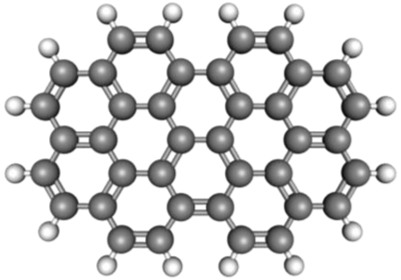
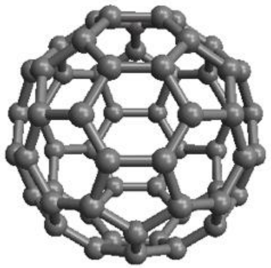
PAHs as tracers of the matter cycle, from evolved stars to the solar system: the contribution of laboratory astrophysics

Christine Joblin





cnrs dépasser les frontières

irap astrophysique & planétologie

cnes

Université de Toulouse

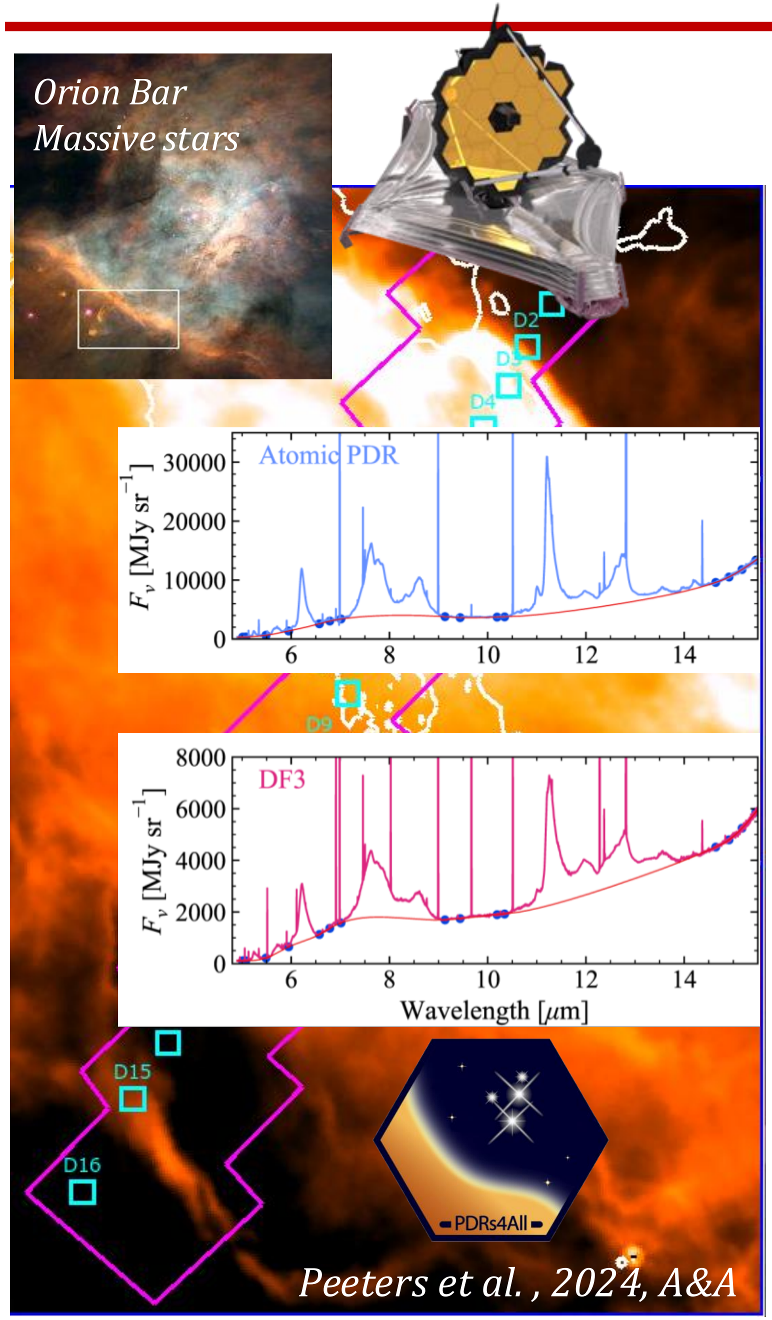
Laboratory astrophysics

- A research field associated with key questions in astrophysics
- Includes experimental, theoretical and modelling work
- Unusual conditions of astrophysical environments (e.g., the interstellar medium) → design of new dedicated laboratory setups
- Diversity of systems and processes
- Use of large facilities/infrastructures (light sources, heavy ions, electrostatic storage rings, analytical tools …)
- Involves several communities (key to its success):
    - Astrophysics: atomic and molecular physics, nuclear physics, plasma physics, surface science, quantum chemistry, …
    - Exploration of the Solar System: analytical chemistry, organic chemistry, cosmochemistry,…

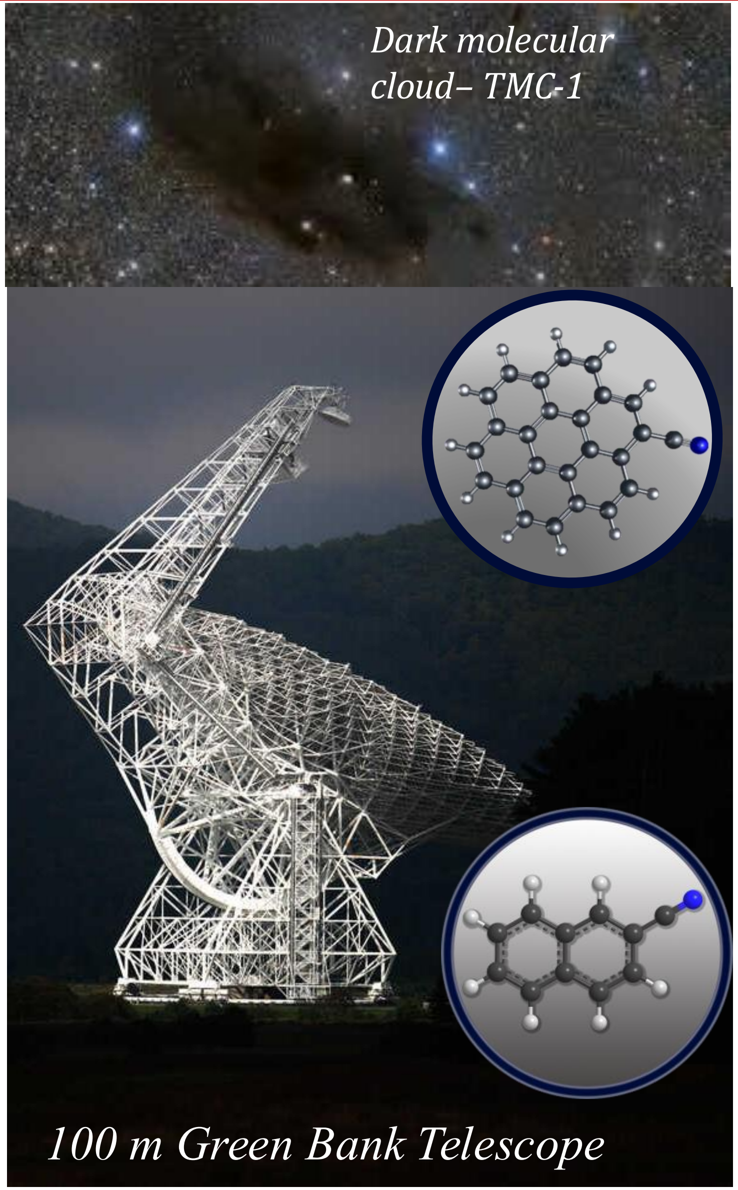
→ "Action Thématique (AT) **PCMI** – Physique et Chimie du Milieu Interstellaire"

pcmi

PAHs: Messengers from Stars to the Solar System

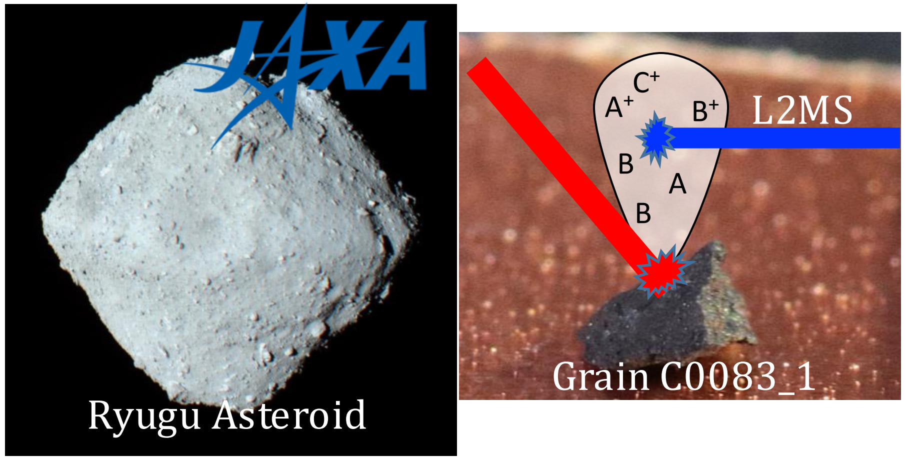


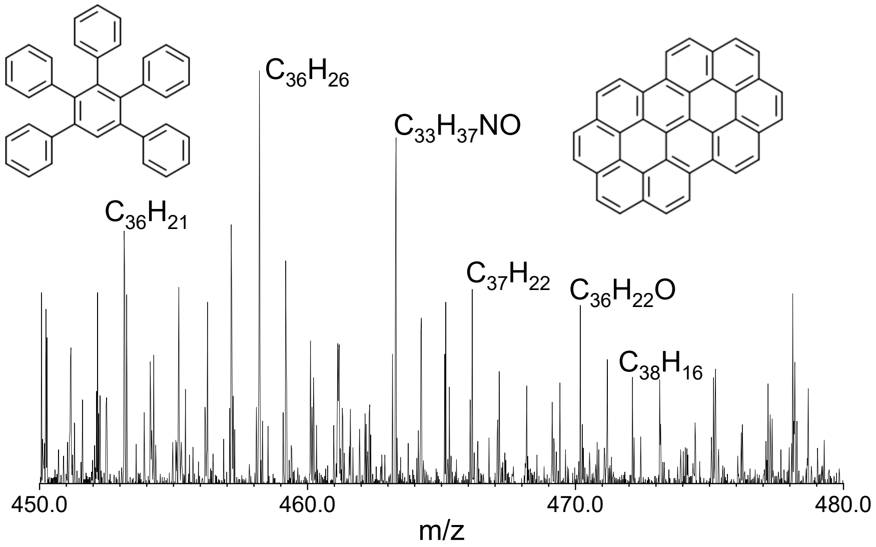
Peeters et al. , 2024, A&A



Wenzel et al. 2025, ApJ Let.

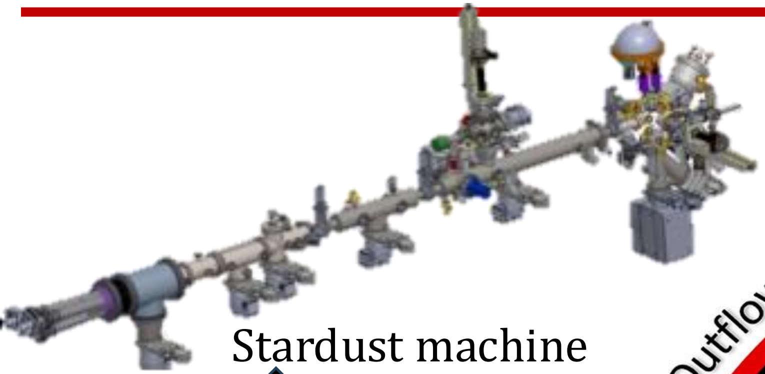
Sample return missions





Sabbah et al. 2024, Nat. Sci.

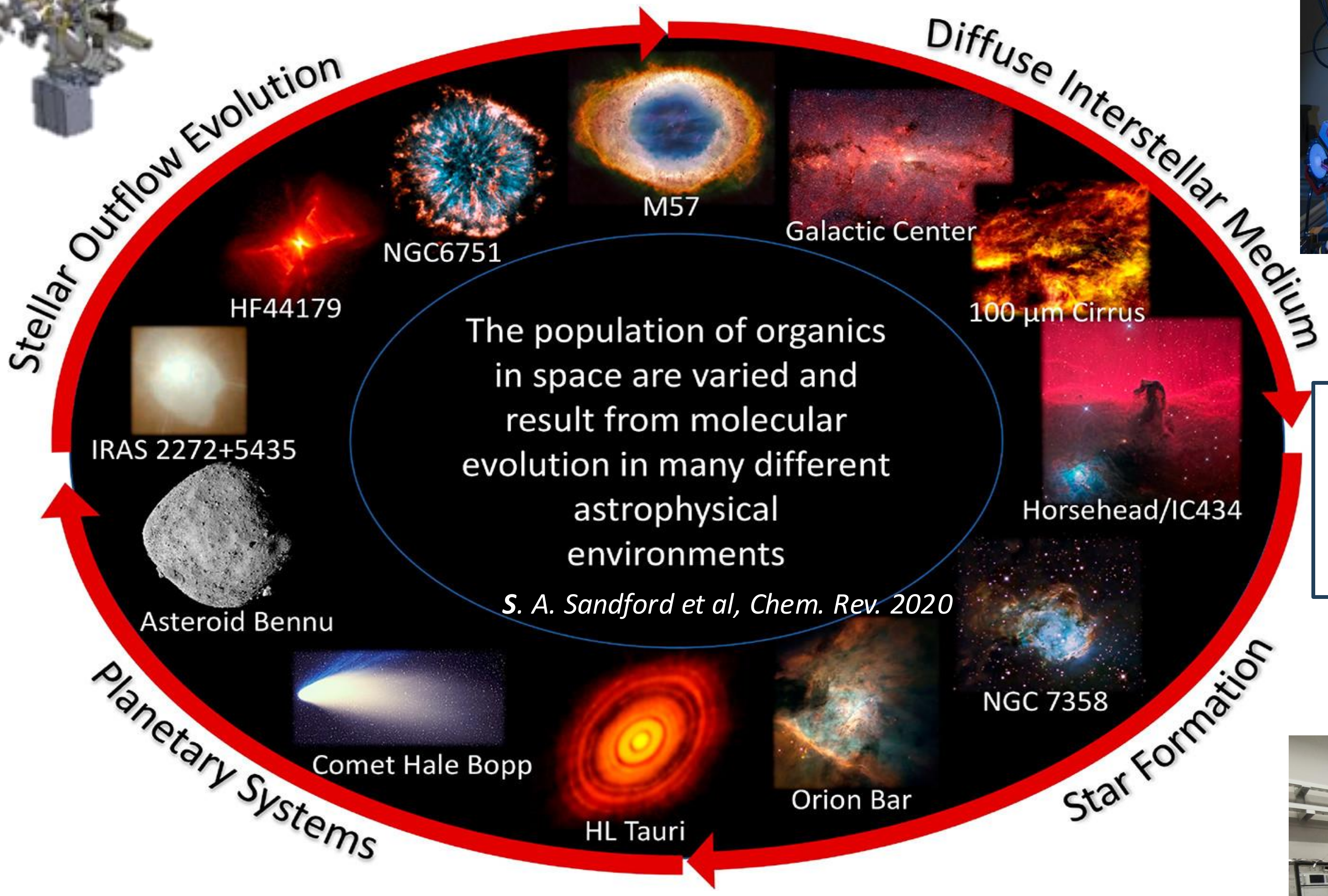
Laboratory astrophysics: Cosmic matter cycle

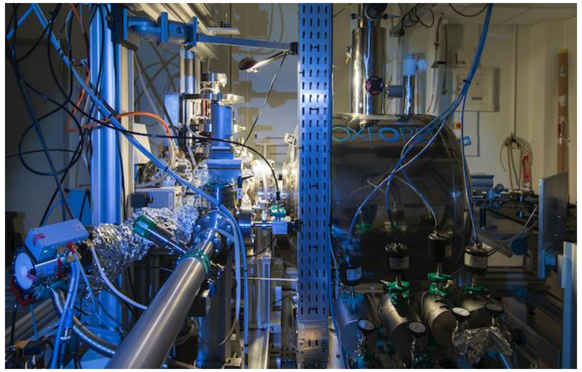


Stardust machine

Production and analysis of stardust analogues
Analysis of Solar System samples

AROMA molecular analyzer

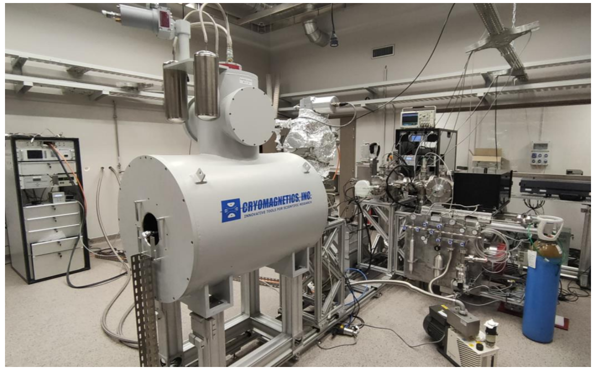




PIRENEA

Simulation chambers
Cryogenic temperatures and ultra-high vacuum
Ultraviolet radiation

PIRENEA 2



CSIC CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

nanoCOSMOS

erc

cnrs dépasser les frontières

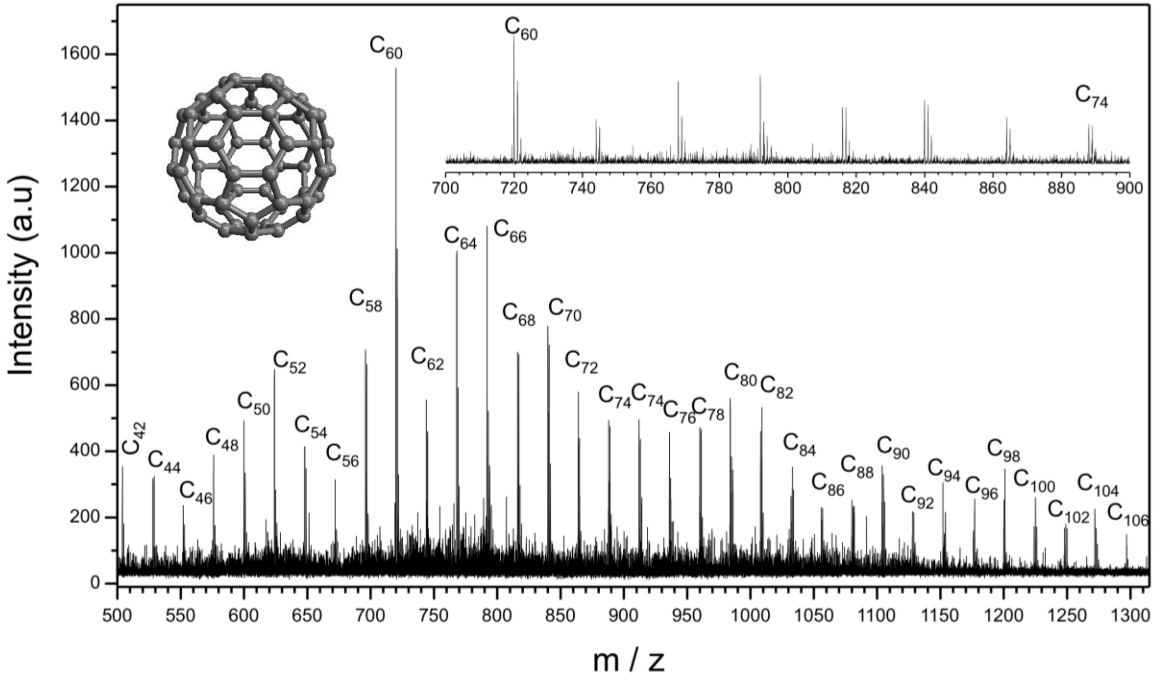
Results: Large PAHs and fullerenes in meteorites/asteroids

AROMA molecular analyzer

THE ASTROPHYSICAL JOURNAL, 931:91 (12pp), 2022 June 1
https://doi.org/10.3847/1538-4357/ac69dd

Detection of Cosmic Fullerenes in the Almahata Sitta Meteorite: Are They an Interstellar Heritage?

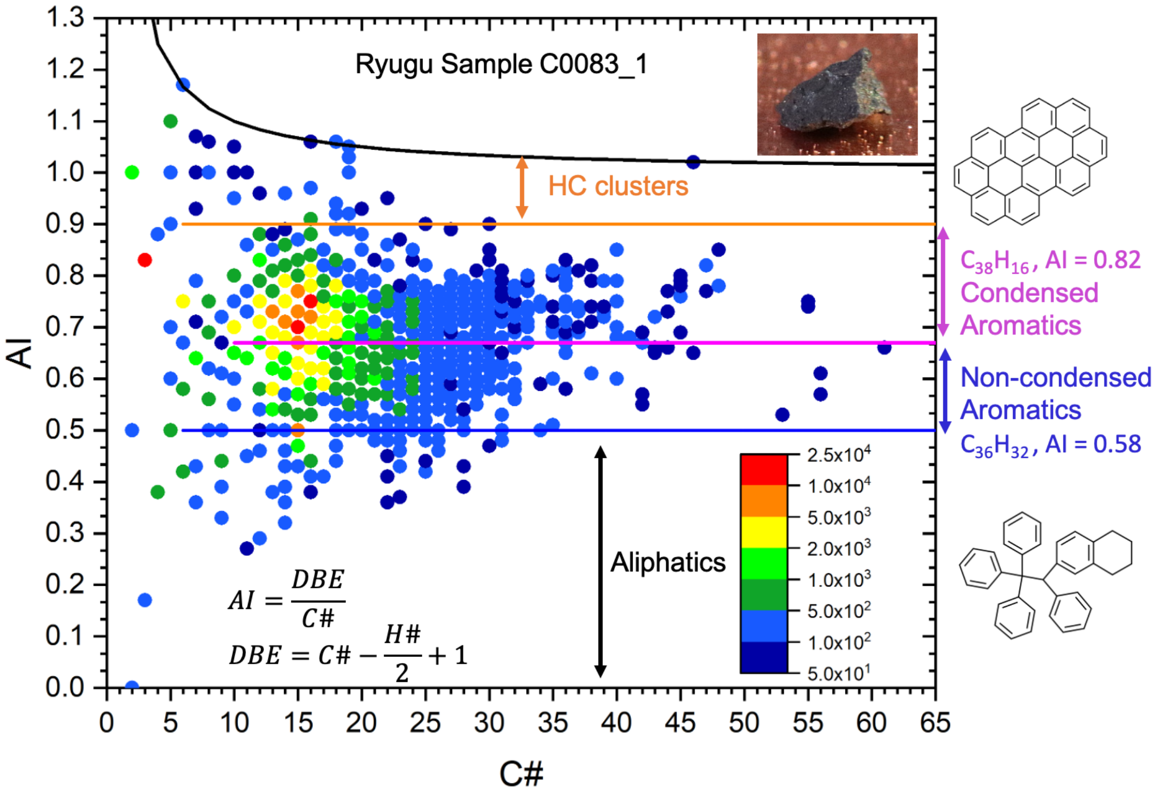
Hassan Sabbah[1], Mickaël Carlos[1], Peter Jenniskens[2], Muawia H. Shaddad[3], Jean Duprat[4], Cyrena A. Goodrich[5], and Christine Joblin[1]



DOI: 10.1002/ntls.20240010
RESEARCH ARTICLE
Natural Sciences

First direct detection of large polycyclic aromatic hydrocarbons on asteroid (162173) Ryugu samples: An interstellar heritage

Hassan Sabbah | Ghylaine Quitté | Karine Demyk | Christine Joblin

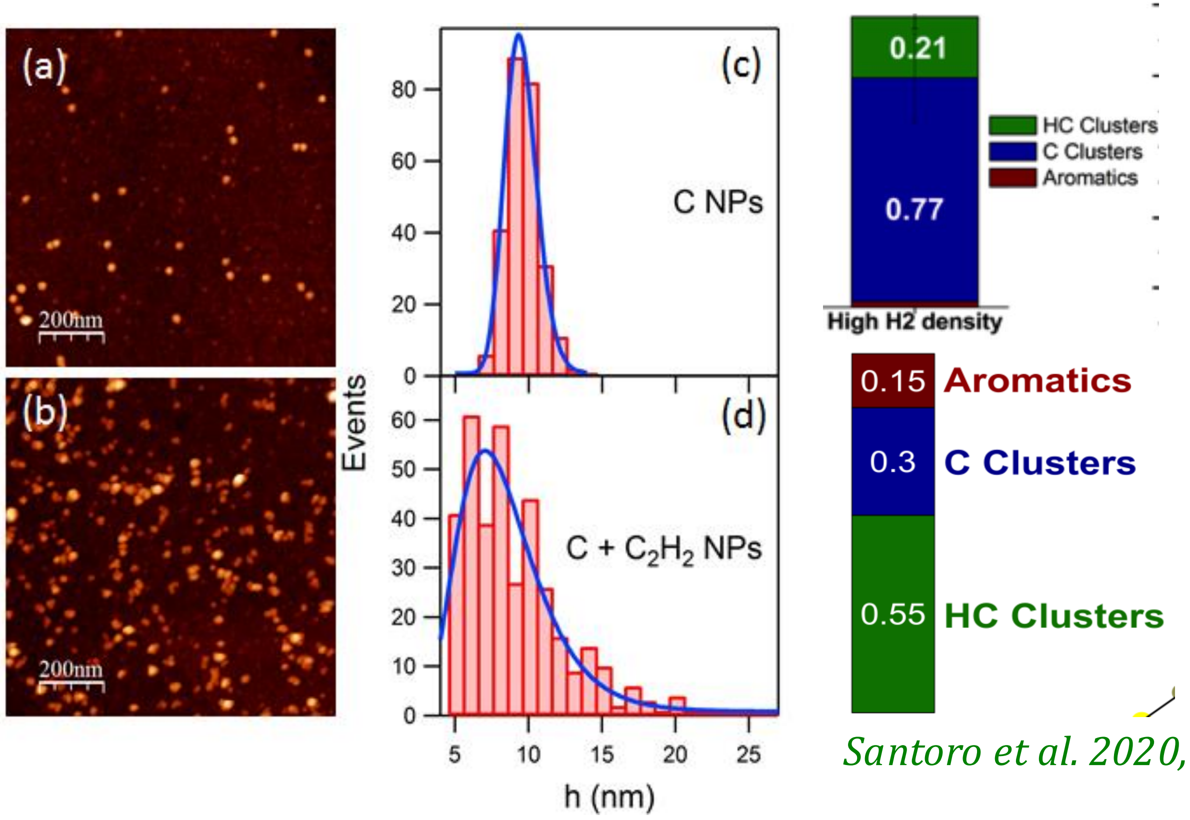


Results: Role of C_2H_2 and metals in PAH formation (high temperatures)

Stardust machine

Prevalence of non-aromatic carbonaceous molecules in the inner regions of circumstellar envelopes

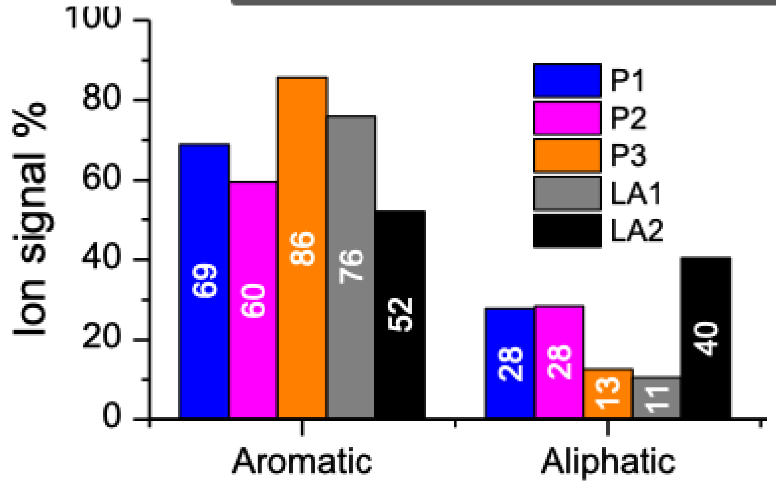
Lidia Martínez[1,9], Gonzalo Santoro[1,9], Pablo Merino[1,2,9], Mario Accolla[1], Koen Lauwaet[3], Jesús Sobrado[4], Hassan Sabbah[5,6], Ramón J. Pelaez[7], Victor J. Herrero[7], Isabel Tanarro[7], Marcelino Agúndez[2], Alberto Martín-Jimenez[3], Roberto Otero[3], Gary J. Ellis[8], Christine Joblin[5*], José Cernicharo[2*] and José A. Martín-Gago[1*]



Santoro et al. 2020, ApJ

Dusty plasma reactor

Laser vaporization



→ Organometallic seeds

$Ag_nC_2H_m$ (n = 1–3; m = 0–2)

Catalysis for hydrocarbon formation

Bérard et al., 2021, Front. Astron. Space Sci. 8:654879

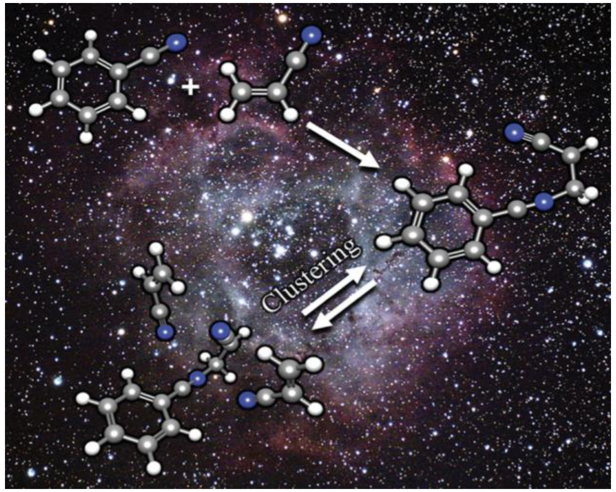
→ Specific role of Fe

Results: different chemistries for PAH formation (low temperatures)

Only two-body collisions are relevant!

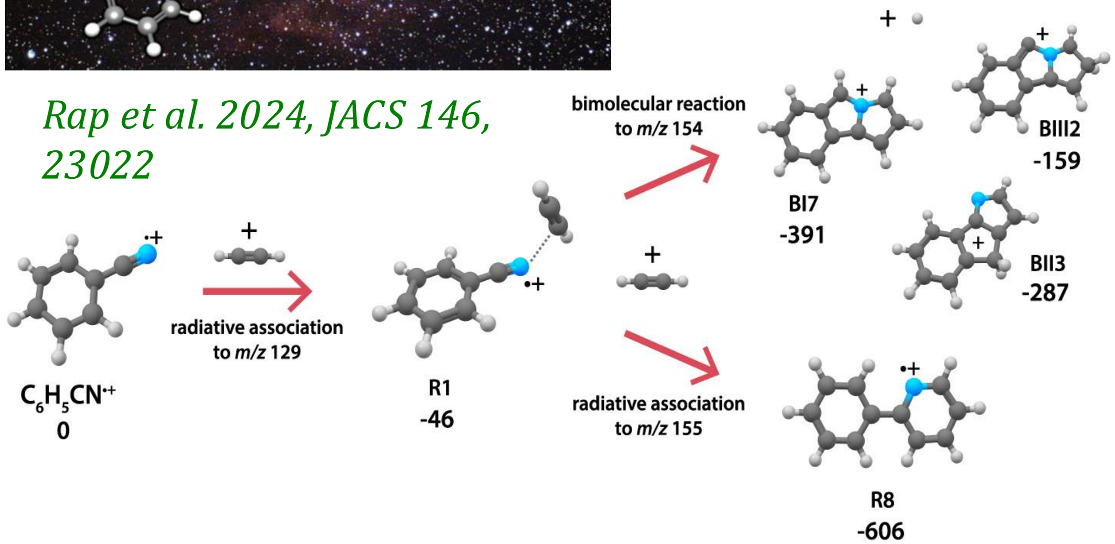
Ion-molecule reactions

- Role of adducts (covalent/non-covalent interactions) – *Moderate (400K) to cold temperatures*



Sutton et al. 2024, PCCP 26, 29708

Rap et al. 2024, JACS 146, 23022

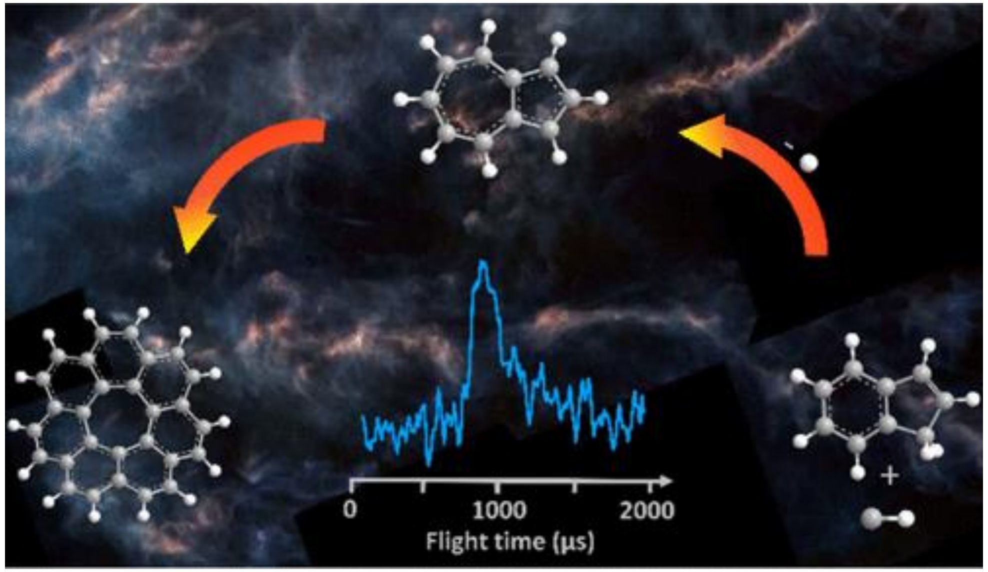


Neutral-neutral reactions

- Barrierless reaction

C_9H_8 + CH → $C_{10}H_8$ (azulene/naphthalene) + H

Low-temperature conditions of TMC-1



Yang et al. 2025, ACS Cent. Sci. 11, 322

Mechanisms of five key reaction pathways discussed.

Kaiser & Hansen 2021, JPCA 125, 3826

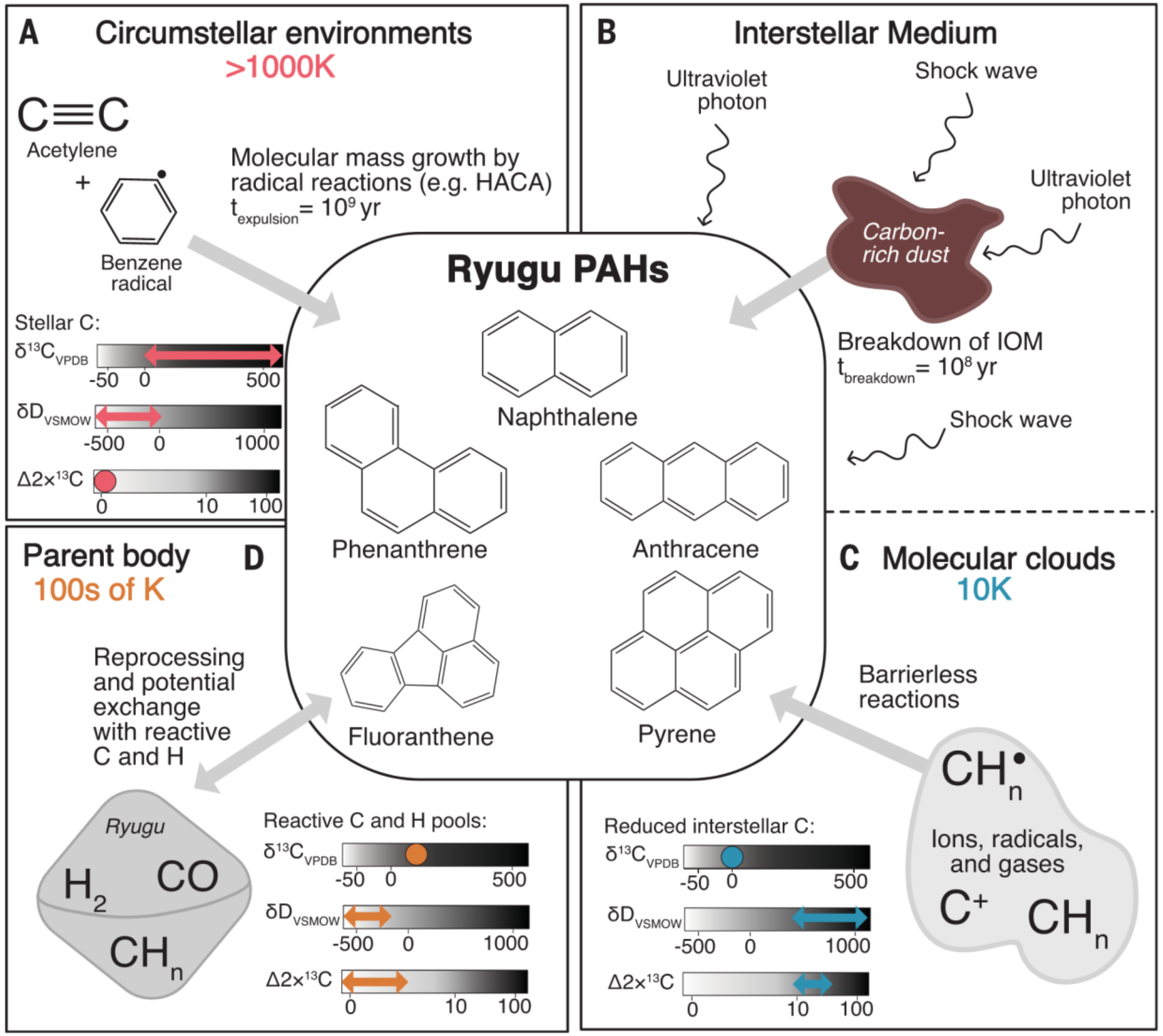
Different environments: different chemistries for PAH formation

ASTROCHEMISTRY

Polycyclic aromatic hydrocarbons in samples of Ryugu formed in the interstellar medium

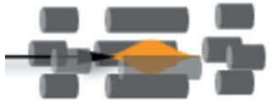
Zeichner et al. 2023, Science 382, 1411

Polycyclic aromatic hydrocarbons (PAHs) contain ≲20% of the carbon in the interstellar medium. They are potentially produced in circumstellar environments (at temperatures ≳1000 kelvin), by reactions within cold (~10 kelvin) interstellar clouds, or by processing of carbon-rich dust grains. We report isotopic properties of PAHs extracted from samples of the asteroid Ryugu and the meteorite Murchison. The doubly-^{13}C substituted compositions ($\Delta 2\times^{13}C$ values) of the PAHs naphthalene, fluoranthene, and pyrene are 9 to 51‰ higher than values expected for a stochastic distribution of isotopes. The $\Delta 2\times^{13}C$ values are higher than expected if the PAHs formed in a circumstellar environment, but consistent with formation in the interstellar medium. By contrast, the PAHs phenanthrene and anthracene in Ryugu samples have $\Delta 2\times^{13}C$ values consistent with formation by higher-temperature reactions.



Laboratory astrophysics: Interaction of PAHs with (VUV) photons

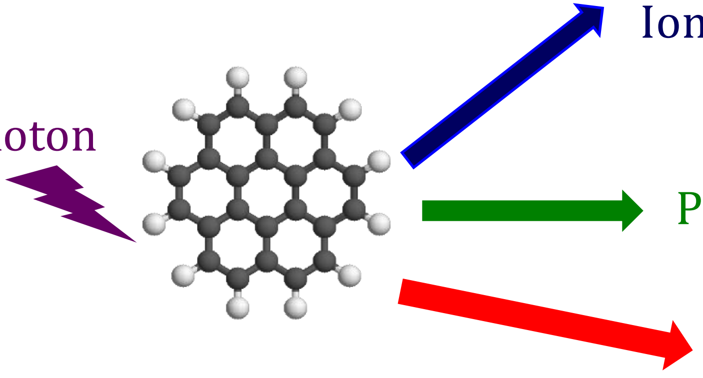
SRMS2@DESIRS



P_{He}=10^{-3} mbar

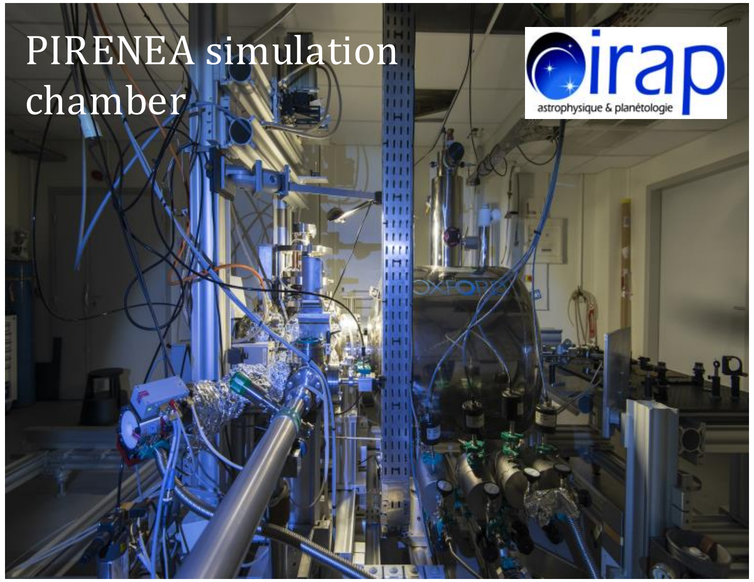
Linear Ion Trap

k_{coll} ~10^4 s^{-1}



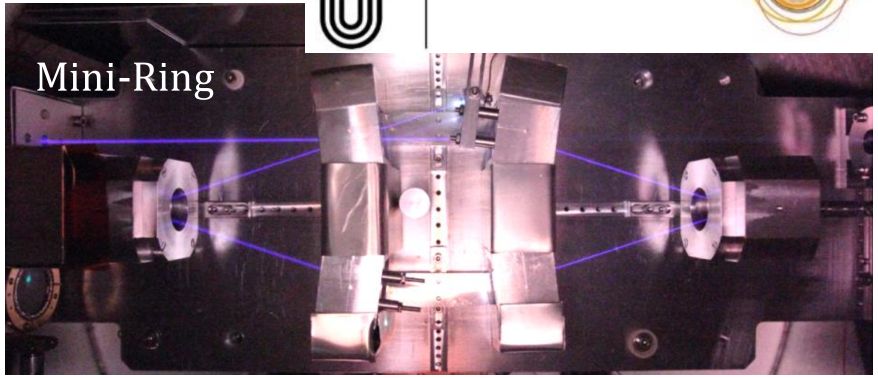
No collision during relaxation

Cryogenic ion trap: T~20 K - P_{res}=10^{-11} mbar



Cryogenic electrostatic storage ring:
T~13 K - P_{res}=10^{-14} mbar → dynamics from 70 µs to hours

Table-top electrostatic storage ring:
T=300 K → dynamics from 10 µs to ~500 ms

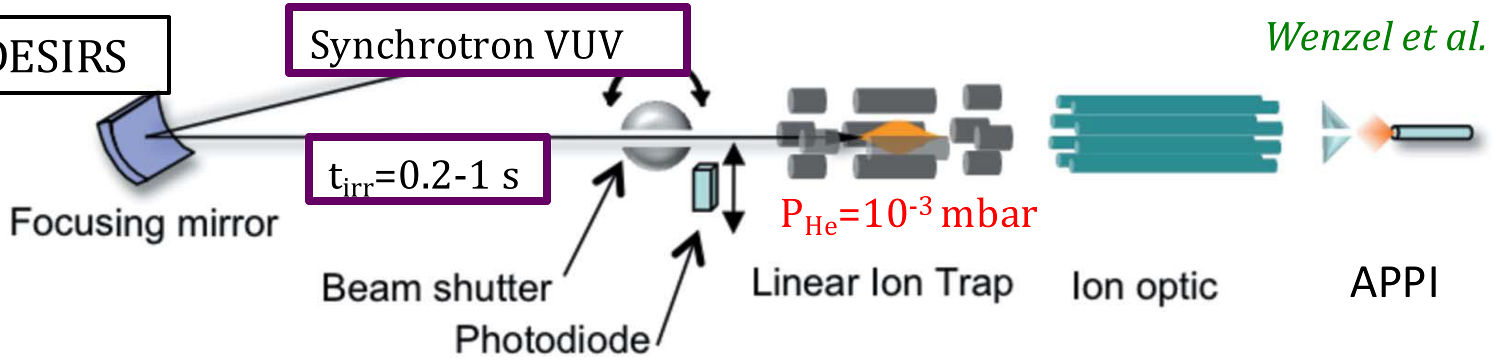


Université Claude Bernard Lyon 1

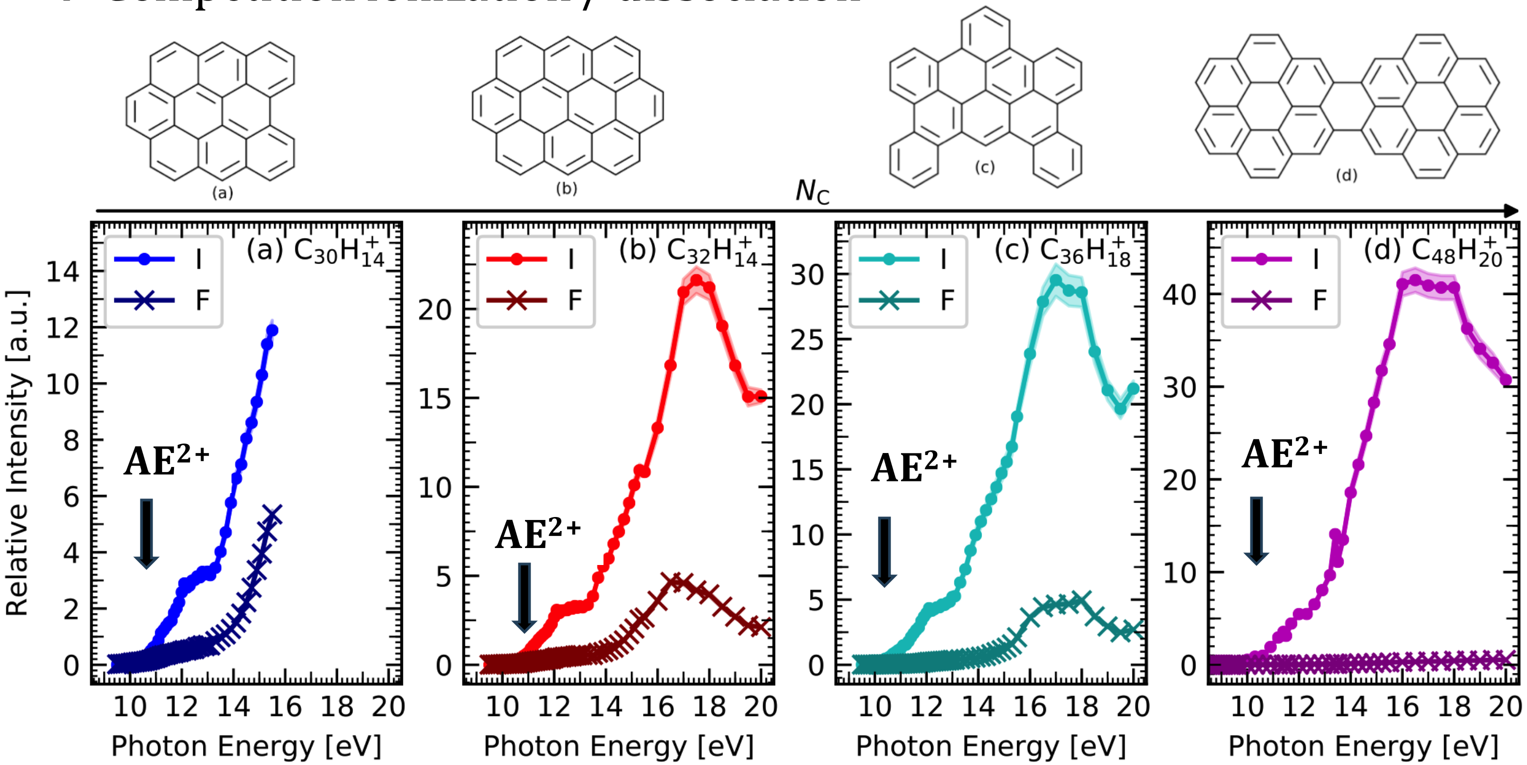
Results: PAH ionization and competition with dissociation

SRMS2@DESIRS

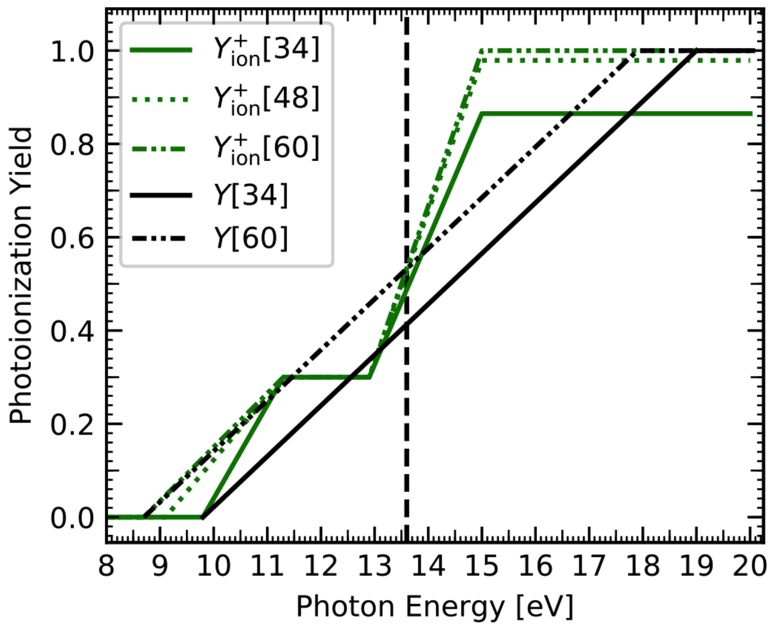
Wenzel et al. 2020, A&A 641, A98



→ Competition ionization / dissociation



→ Ionization yield



For neutrals: *Jochims et al. 1996, A&A 314, 1003; Verstraete et al. 1990, A&A 237, 436*

Application: PAH charge distribution - neutral gas heating

Berné et al. 2022, A&A 667, A159

Observations

PE heating efficiency (limited to PAHs)

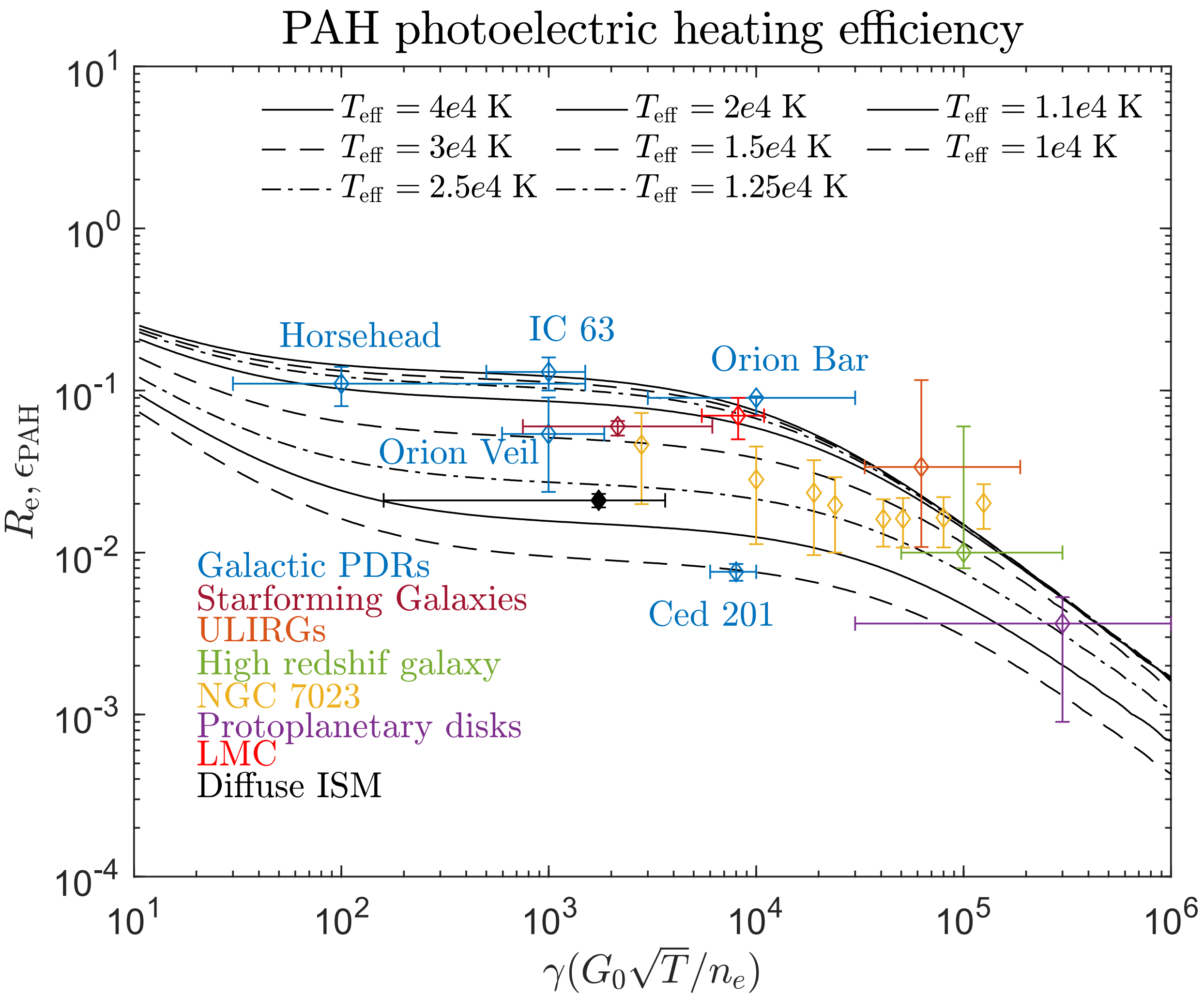
$$R_e = \frac{I_{gas}}{I_{PAH} + I_{gas}},$$

Model

PE heating efficiency

$$\epsilon_{PAH} = \frac{P_e}{P_{Rad}}.$$

Photoelectrons vs total power absorbed by PAHs



→ Molecular physics and observations agree on ionization of PAHs being the major source of neutral gas heating

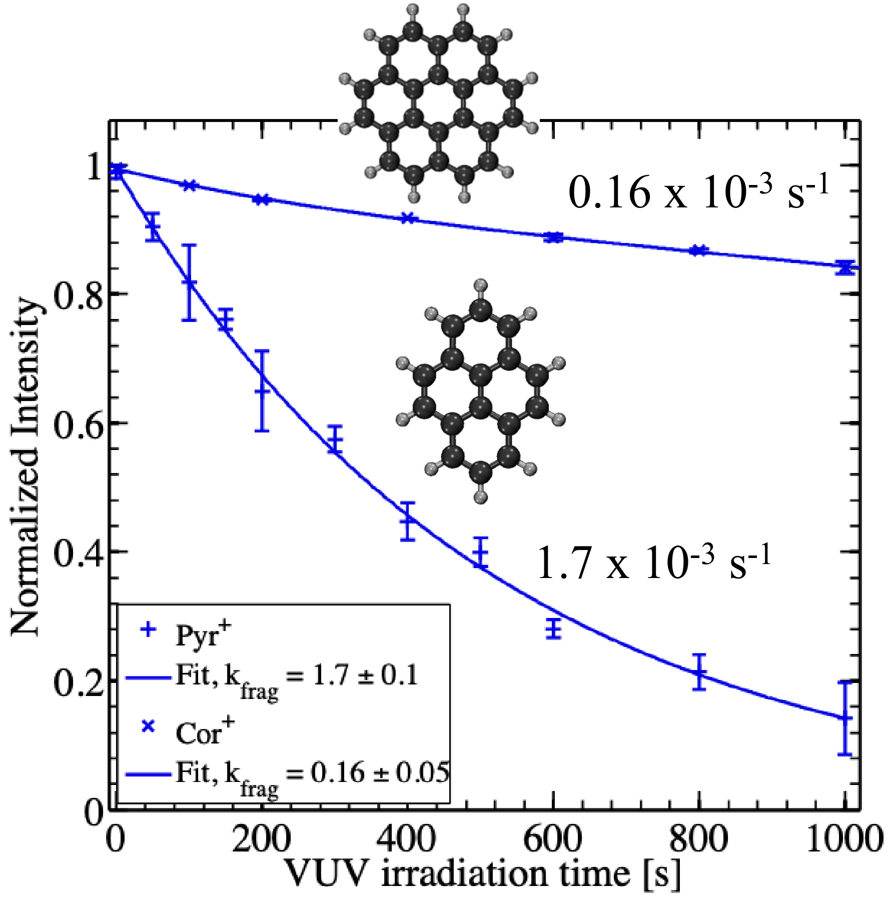
Ionization parameter
- G_0: units of 1.6 10^{-6} W m^{-2} [5.17-13.6 eV]
- T: gas temperature
- n_e: electron density

Results: Photodissociation of PAH cations

PIRENEA

VUV beam – 10.5 eV / ~10^{11} ph.s^{-1}

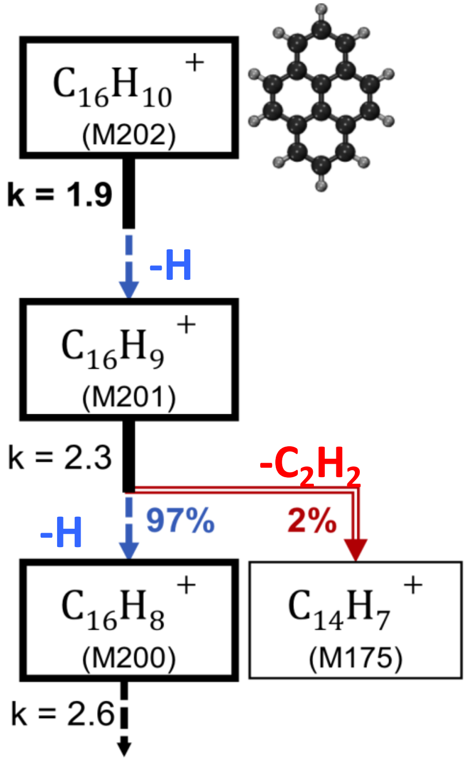
τ_{VUV} ~ 100 s (Orion Bar!)



Marciniak et al. 2021, A&A 652, A42

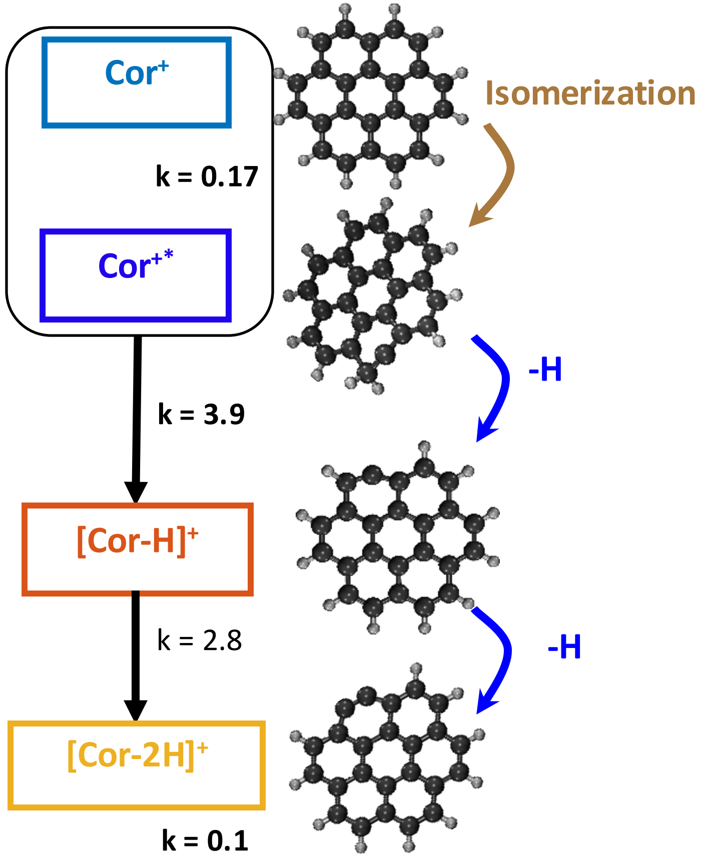
→ Sequential H loss

$2H/H_2$ loss negligible (max 2%)



Vinitha et al. 2022, JPCA 126, 5632

→ Isomerization = H shift



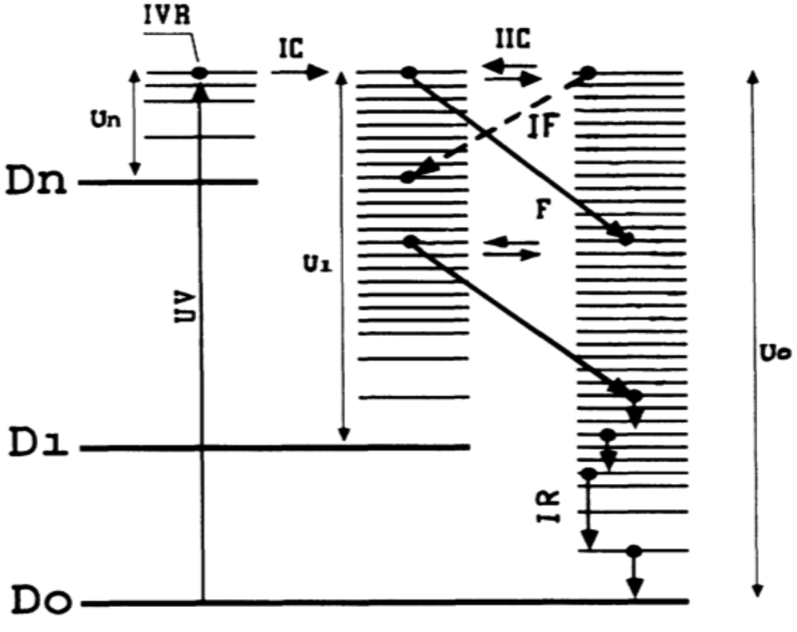
Marciniak et al. 2021, A&A 652, A42

Results: Radiative cooling in electrostatic storage rings

VOLUME 60, NUMBER 10 PHYSICAL REVIEW LETTERS 7 MARCH 1988

Predicted Fluorescence Mechanism in Highly Isolated Molecules: The Poincaré Fluorescence

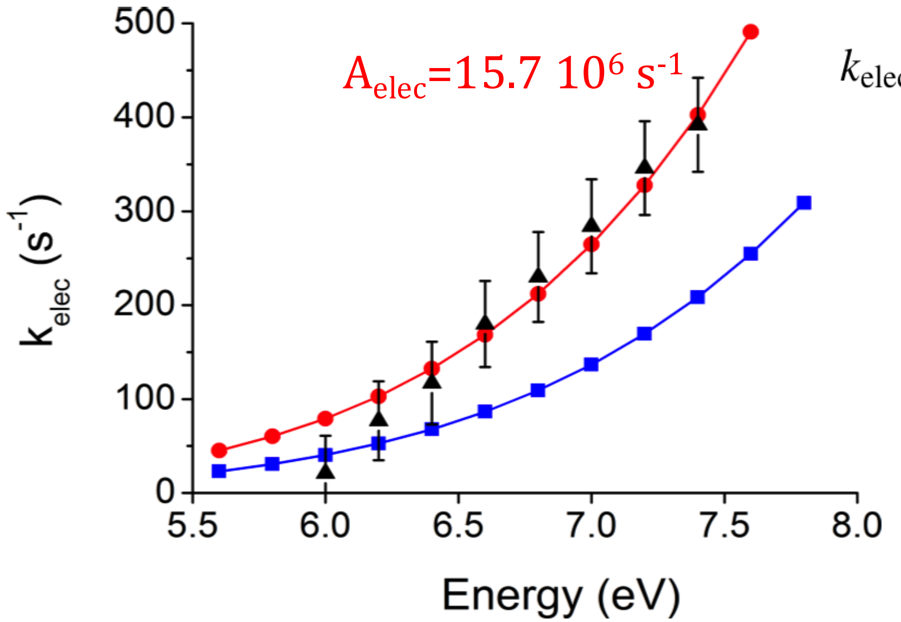
A. Léger,[1] P. Boissel,[2] and L. d'Hendecourt[1]
[1]*Groupe de Physique des Solides de l'Ecole Normale Supérieure, Université Paris VII, 75251 Paris, France*
[2]*Photophysique Moléculaire, Centre National de la Recherche Scientific, Université Paris Sud, 91405 Orsay, France*
(Received 29 October 1987)



$$k_{\mathrm{elec}}(E) \approx A_{\mathrm{elec}} \frac{\rho(E - E_{D_2})}{\rho(E)}$$

Boissel et al. 1997, JPC 106, 4973

Martin et al. 2015, PRA 92, 053425



$$k_{\mathrm{elec}}(E) \approx A_{\mathrm{elec}} \frac{\rho(E - E_{D_2})}{\rho(E)}$$

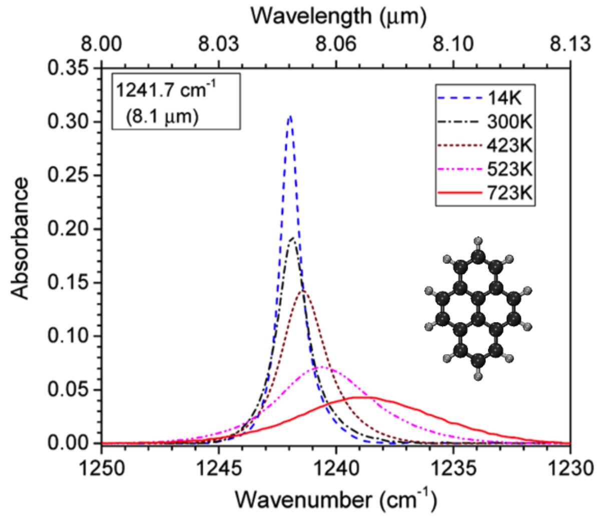
→ When activated, this cooling is much more efficient to compete with dissociation than IR cooling.

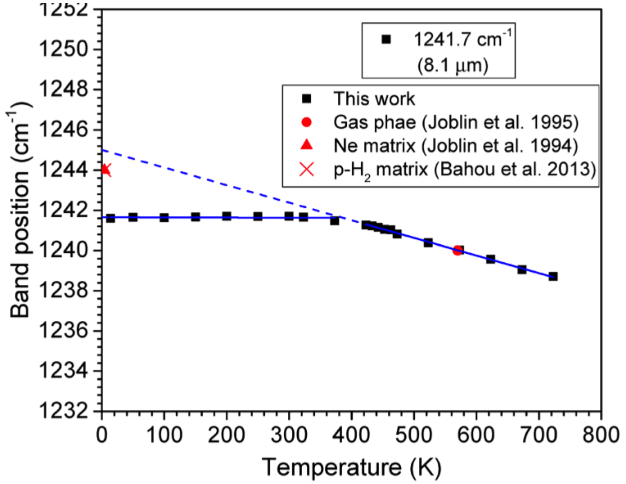
Results: IR spectroscopy of hot PAHs

→ ESPOIRS FTIR setup

→ Theory: AnharmoniCaOS and Molecular Dynamics

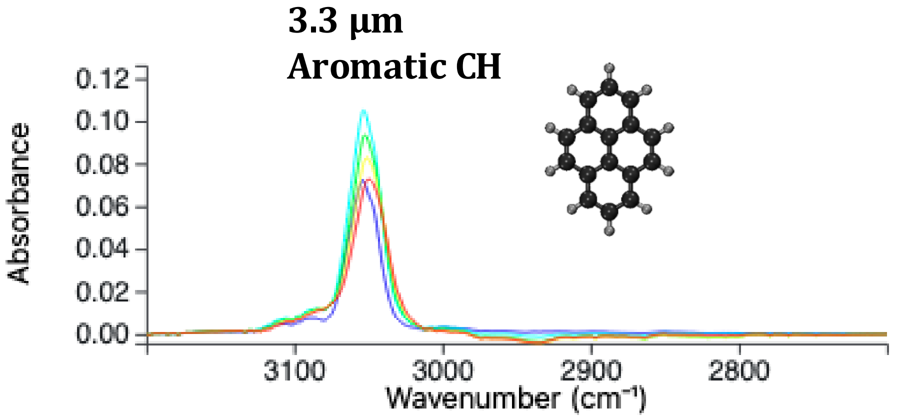
Solid phase (14 -723 K)



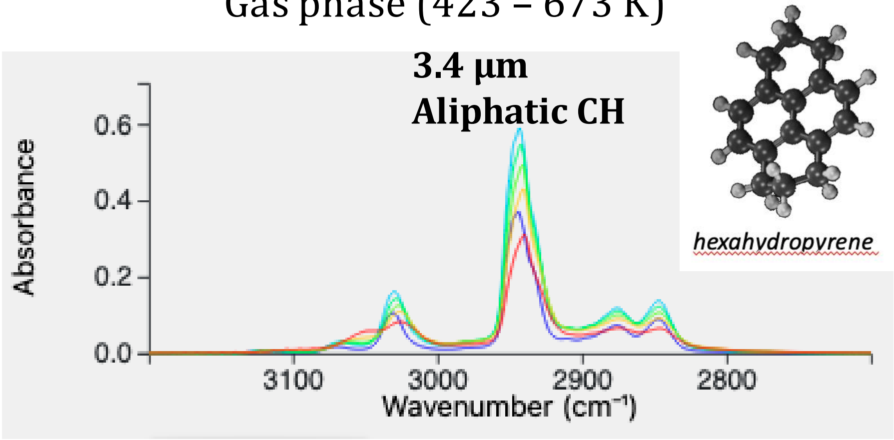


Chakraborty et al., 2019, JPC A 123, 4139

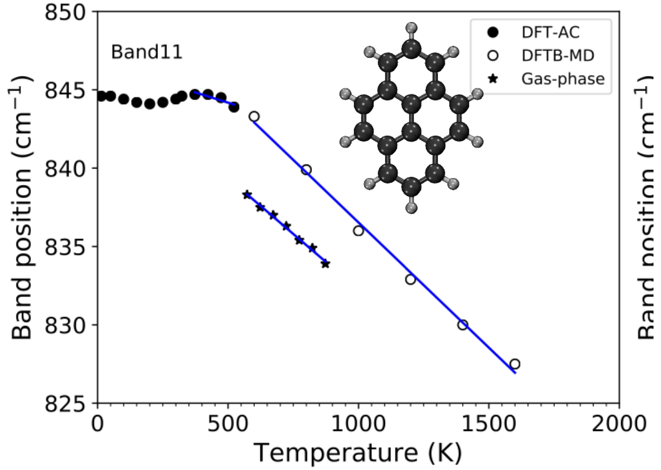
Gas phase (423 – 623 K)

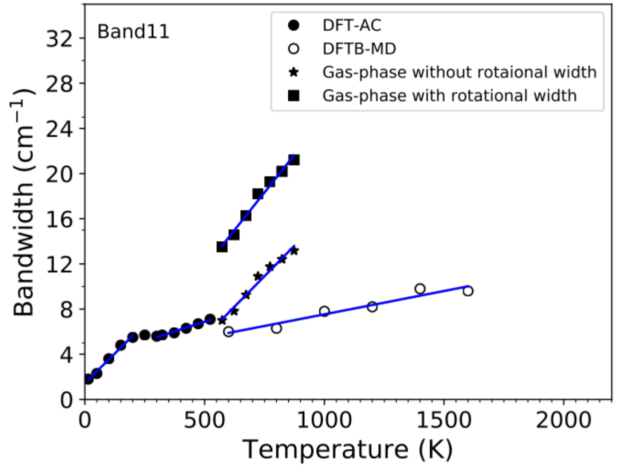


Gas phase (423 – 673 K)



Demyk et al., 2025, in prep.

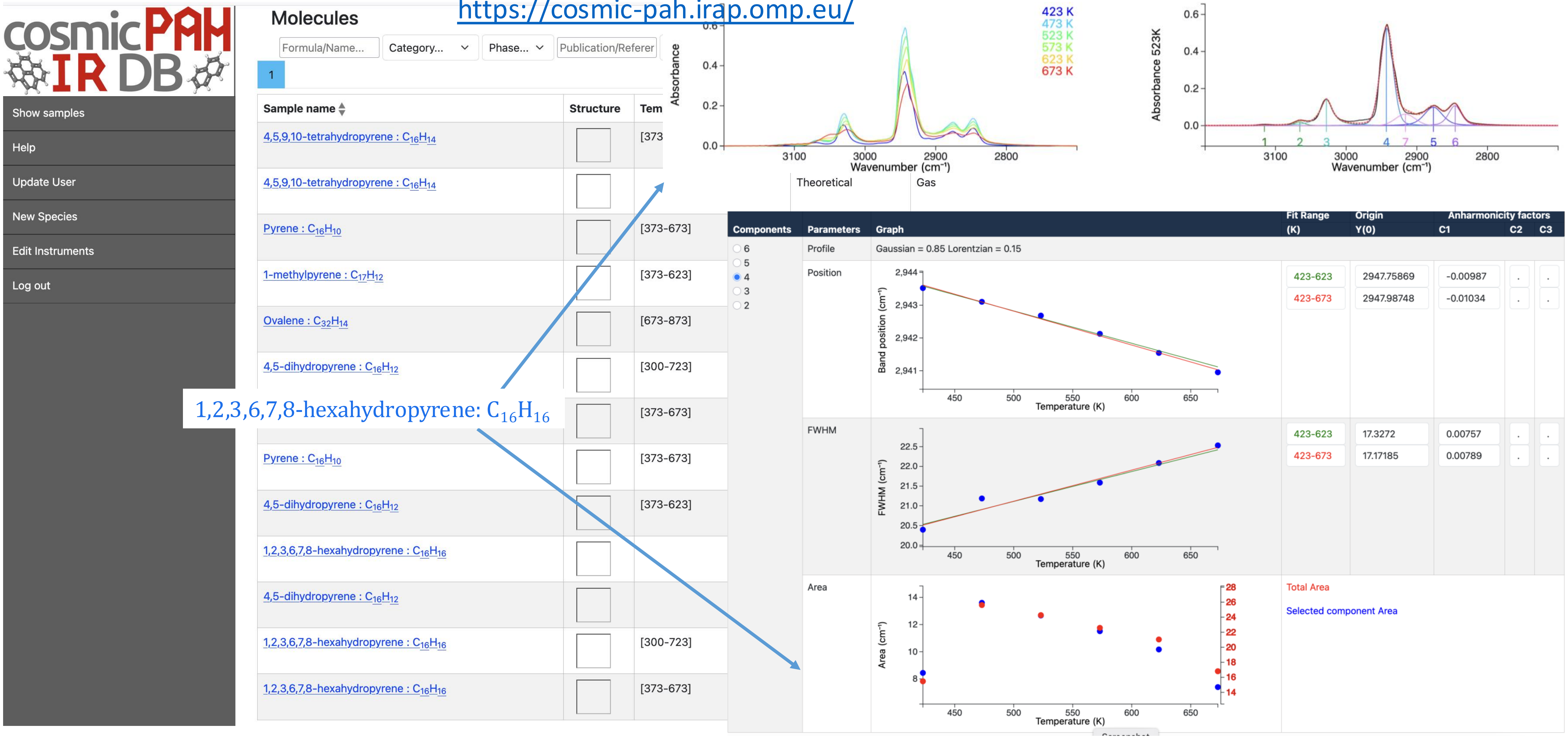




Chakraborty et al. 2021, J. Mol. Spect. 378, 111466

Results: CosmicPAH database of anharmonic infrared spectra

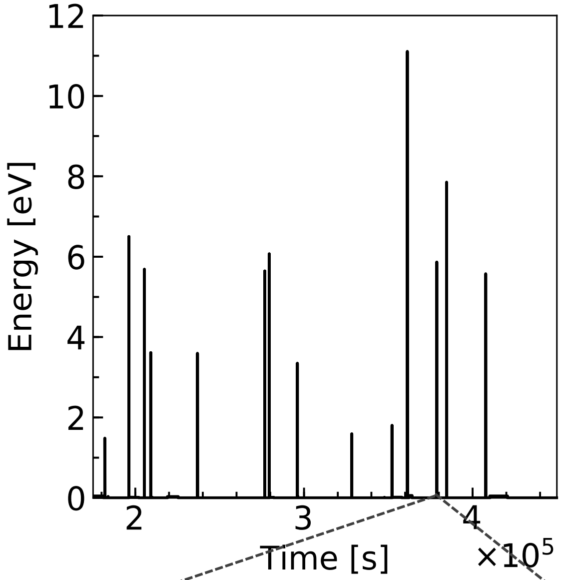
https://cosmic-pah.irap.omp.eu/

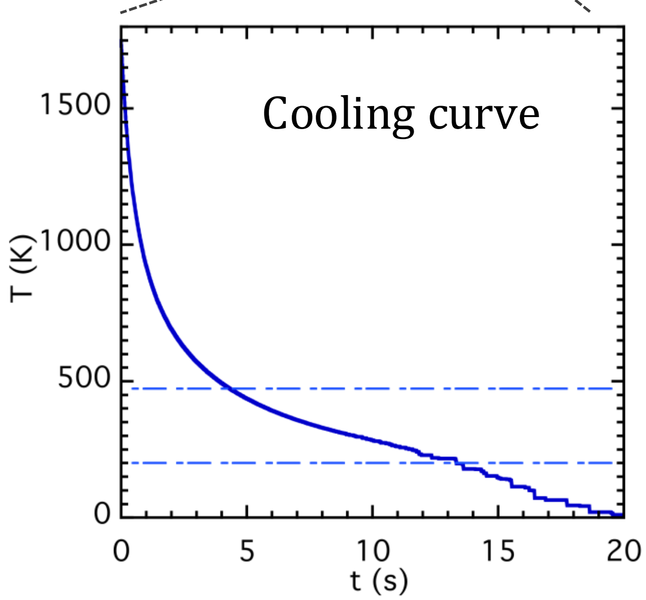


De Bentzmann et al., 2025, in prep

Application: Modelling the IR emission spectrum of interstellar PAHs

UV photon absorption rate





Simulation of PAH physics

Monte Carlo code

Environment

UV radiation field

Spectroscopy & Molecular properties

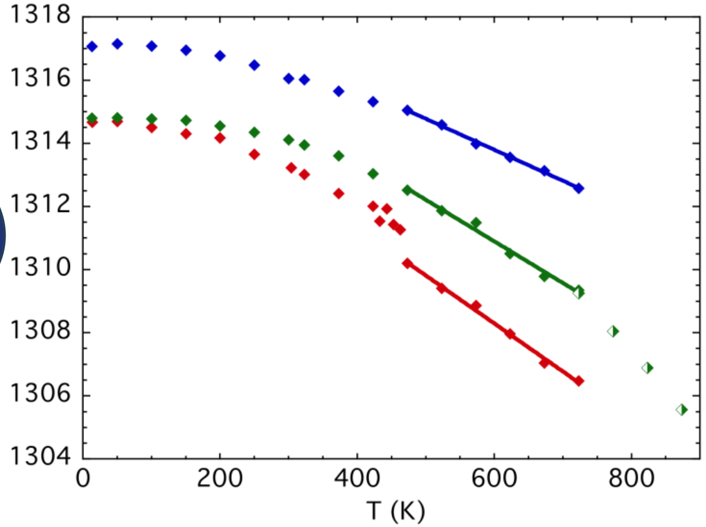
Quantum Chemistry DB
Experimental DBs

Comparison with Astronomical Observations

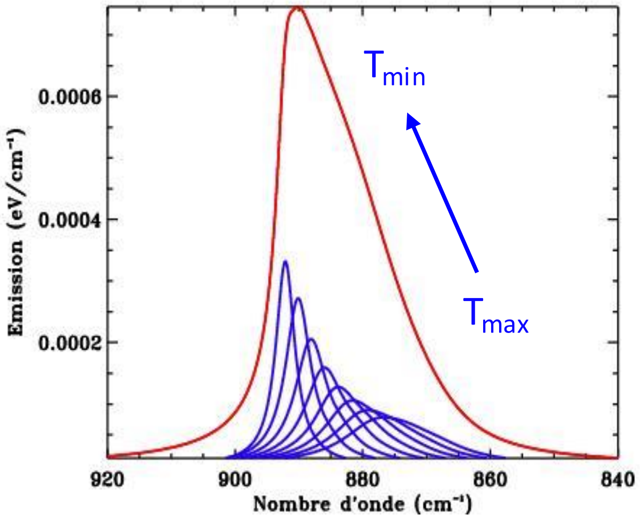
The AIBs / JWST

→ The LAIBrary project

Spectral parameters – T evolution



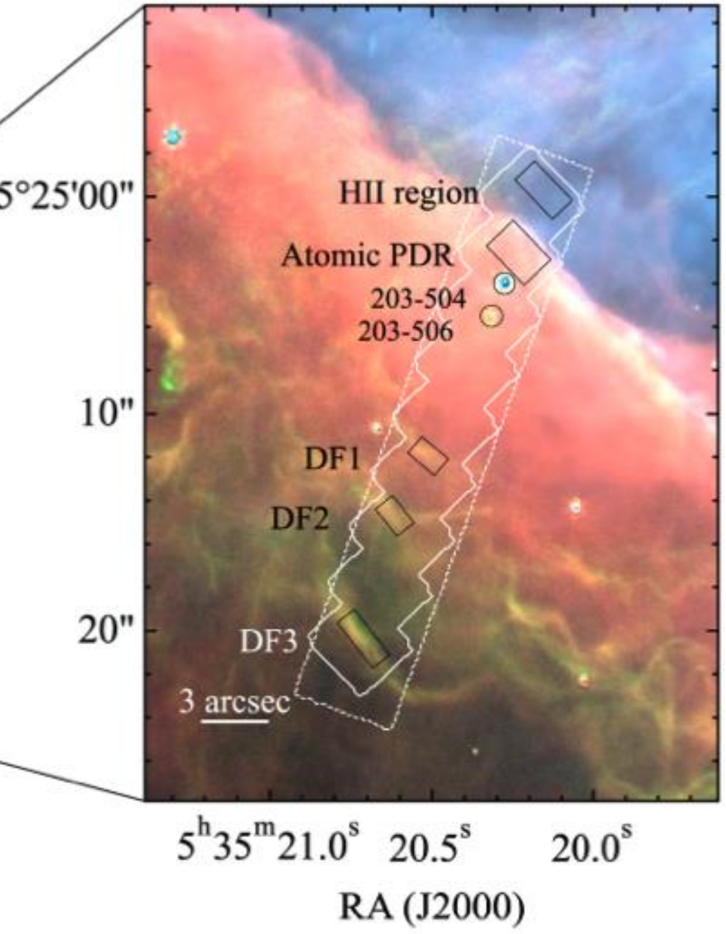
IR band profiles

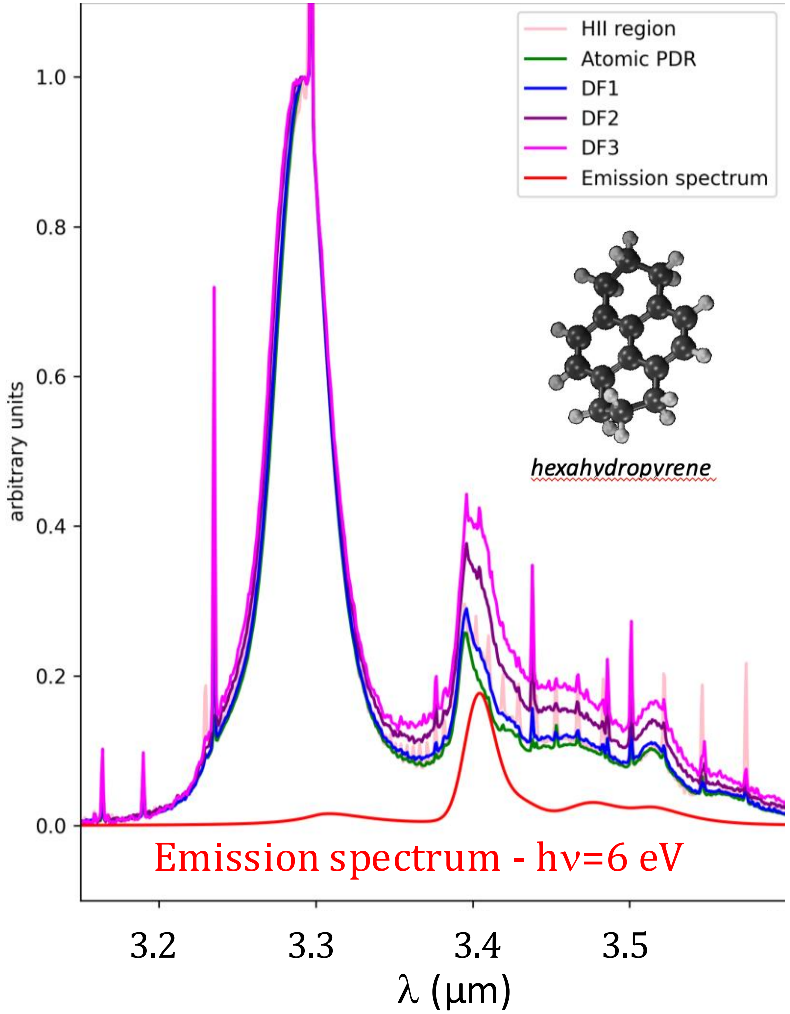


Application: comparison with JWST observations (PDRs4All)

Peeters, Berné, Habart & the PDRs4All team, 2024, A&A, 685, A74
Chown, Sidhu, Peeters, et al. 2024, A&A, 685, A75

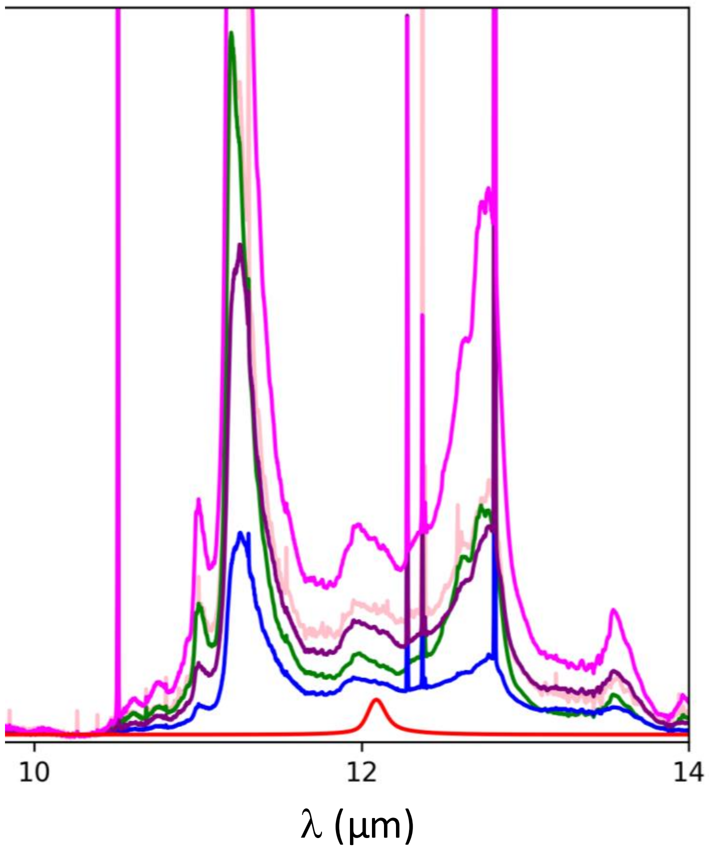
www.pdrs4all.org





Emission spectrum - hν=6 eV

Emission spectrum / LAIBrary project



Demyk et al., 2025, in prep.

Final remarks and perspectives

- Key questions in astrophysics
  - Derive local physical conditions from the AIBs
  - Formation and chemical evolution of PAHs: messengers from stars to the Solar System
  - Role of PAHs in star-forming and planet-forming regions. Interaction with water, deuteration, molecular complexity → link with the PEPR Origin (France 2030)

- Study at the interface of disciplines / communities (key to its success):
  - Astrophysics, planetology, cosmochemistry
  - Molecular physics, quantum chemistry, plasma physics, surface science, analytical chemistry, organic chemistry, …

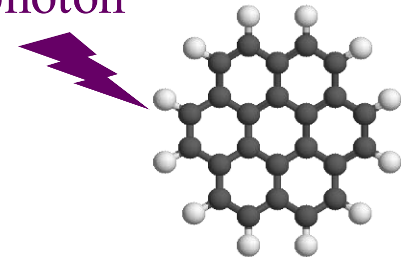
- Use of large facilities/infrastructures (light sources, heavy ions, electrostatic storage rings, analytical tools …)

- Unusual conditions of astrophysical environments (e.g., the interstellar medium)

→ design of new dedicated laboratory setups

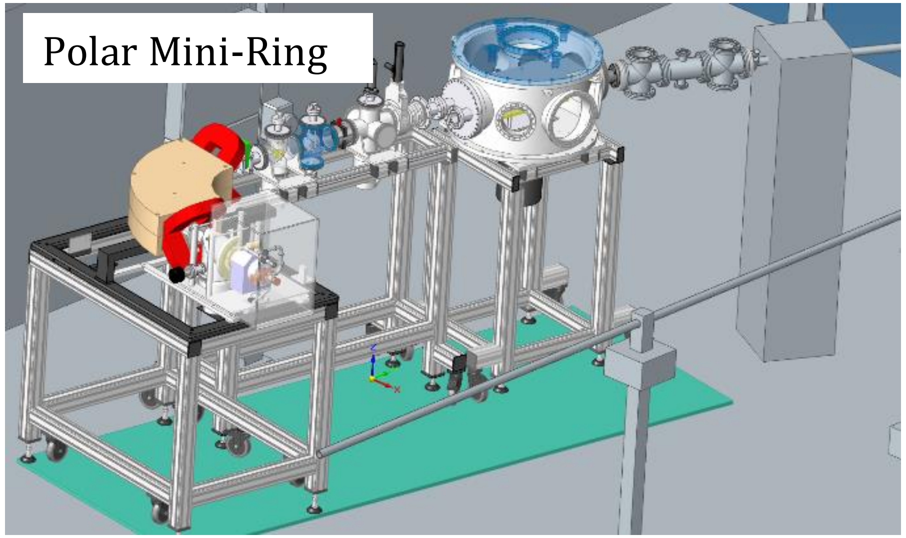
Laboratory astrophysics: (some) new dedicated setups

VUV photon



Cryogenic electrostatic storage ring: T~20 K

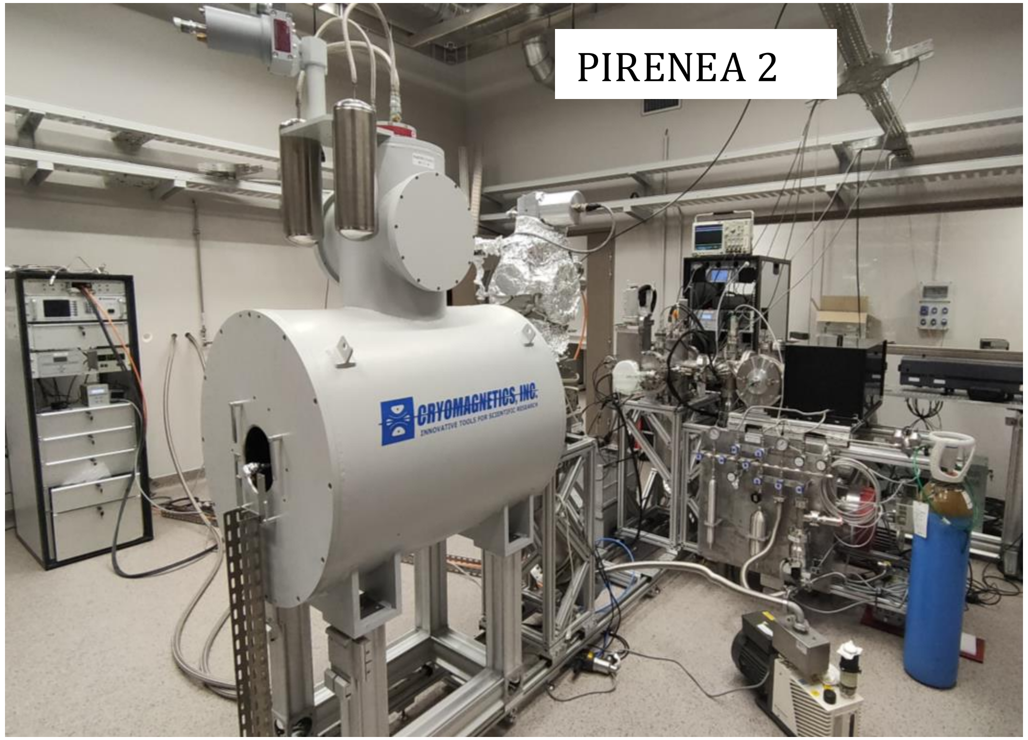
→ dynamics from 10 μs to > 1 min. as a function of $h\nu_{UV}$



ANR SynPAHcool

Study of gas-nanograin-photon interactions in conditions of star- and planet-forming regions

- Two sources of clusters/nanograins:
  - LVAP (high T): stardust – role of metals
  - Molecular aggregation (low T): water-carbonaceous nanograins
- Simulation of interstellar conditions (PIRENEA)



- ANR JCJC CASSOULExp (A. Marciniak); AT PCMI
- Future project?

Acknowledgements

Main long-term collaborators/ permanent staff

IRAP (UT/CNRS, Toulouse) H. Sabbah, K. Demyk, O. Berné, G. Quitté, *A. Bonnamy*, L. Noguès, D. Murat, O. Coeur-Joly

FeRMI (UT/CNRS, Toulouse) A. Marciniak, S. Zamith, D. Toublanc, A. Bonnamy (LCAR), A. Simon, M. Rapacioli (LCPQ)

LAPLACE (UT/CNRS, Toulouse) K. Makasheva

Osservatorio Astronomico di Cagliari (Italy) G. Mulas

Synchrotron SOLEIL A. Giuliani, G. Garcia, L. Nahon

ILM (Univ. Lyon1) S. Martin, J. Bernard

DESIREE (Univ. Stockholm) H. Schmidt, H. Zettergren, M. Ji, M. Stockett

NANOCOSMOS ERC SYNERGY (CSIC Madrid) J. Cernicharo, J. A. Martín-Gago

euroPAH
the extensive and ubiquitous role of polycyclic aromatic hydrocarbons in space

nanoCOSMOS

erc

Université de Toulouse

anr agence nationale de la recherche AU SERVICE DE LA SCIENCE

cnes

cnrs dépasser les frontières

pcmi