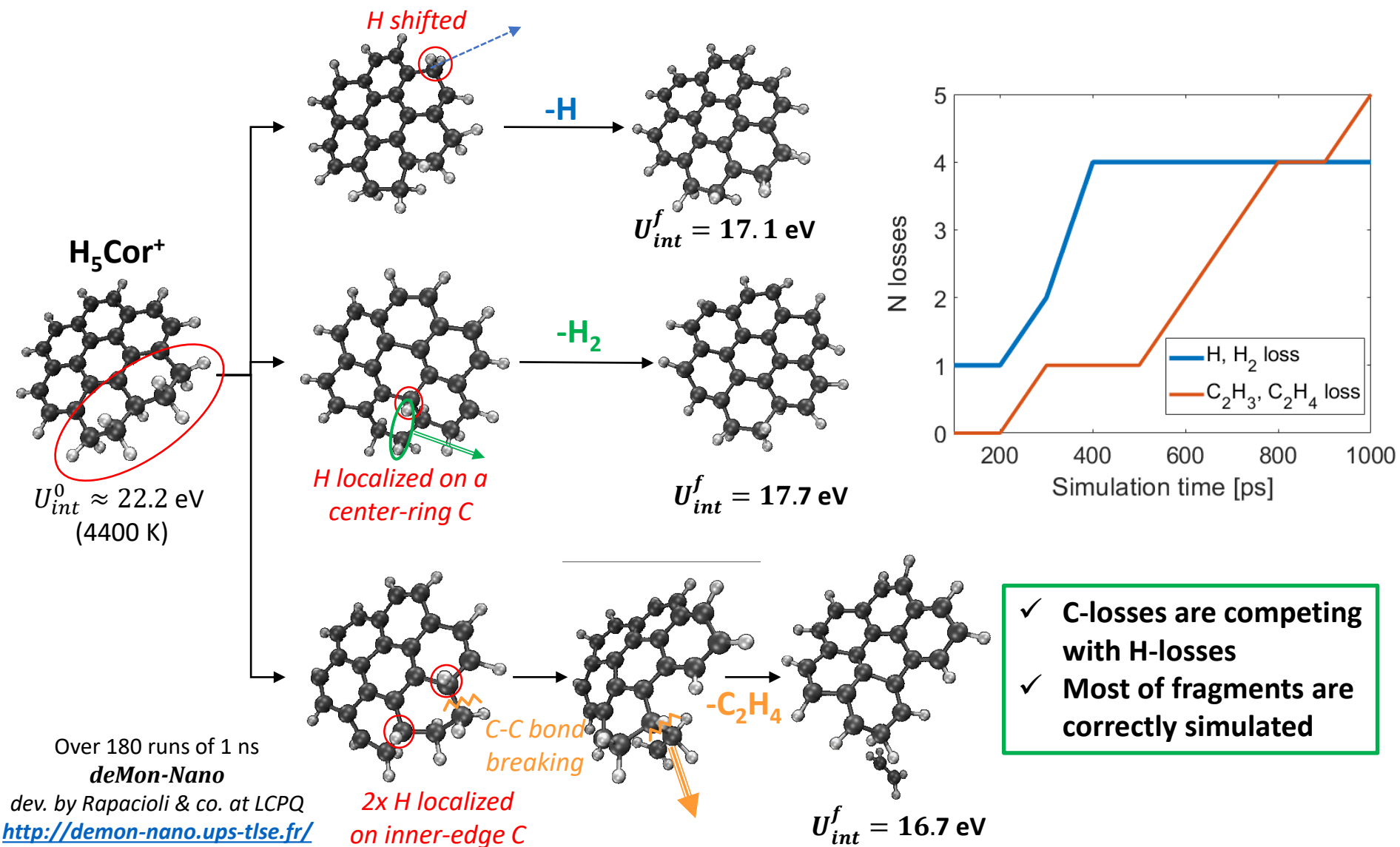
Over 180 runs of 1 ns
deMon-Nano

dev. by Rapacioli & co. at LCPQ
<http://demon-nano.ups-tlse.fr/>

Fragmentation mechanisms of H_5Cor^+



SCC-DFTB + MD simulations at low internal energy (Coll. A. Simon)

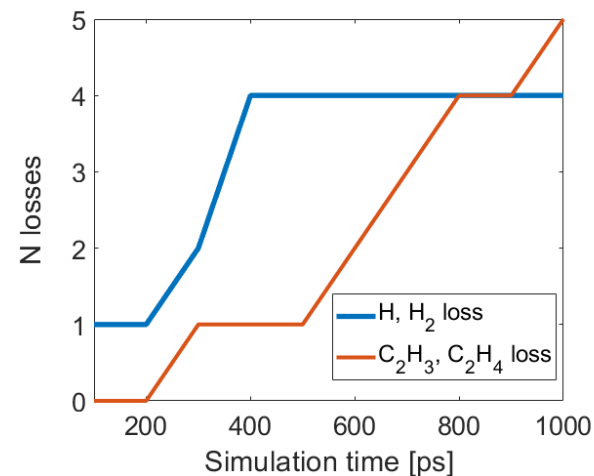
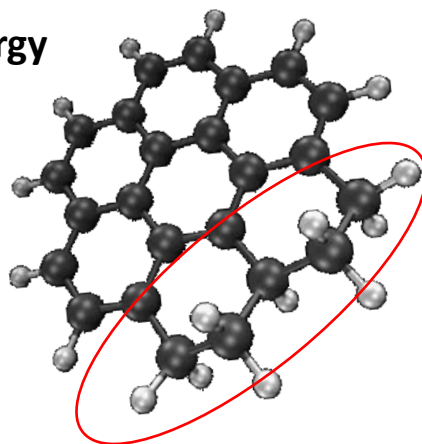


Isomer effect in MD simulation of H_5Cor^+

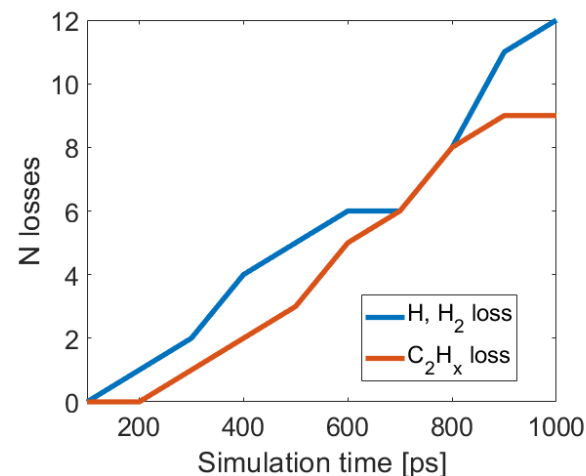
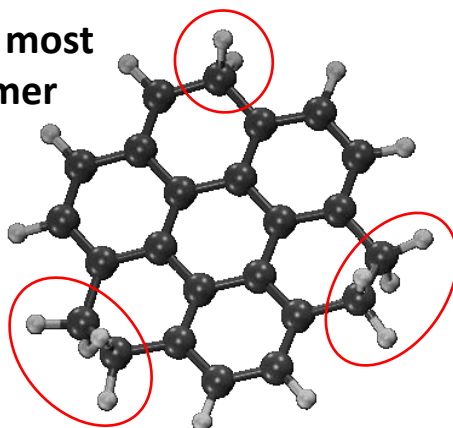
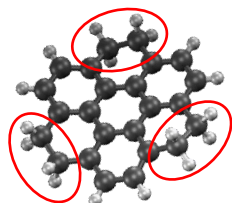


$U_{int}^0 \approx 22.2$ eV
(4400 K)

Lowest energy
isomer

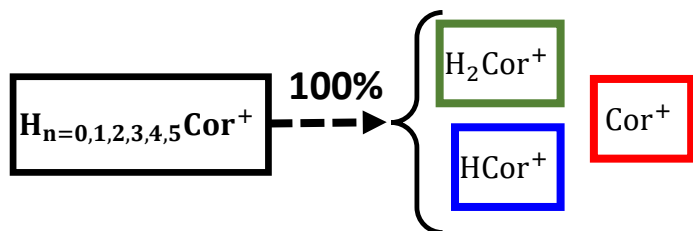


Experimentally most
probable isomer



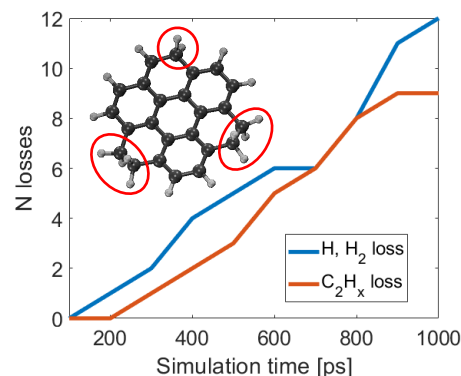
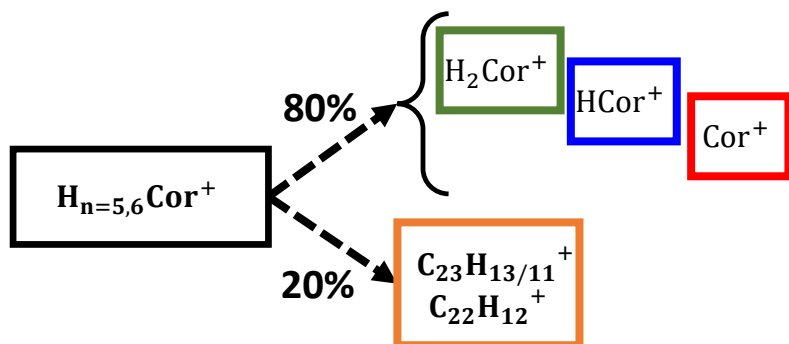
The initial H locations of H_n -PAH⁺ have an impact on the VUV fragmentation

Conclusion about $H_n\text{Cor}^+$



only H-losses (H_2 ?) and/or sequential H-loss

C-loss limit $n \geq 5$

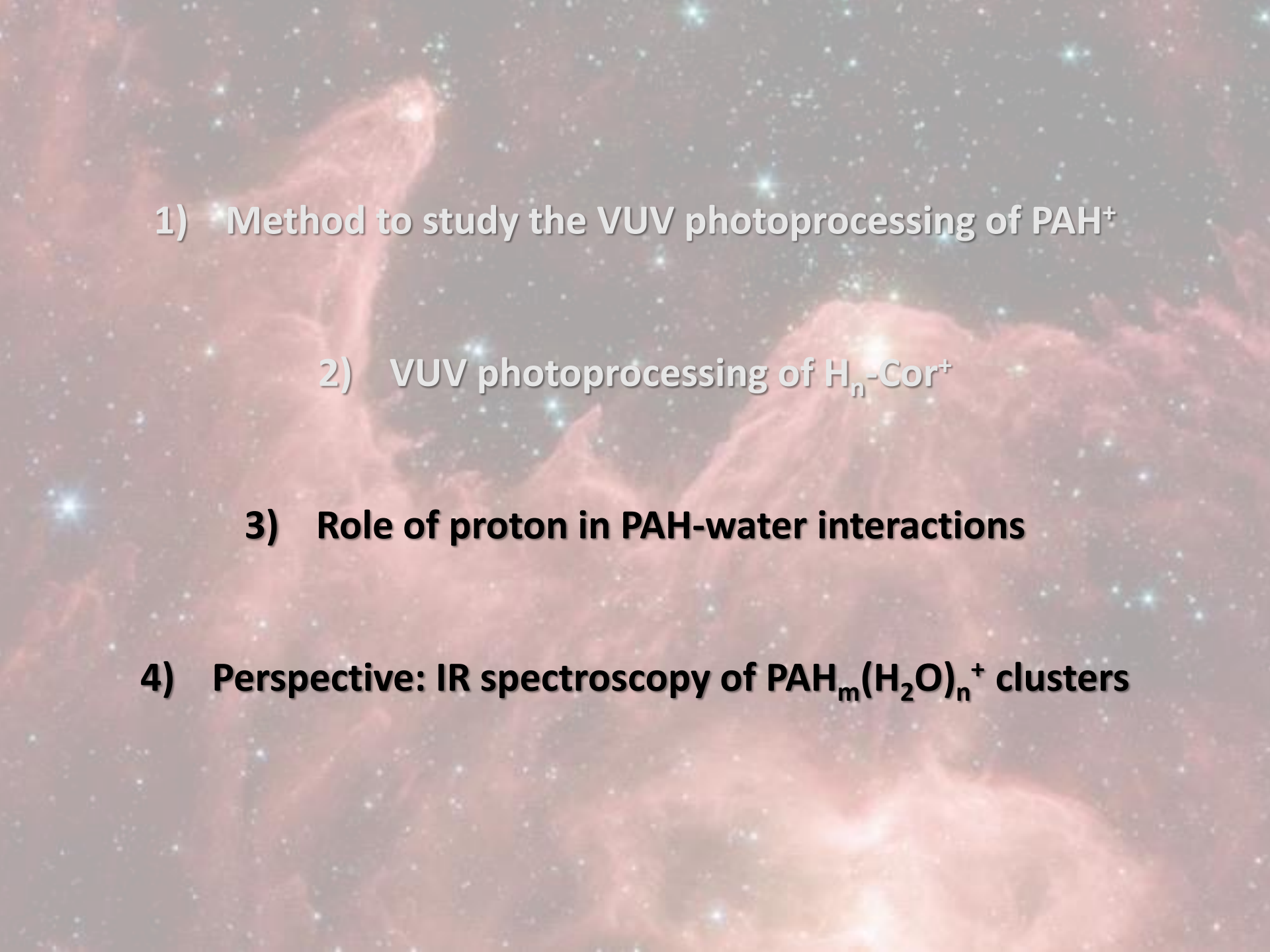


Take home messages

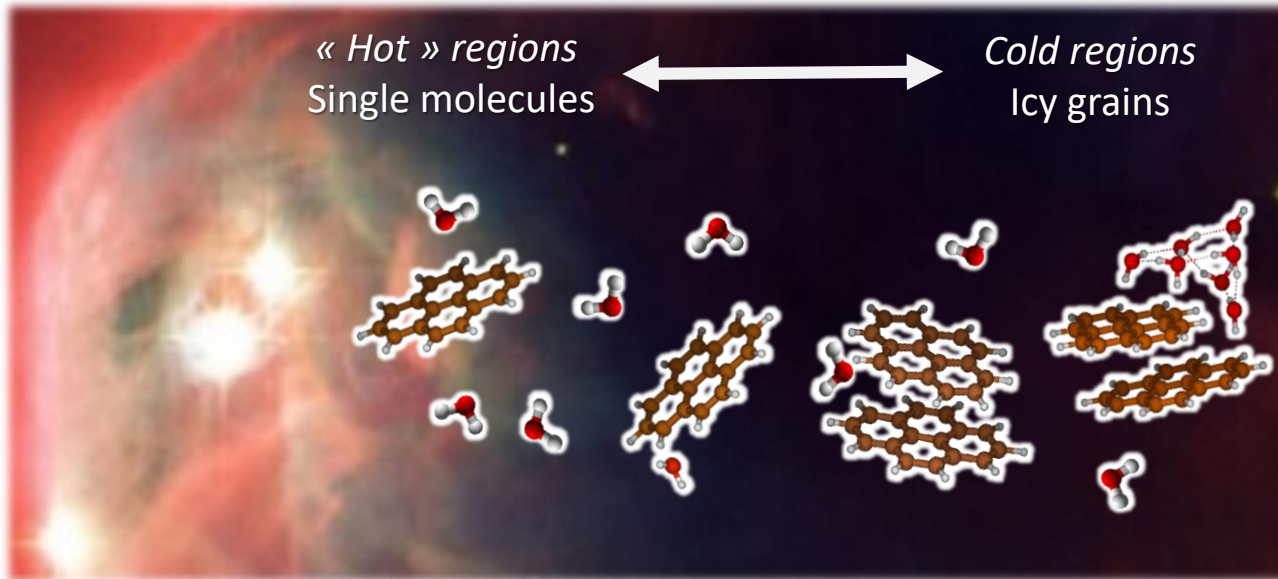
- ❖ Super-hydrogenation protects Cor^+ up to $n=4$
- ❖ Release H_2 and C_2H_x by VUV photoprocessing of $H_n\text{PAH}^+$

Phenomena to be investigated

- Extrapolation of the nH -protection to larger PAH ?
- Initial isomer effects ? Role of H migration ?

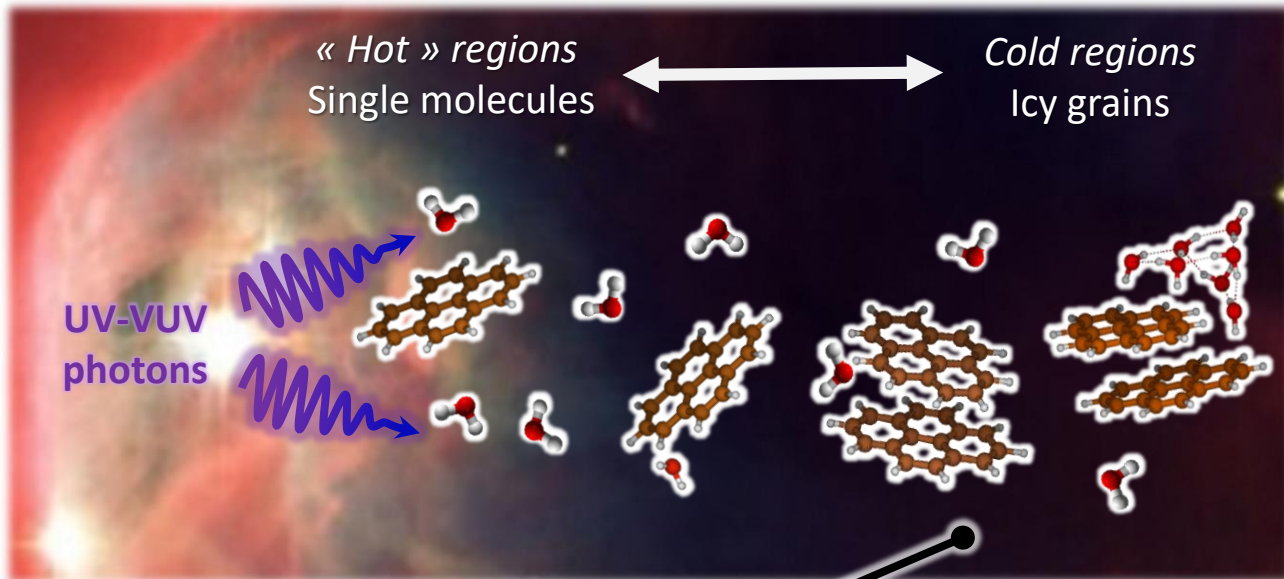
- 
- 1) Method to study the VUV photoprocessing of PAH⁺
 - 2) VUV photoprocessing of H_n-Cor⁺
 - 3) Role of proton in PAH-water interactions
 - 4) Perspective: IR spectroscopy of PAH_m(H₂O)_n⁺ clusters

Example of PAH-water interactions in astrochemistry

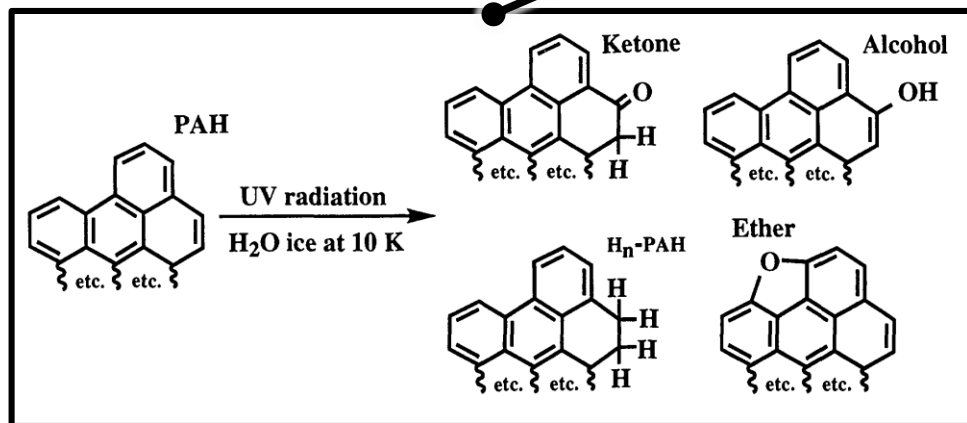


See e.g. D. J. Burke et al., *PCCP*, **12**:5947 (2010), Guélin & Cernicharo, *Front. Astron. Space Sci.* **9** (2022)

Example of PAH-water interactions in astrochemistry

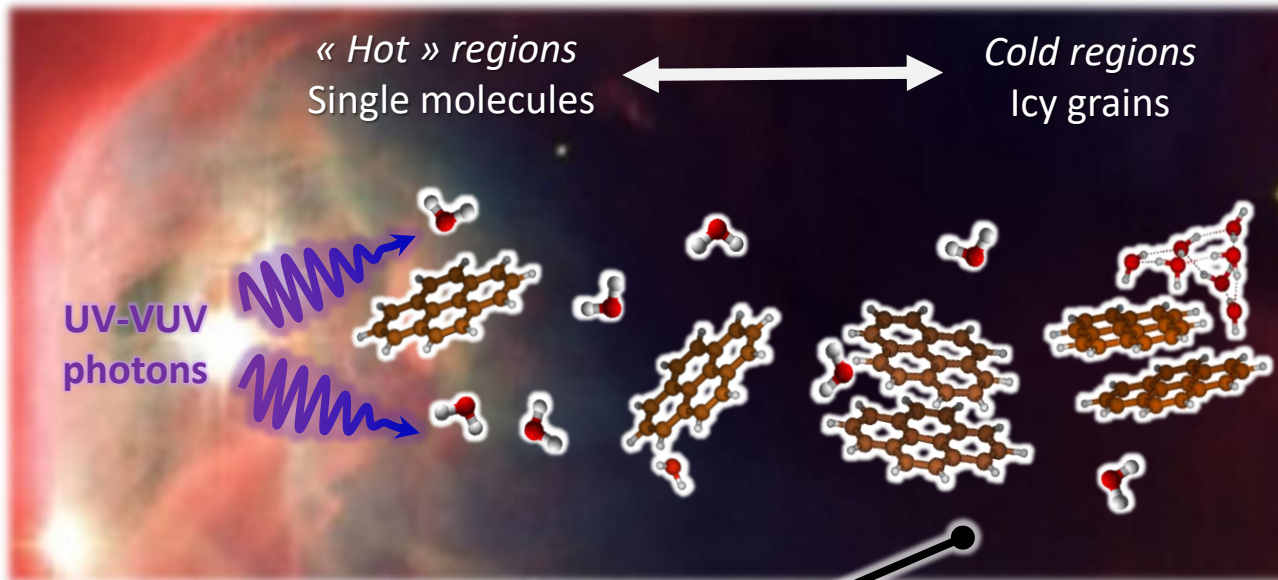


See e.g. D. J. Burke et al., *PCCP*, **12**:5947 (2010), Guélin & Cernichou, *Front. Astron. Space Sci.* **9** (2022)

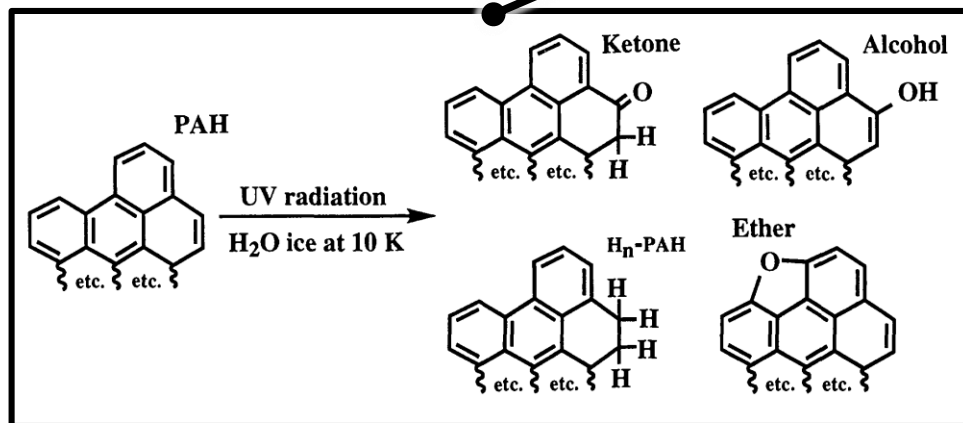


M. P. Bernstein et al., *Science*, **283**, 1135 (1999), S. A. Sandford et al., *ApJ*, **538**, 691 (2000)

Example of PAH-water interactions in astrochemistry



See e.g. D. J. Burke et al., *PCCP*, **12**:5947 (2010), Guélin & Cernichou, *Front. Astron. Space Sci.* **9** (2022)



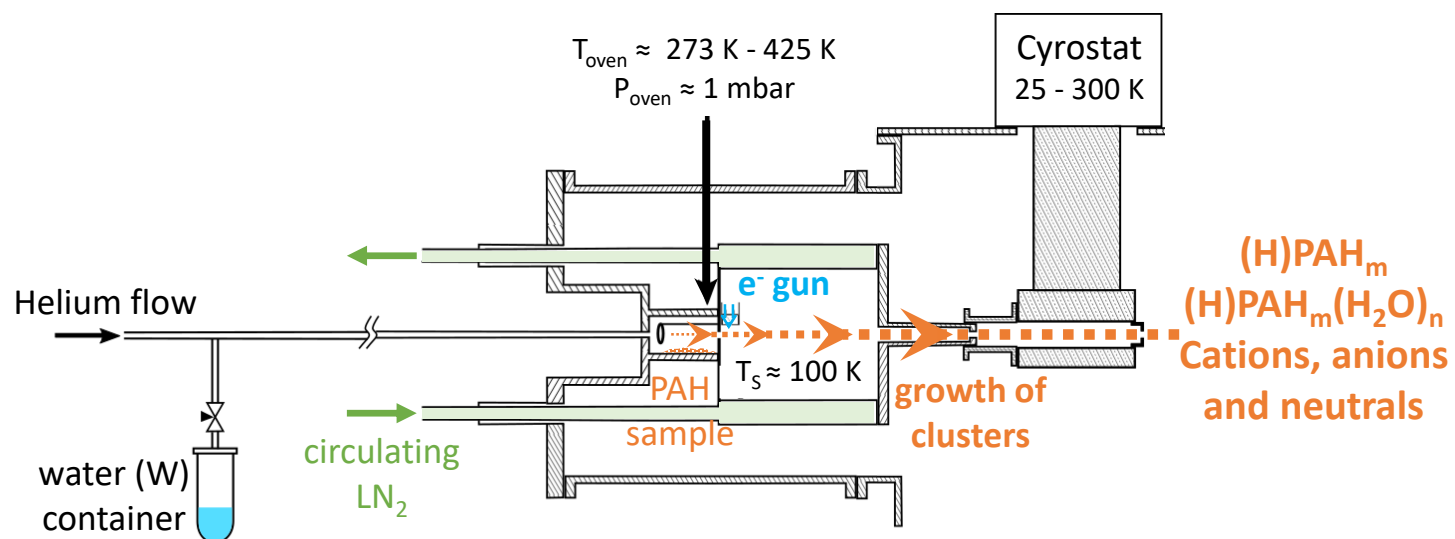
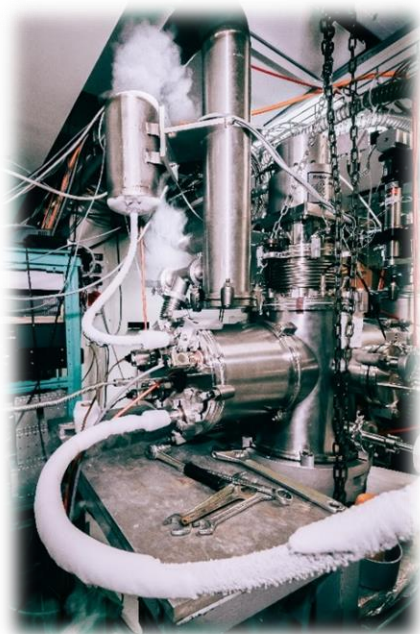
M. P. Bernstein et al., *Science*, **283**, 1135 (1999), S. A. Sandford et al., *ApJ*, **538**, 691 (2000)

Context: molecular complexification in astro-relevant environment

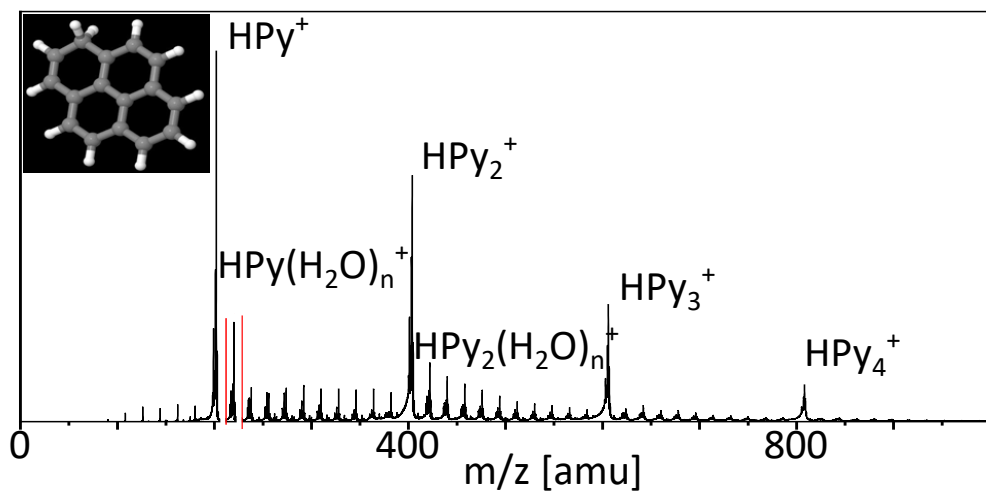
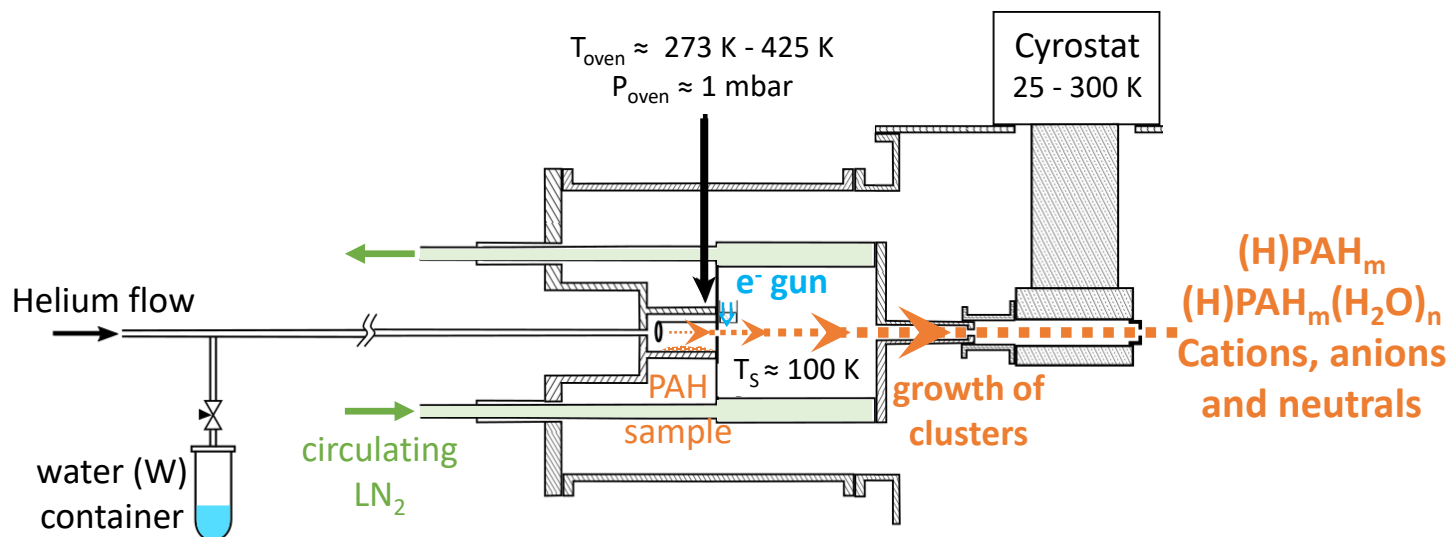
Aim: better understand the reaction at the quantum level including proton migration which seems to have a key role

Target systems: (H)PAH_m(H₂O)_n⁺ clusters studied by systematically adding PAH units or H₂O units

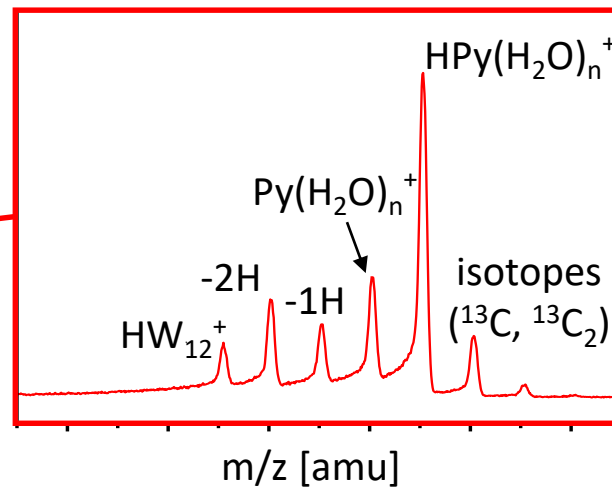
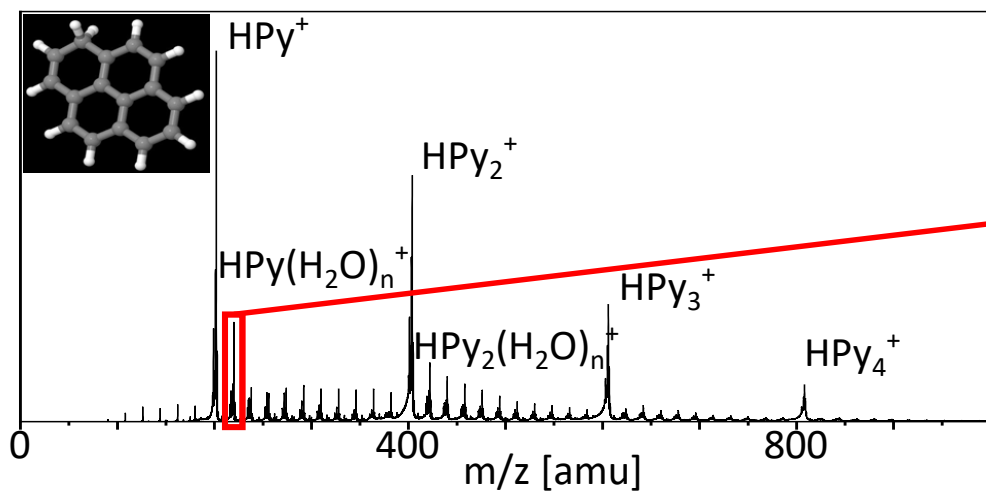
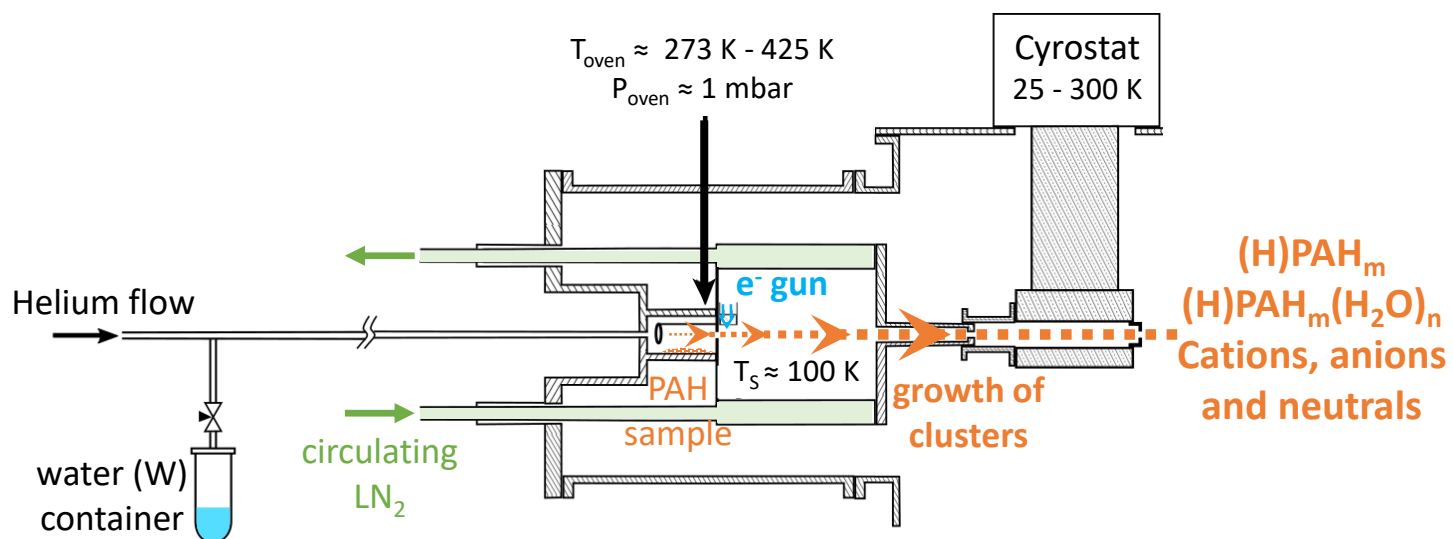
A molecular aggregation source to produce PAH-water clusters



A molecular aggregation source to produce PAH-water clusters

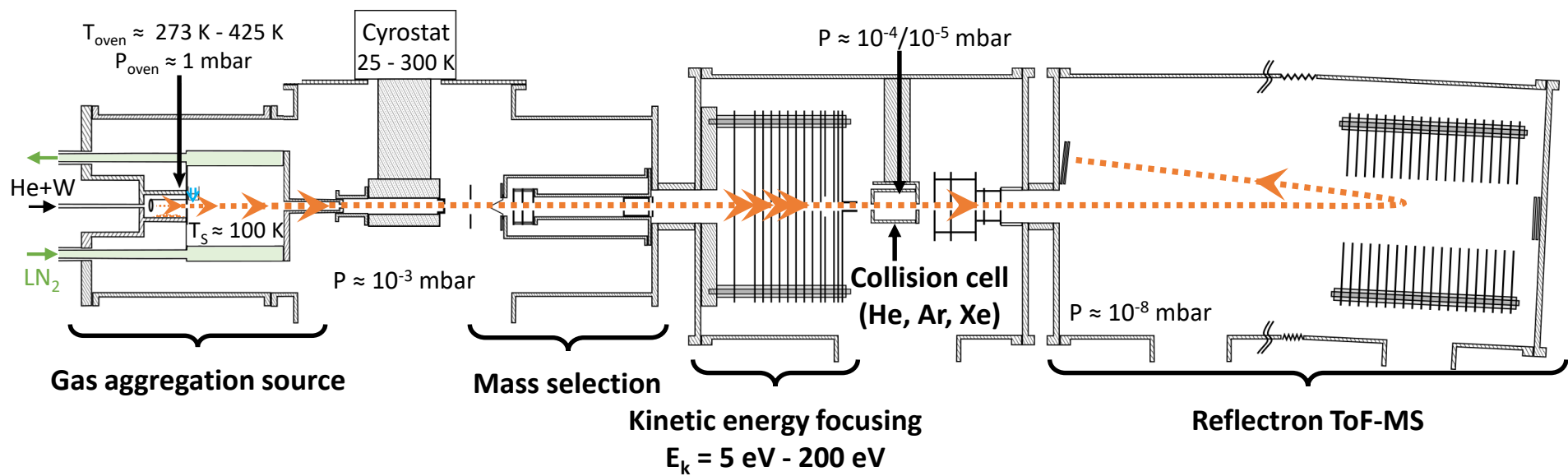


A molecular aggregation source to produce PAH-water clusters

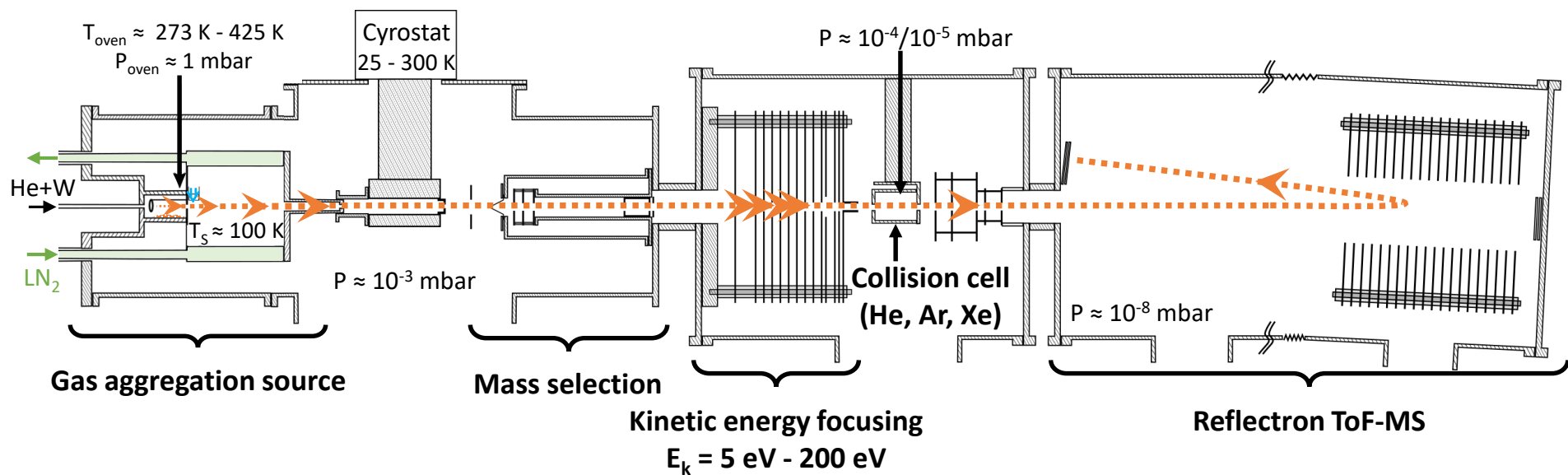


Braud, I. et al. *Rev. Sci. Instr.* **88**, 043102 (2017)

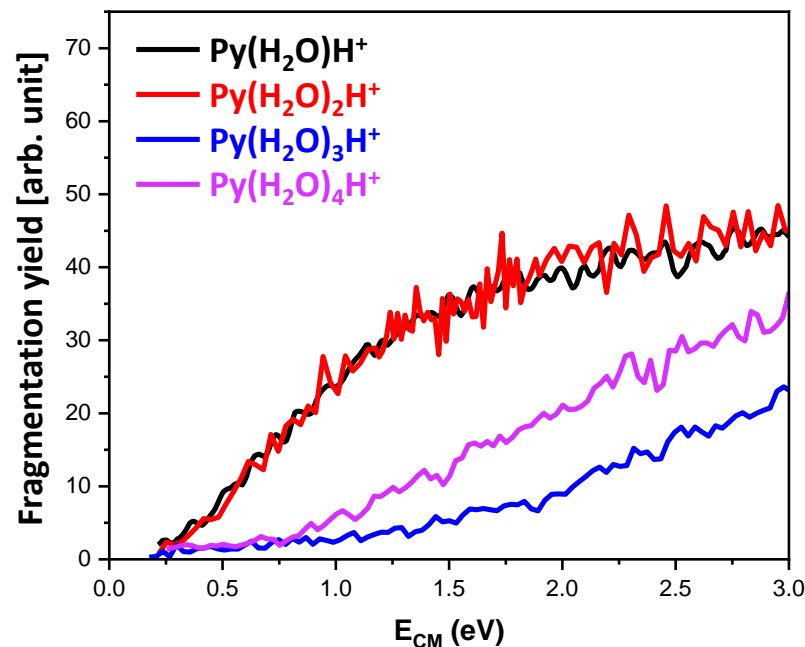
Collision induced dissociation at controlled kinetic energy



Collision induced dissociation at controlled kinetic energy

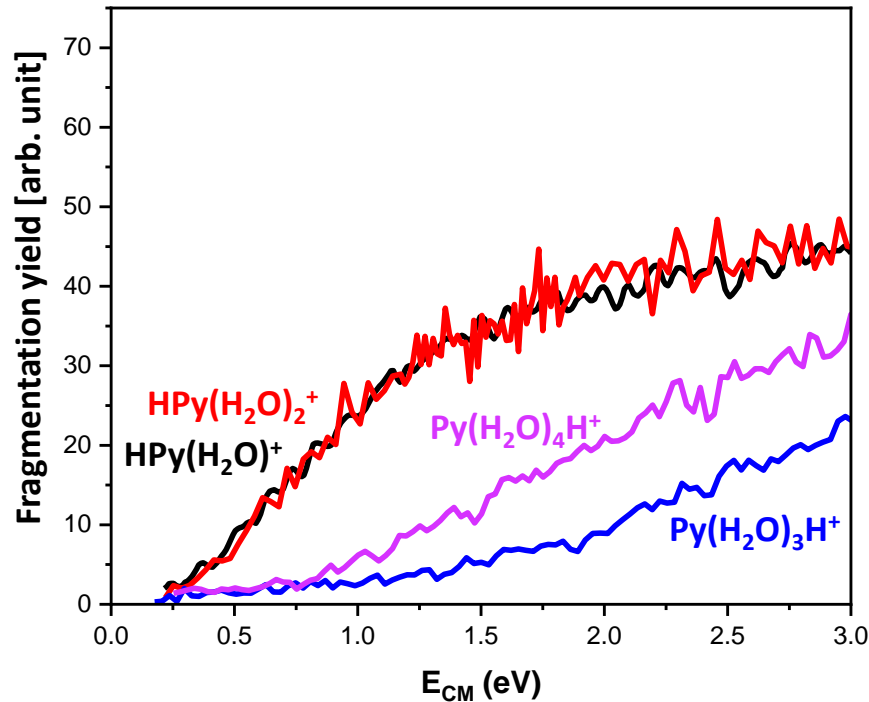


$$E_{\text{CM}} \propto \frac{m_{\text{col.}}}{m_{\text{col.}} + M_{\text{ion}}} E_k$$



Nair, A. M. et al. *PCCP* **26**, 5947 (2024)

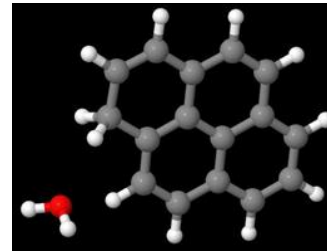
Proton localization in Pyrene(H₂O)_nH⁺



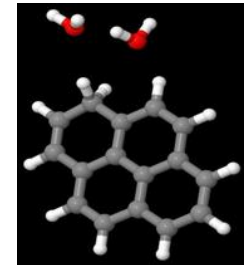
Experiment (TCID)

Specific dissociation behaviors for Py(H₂O)_nH⁺, with a “switch” from n = 3

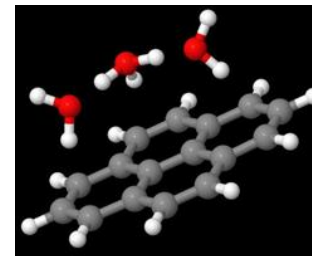
HPy(H₂O)⁺
E_D = 0.3 eV



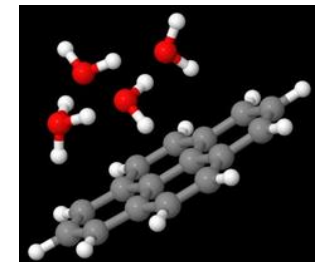
HPy(H₂O)₂⁺
E_D = 0.26 eV



Py(H₂O)₃H⁺
E_D = 0.83 eV



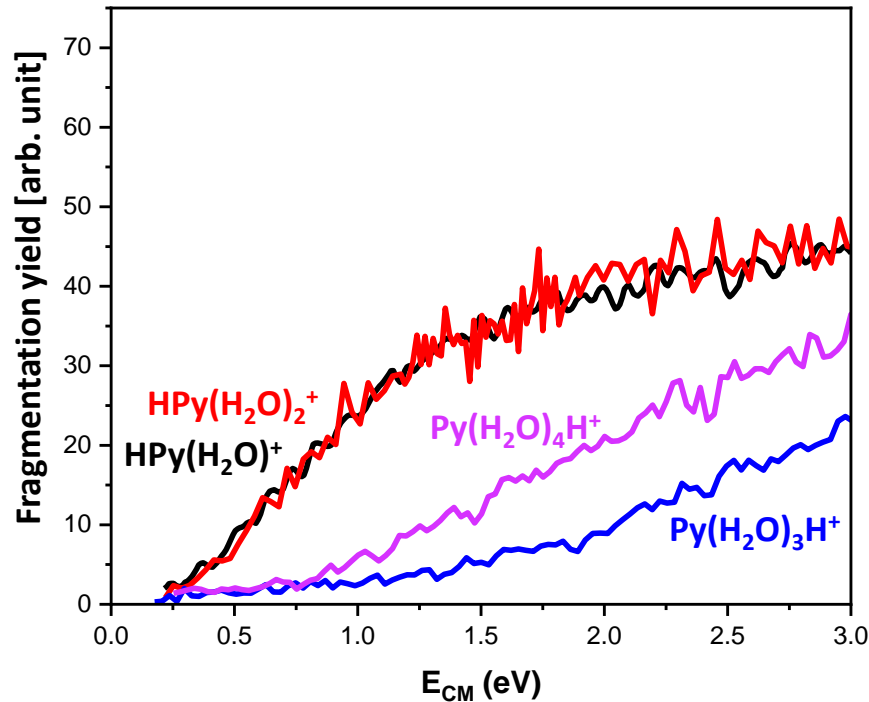
Py(H₂O)₄H⁺
E_D = 0.5 eV



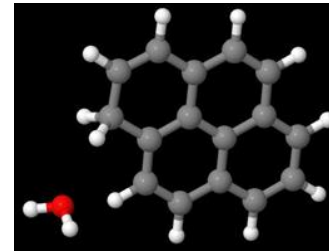
Theory (DFTB)

Structures and dissociation energies show that proton affinity evolves with n

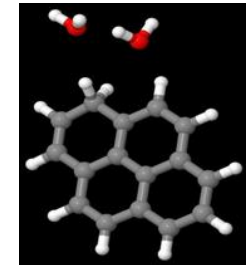
Proton localization in Pyrene(H₂O)_nH⁺



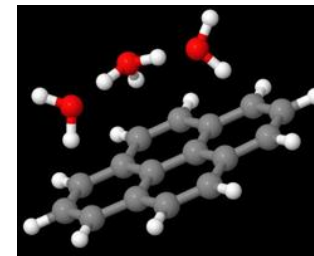
HPy(H₂O)⁺
E_D = 0.3 eV



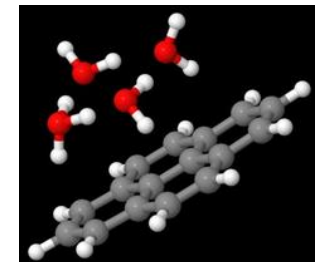
HPy(H₂O)₂⁺
E_D = 0.26 eV



Py(H₂O)₃H⁺
E_D = 0.83 eV



Py(H₂O)₄H⁺
E_D = 0.5 eV



Experiment (TCID)

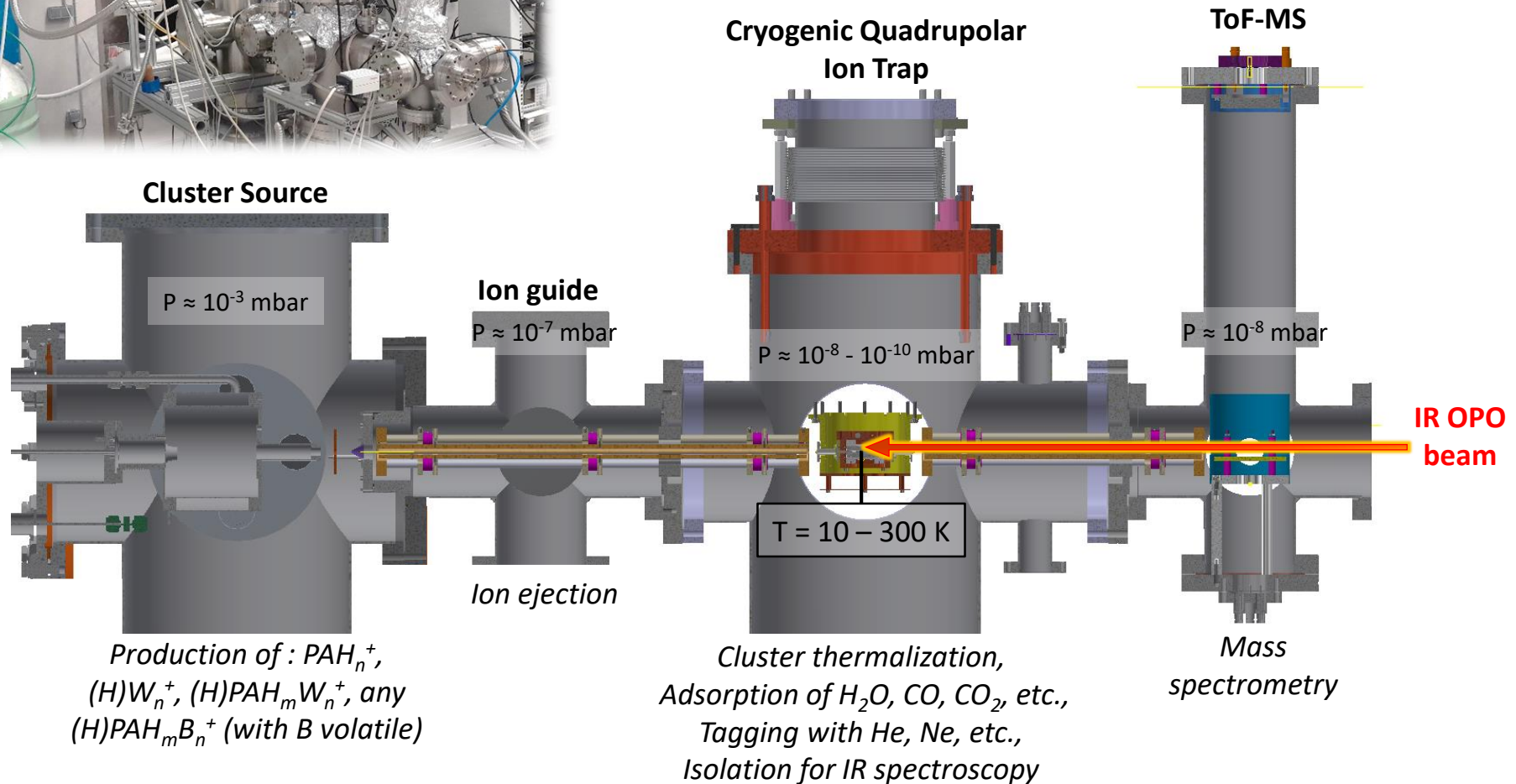
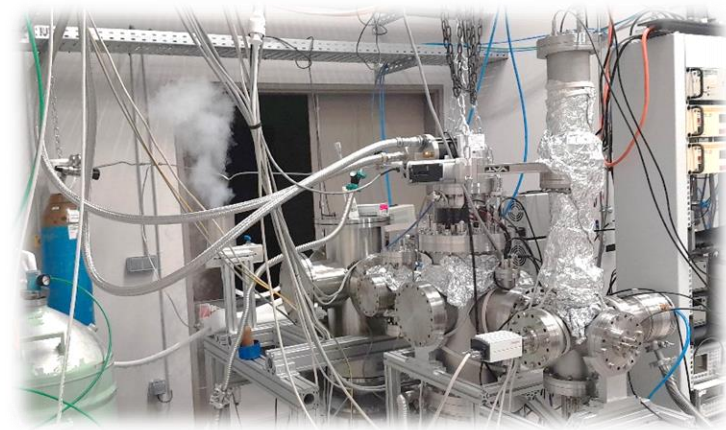
Specific dissociation behaviors for Py(H₂O)_nH⁺,
with a “switch” from n = 3

Theory (DFTB)

Structures and dissociation energies show
that proton affinity evolves with n

➔ More details about theory in the talk of **Heloïse Leboucher (tomorrow, 2:30 pm)** ←

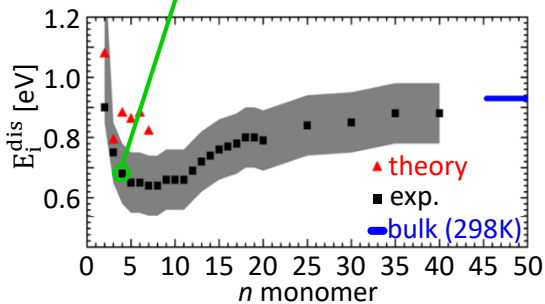
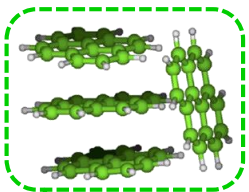
Perspective: measuring the IR spectra of tagged $\text{PAH}_m(\text{H}_2\text{O})_n^+$ clusters



Perspective: measuring the IR spectra of tagged PAH_m(H₂O)_n⁺ clusters

Production with the molecular cluster source

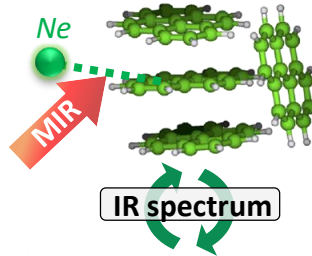
Pyr₄⁺



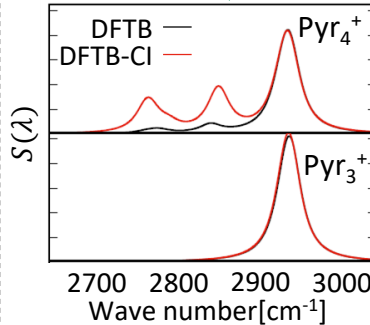
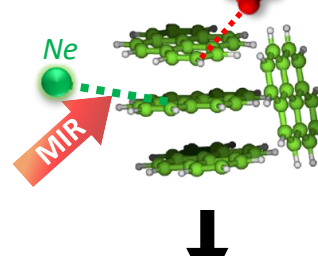
Zamith, S. et al., *J. Chem. Phys.* **151**, 1943303 (2019)

Exp. vs. Theory - Computation with DFTB

Pyr₄⁺ · Ne



(Pyr₄H₂O)⁺ · Ne



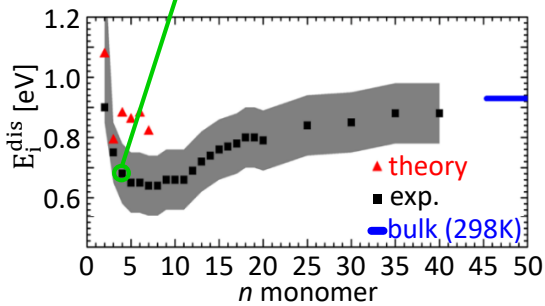
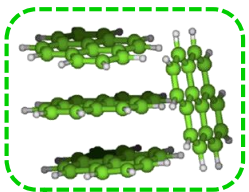
Dontot, L. et al. *EPJD.* **74**, 216 (2020)

Spectral signature
+
Adsorption site

Perspective: measuring the IR spectra of tagged PAH_m(H₂O)_n⁺ clusters

Production with the molecular cluster source

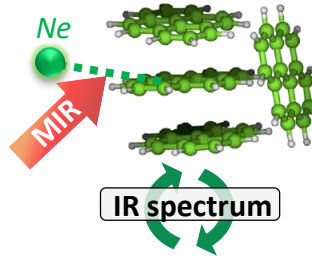
Pyr₄⁺



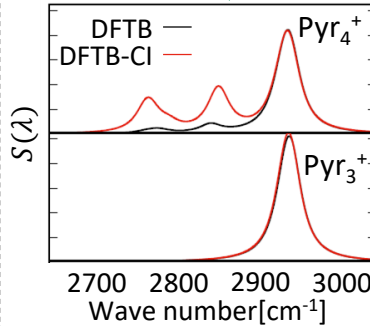
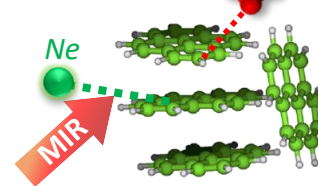
Zamith, S. et al., *J. Chem. Phys.* **151**, 1943303 (2019)

Exp. vs. Theory - Computation with DFTB

Pyr₄⁺ · Ne



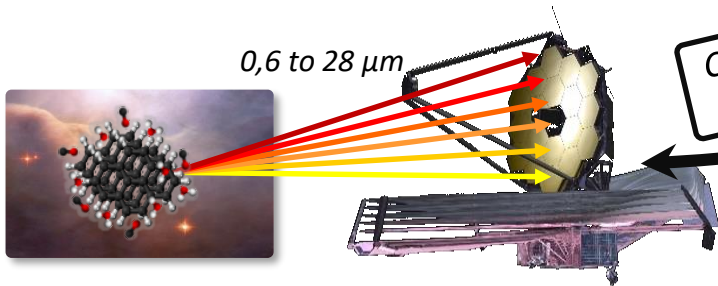
(Pyr₄H₂O)⁺ · Ne



Dontot, L. et al. *EPJD.* **74**, 216 (2020)

Spectral signature
+
Adsorption site

0,6 to 28 μm



Complementary
with JWST

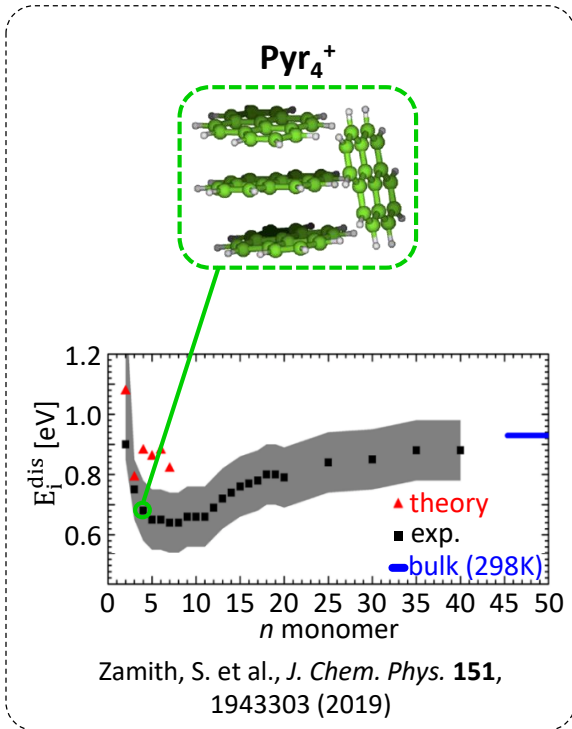
PDRs4all JWST Program

Berné, O. et al., *PASP* **134**, 054301 (2022)

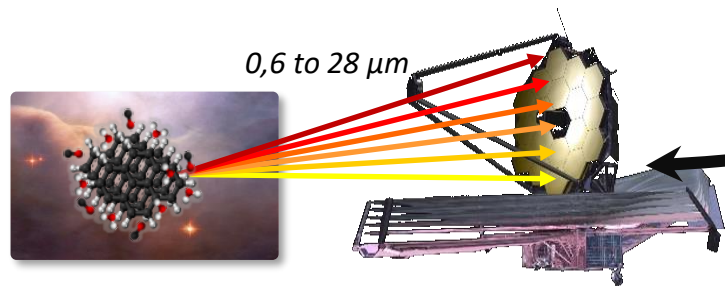
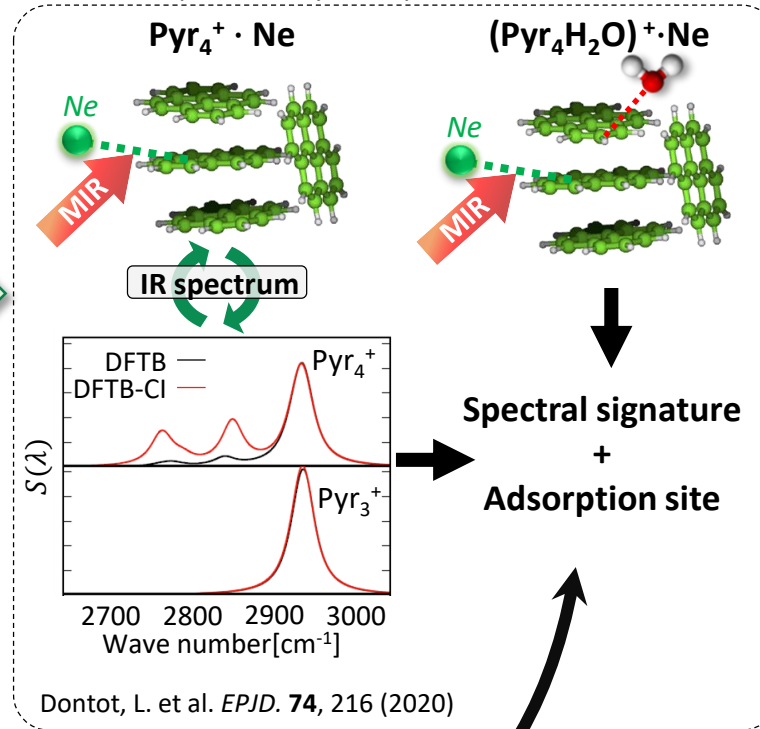
Marciniak, A. et al. *Eur. Conf. on Lab. Astrophys.* **59** (2023)

Perspective: measuring the IR spectra of tagged PAH_m(H₂O)_n⁺ clusters

Production with the molecular cluster source



Exp. vs. Theory - Computation with DFTB



PDRs4all JWST Program
Berné, O. et al., *PASP* **134**, 054301 (2022)

ANR JCJC CASSOULExp
ChAracterizing the Spectral Signatures of astrO-relevant carbonaceoUs cLusters Experimentally

anr® → PhD position will open in September 2025 ← anr®

Contact me at alexandre.marciniak@irsamc.ups-tlse.fr

Acknowledgments



S. Zamith



F. Baterdouk



A. Nair

P. Moretto-Capelle, J.-M. L'Hermite



V. Rao Mundlapati, V. Meloottayil & C. Joblin

Support : A. Bonnamy, L. Nogues, O. Coeur-Joly, D. Murat



Laboratoire de Chimie et Physique Quantiques



*A. Simon,
H. Leboucher,
M. Rapacioli,
F. Spiegelman*



G. Mulas



*M. Vilas-Varela,
D. Peña*



UNIVERSITÉ
TOULOUSE III
PAUL SABATIER



nanocosmos



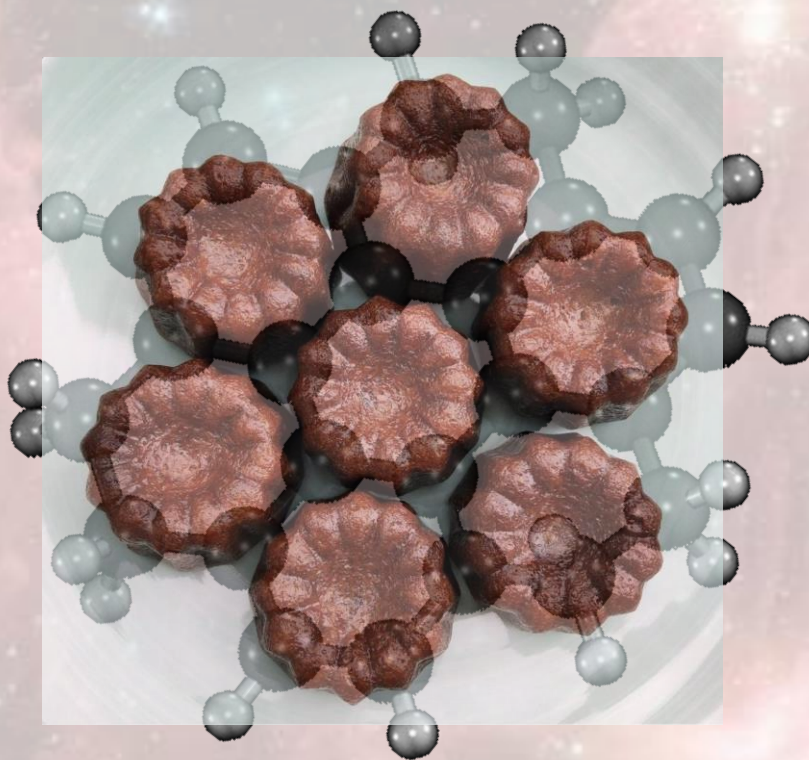
European Research Council
Established by the European Commission



FÉDÉRATION DE RECHERCHES HAUTE ÉNERGIE ET INTERACTIONS



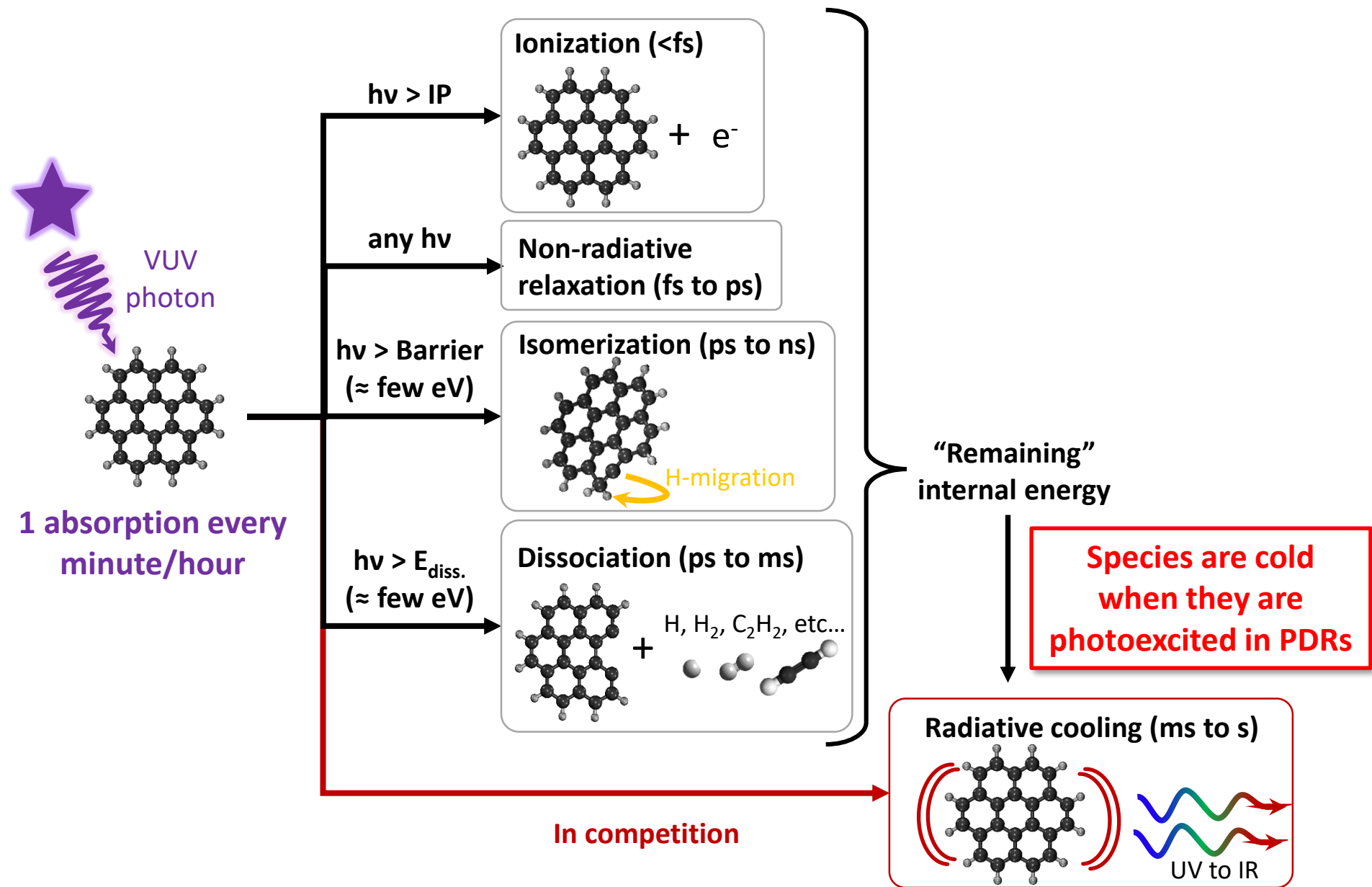
Thanks for your attention !



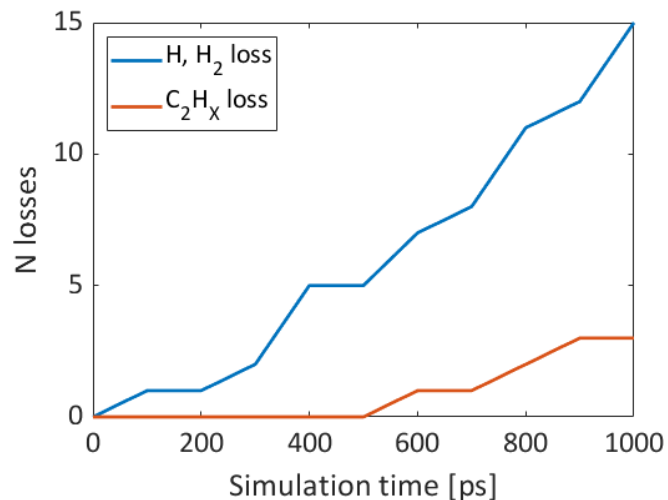
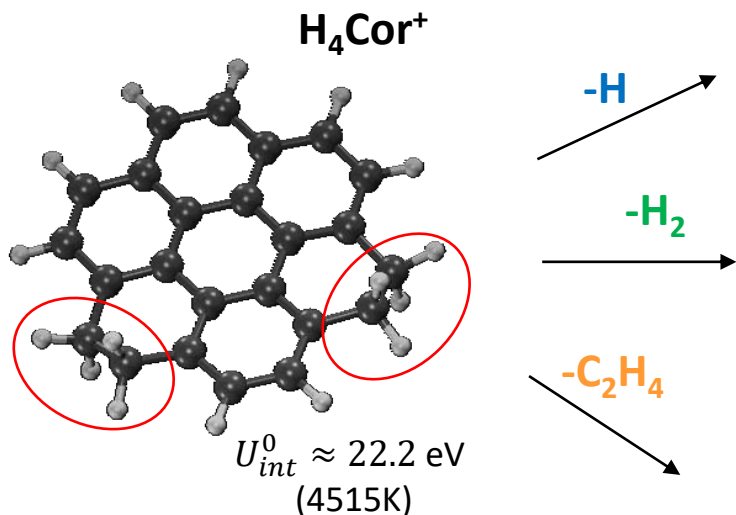


Annexes

Relaxation of a photoexcited PAH in photodissociation regions



But... MD simulations for H_4Cor^+

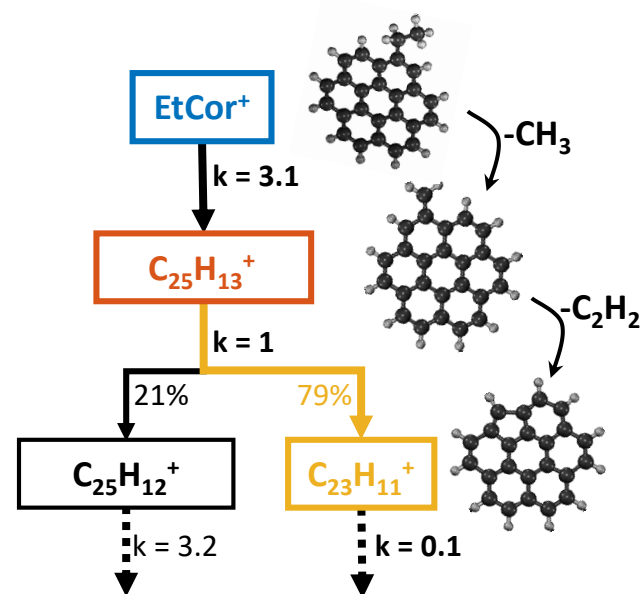
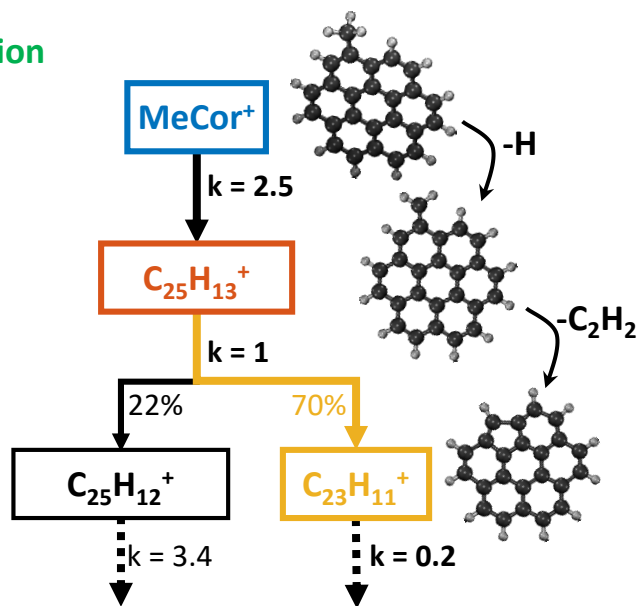
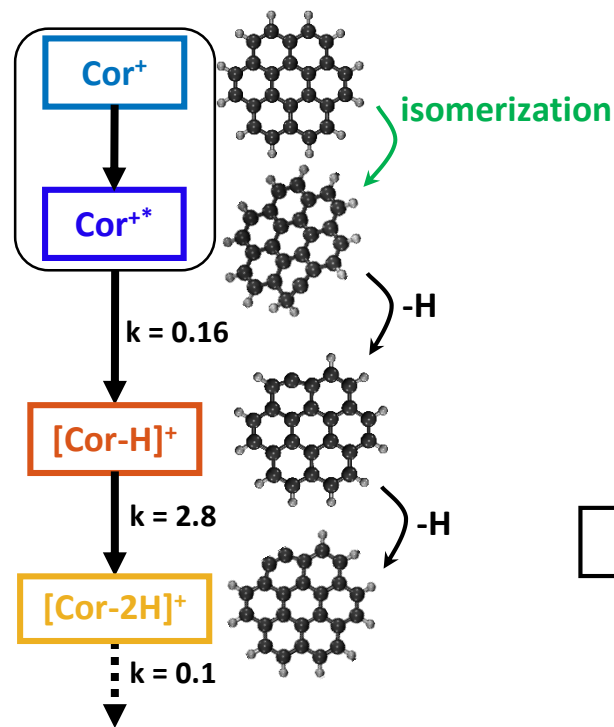
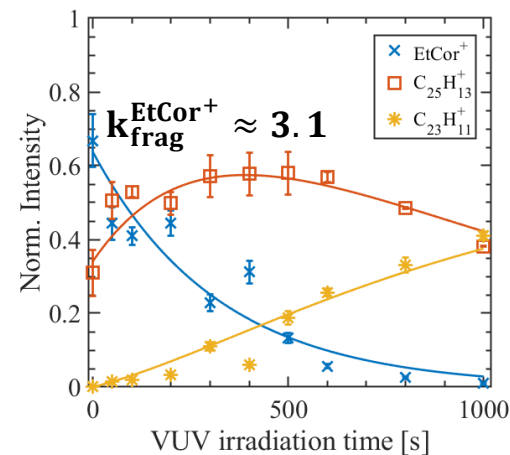
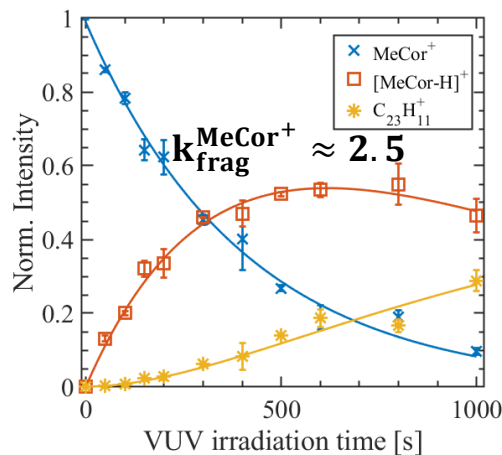
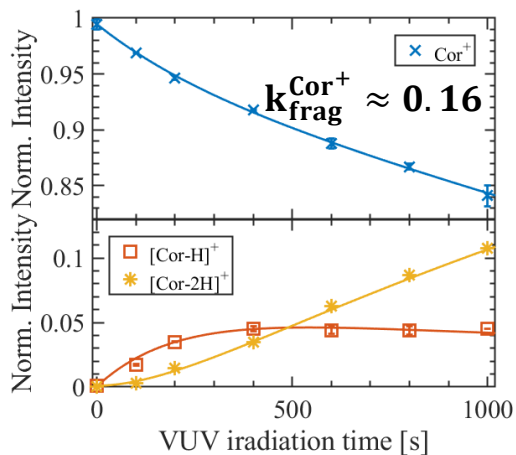


180 runs of 1 ns
eMon-Nano

✗ Carbon fragmentation channels for H_4Cor^+ not observed experimentally

✓ C-losses are neglectable with respect to H-losses

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



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

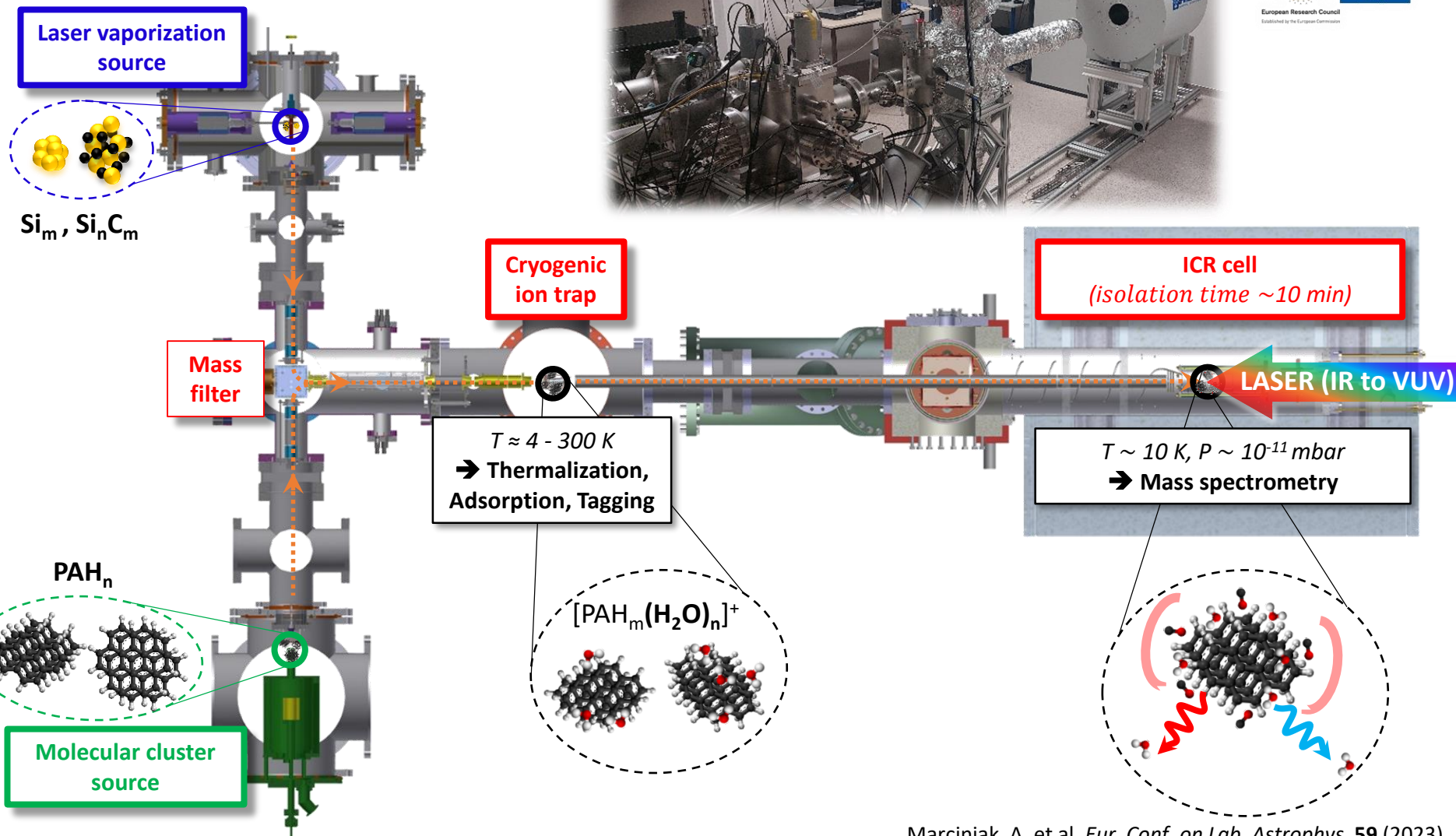
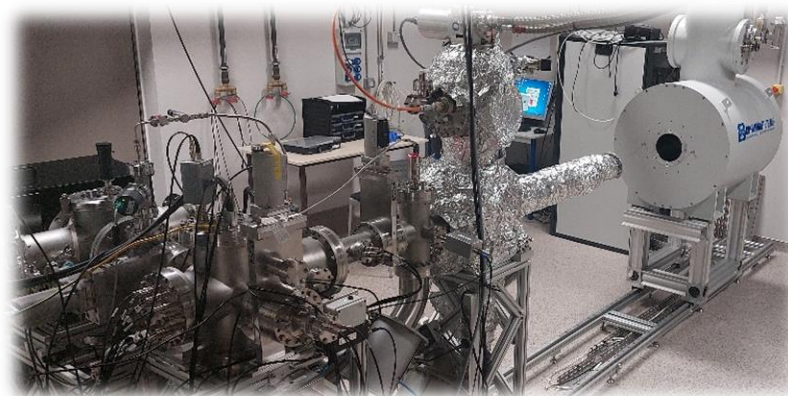
Marciniak, A. et al. A&A 642, A42 (2021)

Simulating photon-gas-nanograin interactions with PIRENEA 2

nanocosmos



European Research Council
Established by the European Commission



Marciniak, A. et al. *Eur. Conf. on Lab. Astrophys.* **59** (2023)