Astro-PAHs: a journey from space to the laboratory

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The physics and chemistry of the ISM
XT2019

Avignon (2-6/09/2019)

Outline

- The interstellar PAH model
  - The Aromatic Infrared Bands
  - Spectral diversity
  - Identification of the IR emission bands of C_{60}

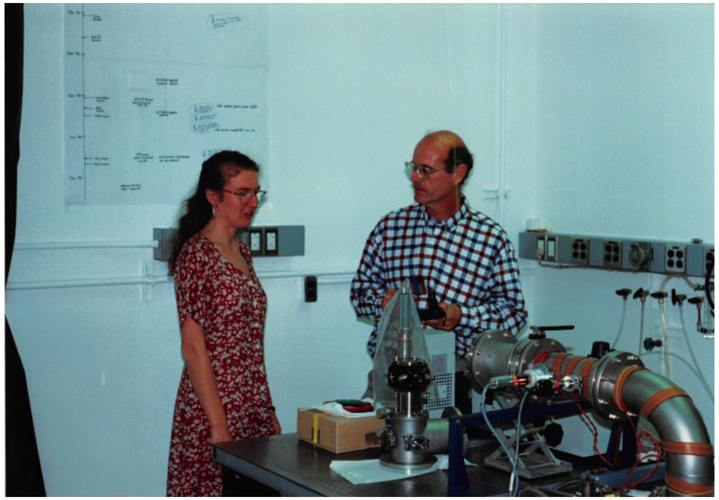
Let's celebrate Xander

** From space to the laboratory **

- Interaction of a PAH with a VUV photon
  - From cosmic conditions to key molecular timescales
  - Unimolecular dissociation
  - Radiative cooling

- Formation of PAHs and fullerenes in evolved stars
  - Context: from evolved stars to laboratory analogues
  - The Nanocosmos ERC Synergy
  - First results on meteorites and stardust analogues

NASA Ames 1993 - 1995



THE ASTROPHYSICAL JOURNAL, 458:610–620, 1996 February 20

SPATIAL VARIATION OF THE 3.29 AND 3.40 MICRON EMISSION BANDS WITHIN REFLECTION NEBULAE AND THE PHOTOCHEMICAL EVOLUTION OF METHYLATED POLYCYCLIC AROMATIC HYDROCARBONS

C. JOBLIN,[1] A. G. G. M. TIELENS,[1] L. J. ALLAMANDOLA,[1] AND T. R. GEBALLE[2]
Received 1995 April 6; accepted 1995 July 28

THE ASTROPHYSICAL JOURNAL, 460:L119–L122, 1996 April 1

VARIATIONS OF THE 8.6 AND 11.3 μm EMISSION BANDS WITHIN NGC 1333: EVIDENCE FOR POLYCYCLIC AROMATIC HYDROCARBON CATIONS

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Received 1995 December 6; accepted 1996 January 19

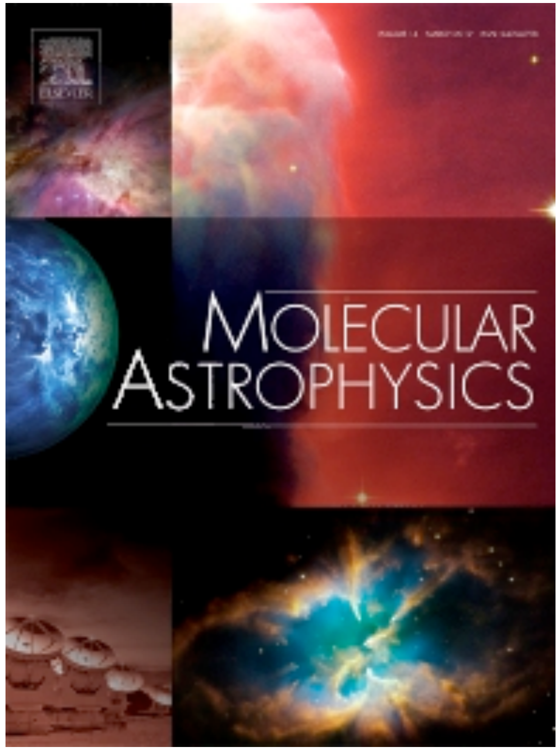
PAHs and the Universe: the 25th anniversary
Toulouse 31/05- 4/06 2010

PAHs and the Universe: the 25th anniversary
Toulouse 31/05- 4/06 2010

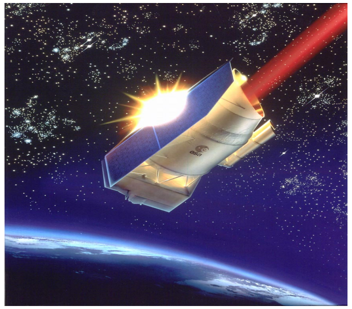

And much more

- Herschel/HIFI – Preparatory work – key programs (from 1995)
- Research Training Network (FP6) *Molecular Universe* (2004-2007)
- *Energetic processing of large molecules international meetings:* EPoLM-3 (Toulouse 2017), EPoLM-4 (Madrid 2019)
- *Innovative Training Network* EUROPAH (2016-2020)
- Molecular Astrophysics (Elsevier) since 2015

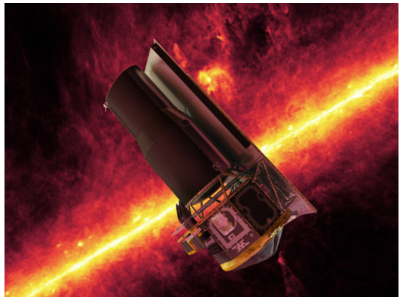
    Editor-in-chief: Xander Tielens



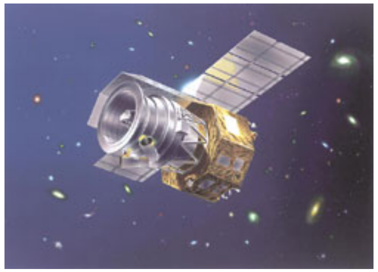
The Aromatic Infrared Bands (AIBs)



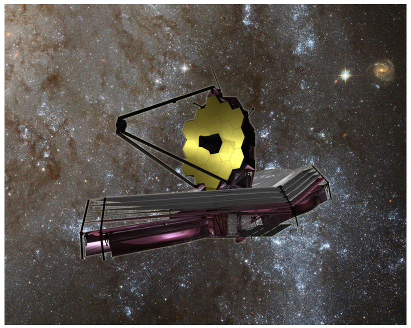
Infrared Space Observatory
ESA; 1995-1998



Spitzer Space Telescope
NASA; 2003-2009

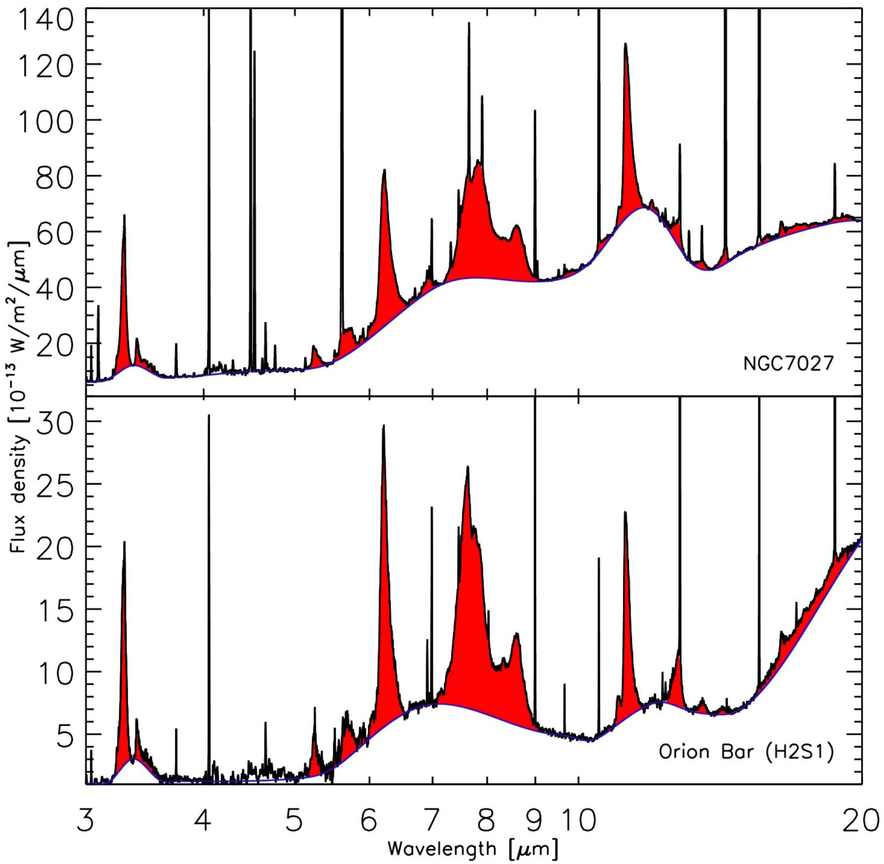


AKARI
JAXA; 2006-2011



James Webb Space Telescope
NASA; 2021-2025?

ISO SWS spectra



Peeters et al., 2004, Astrophysics of Dust vol 309, p141

The Aromatic Infrared Bands (AIBs) → The PAH model

3.3 μm (3050 cm^{-1}); 6.2 μm (1610 cm^{-1});
'' 7.7 '' μm (1300 cm^{-1}); 8.6 μm (1160 cm^{-1});
11.3 μm (890 cm^{-1}); 12.7 μm (785 cm^{-1})

CH and CC aromatic modes

\+

- Stochastic heating – absorption of a single UV photon → N~50 ; T~1000 K

Sellgren 1984, ApJ 277, 623

↓

Léger & Puget 1984, A&A 137, L5
Allamandola, Tielens & Barker 1985, ApJ 290, L25

- Candidates: PAH molecules

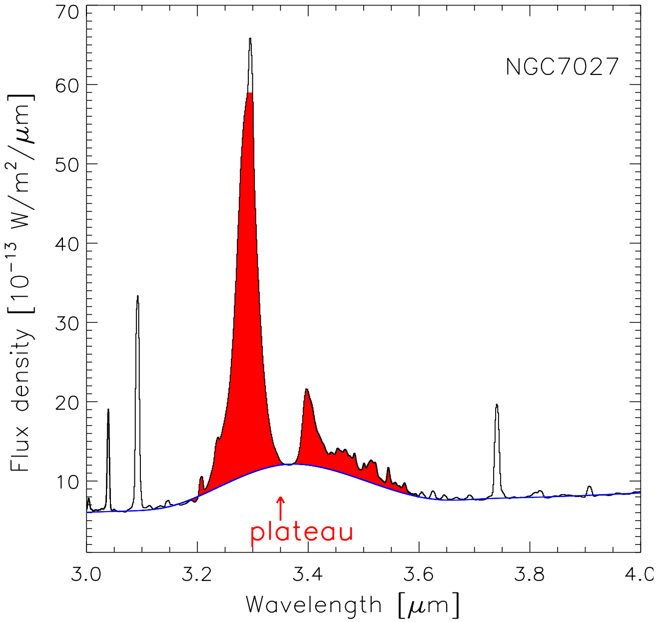
Joblin et al. 1992, ApJ 393, L79
Li & Draine 2001, ApJ, 554, 778
Draine & Li 2007, ApJ 657, 810

- Energetic budget: 10 to 20% of total C
→ ~ 0.1 ppm (N_C~50) relative to H

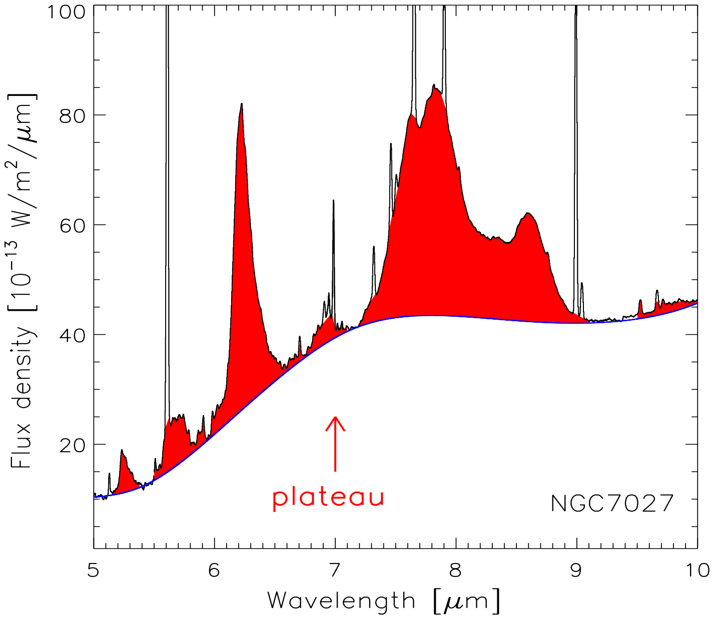
The richness of the AIB spectra: identification of carriers

Peeters et al., 2004, Astrophysics of Dust vol 309, p141;Peeters 2011, EAS Pub. Ser. vol. 46, p13

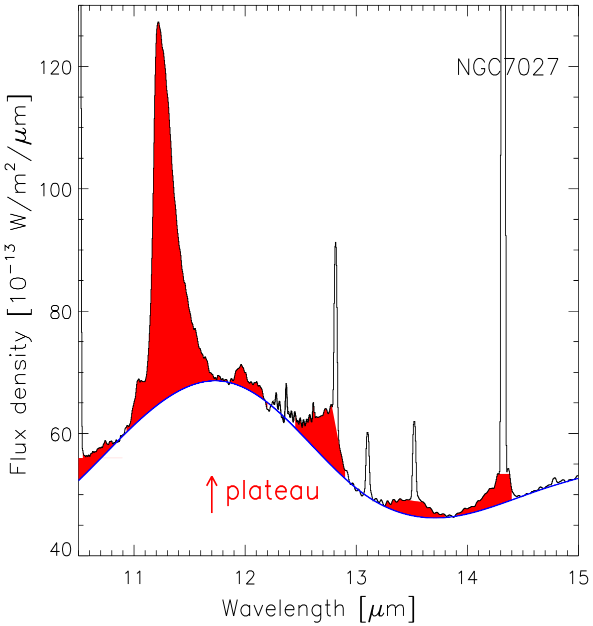
CH stretch



CC stretch, CH bend



CH out-of-plane bend



Aromatics + aliphatic bonds (CH_3 sidegroups? Superhydrogenated?)

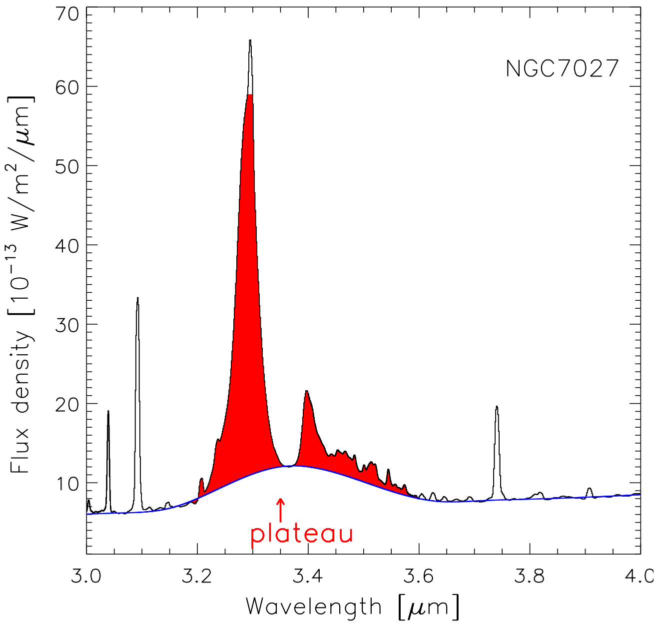
Structure and charge (+/0).
6.2 µm band: PAHs with nitrogen?
Fe-PAH complexes? Protonated PAHs?

→ Strong contribution of solo H. Structure and size

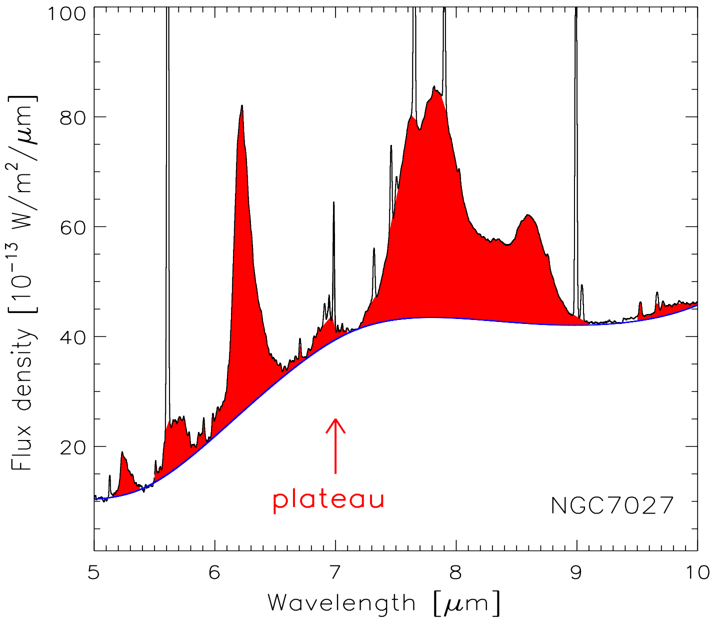
The richness of the AIB spectra: identification of carriers

Peeters et al., 2004, Astrophysics of Dust vol 309, p141;Peeters 2011, EAS Pub. Ser. vol. 46, p13

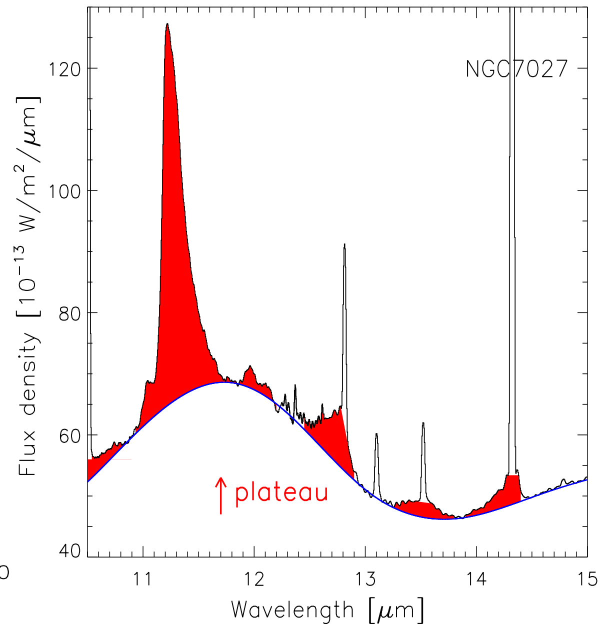
CH stretch



CC stretch, CH bend



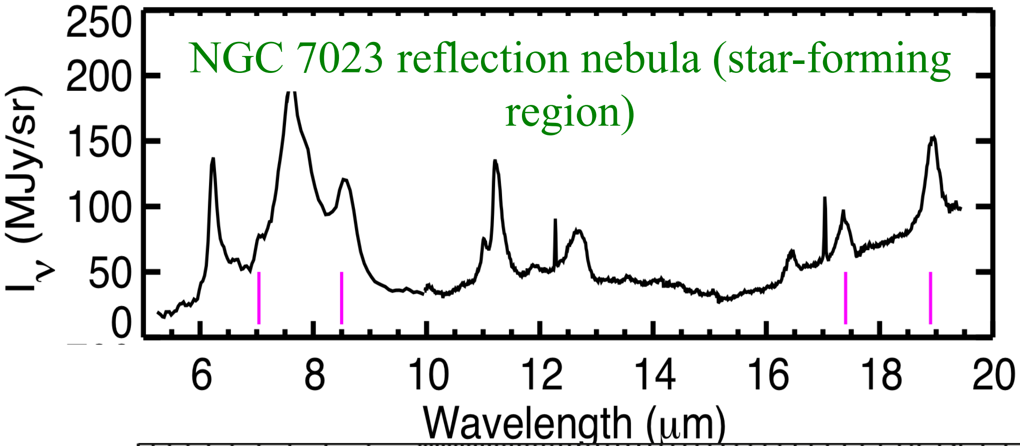
CH out-of-plane bend



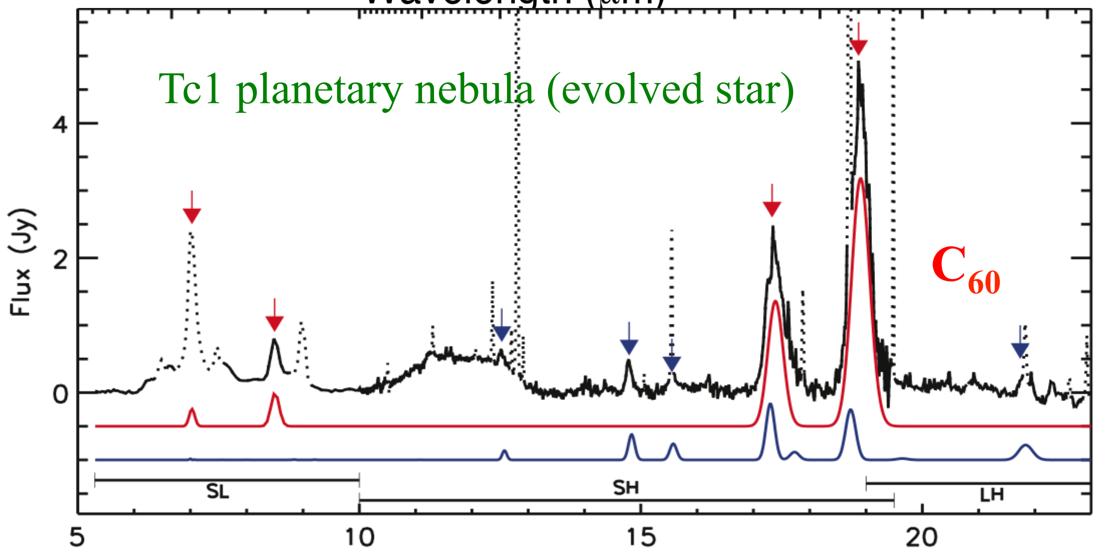
→ Experimental and theoretical work to progress on the spectral identification:

L. Allamandola, *J. Bouwman,* *Mascetti et al.,* *Petrignani et al.,* *C. Boersma,* *Buragohain et al.,* *Chakraborty et al.,* *Endo et al.,* *Velásquez et al.,* *Wenzel et al.*

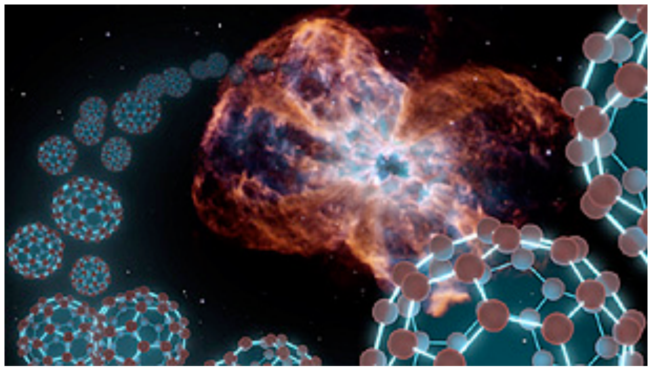
Identification of the IR emission of fullerenes (C_{60})



Sellgren et al. 2010, ApJL 722, L54

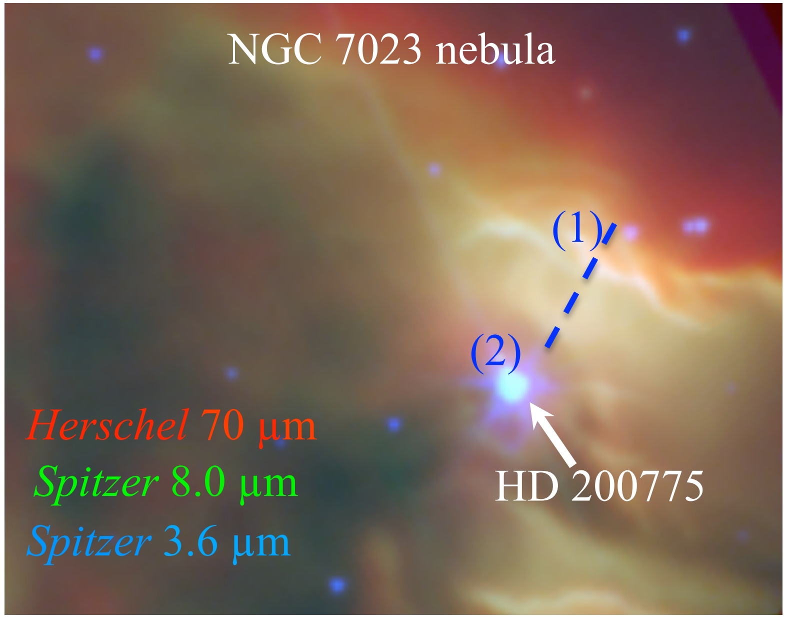


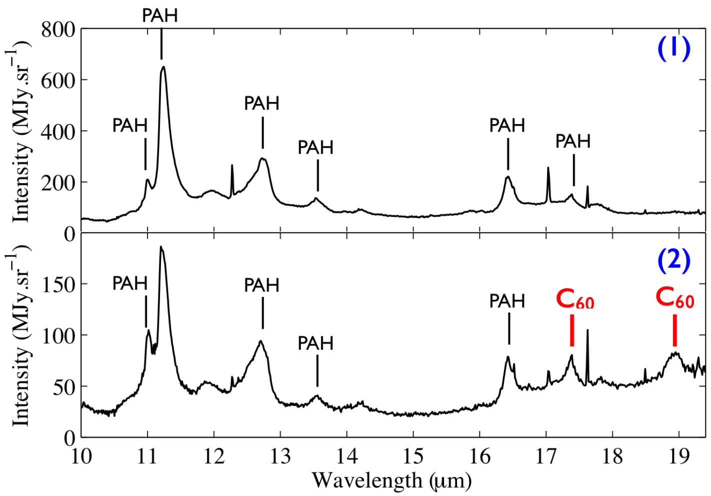
Cami et al. 2010, Science 329, 1180

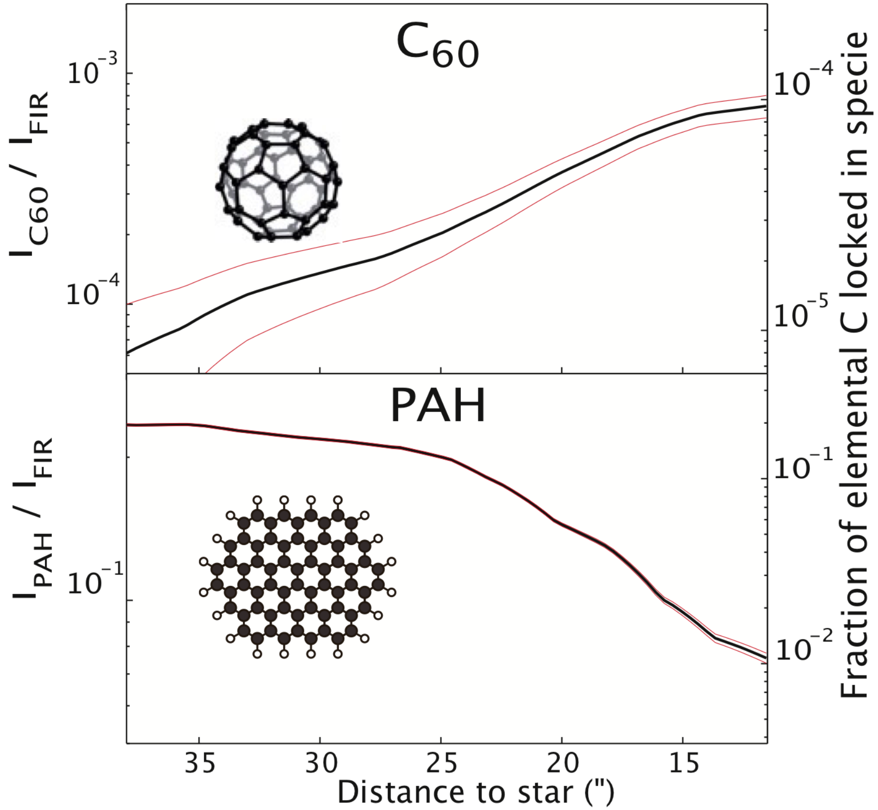


Chemical relation between PAHs and C_{60}?

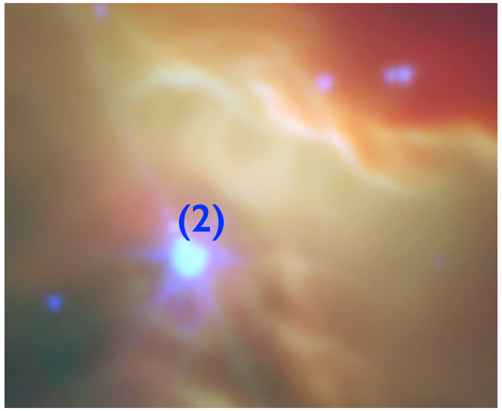
Berné & Tielens 2012, PNAS 109, 401





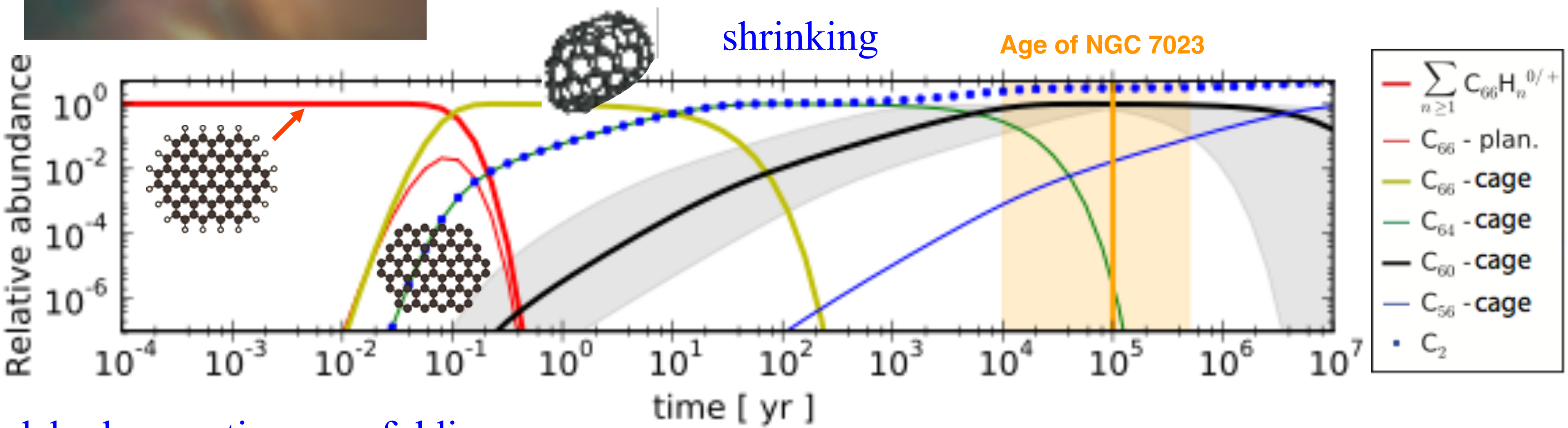


Photochemical evolution of $C_{66}H_{20}$ and formation of C_{60}



Berné, Montillaud, Joblin, 2015, A&A 577, A133

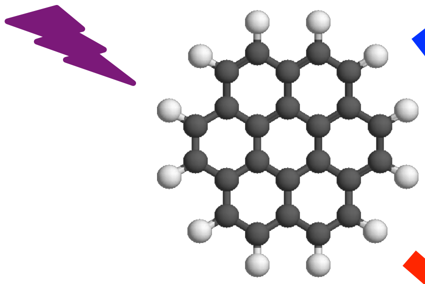
At 10’’ from the star
Go ~ 4 10^4
n_H ~ 2000 cm^{-3}



dehydrogenation   folding

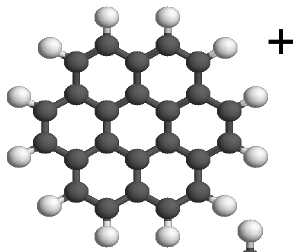
The key role of the interaction of PAHs with VUV photons

VUV photon



Ionization

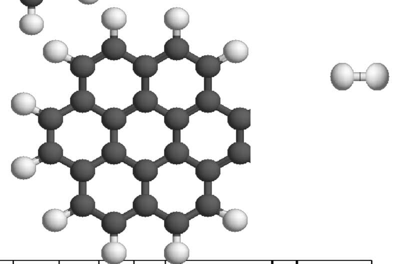
Photoelectric effect/ Gas heating



$+ e^-$

Photodissociation

PAH lifetime

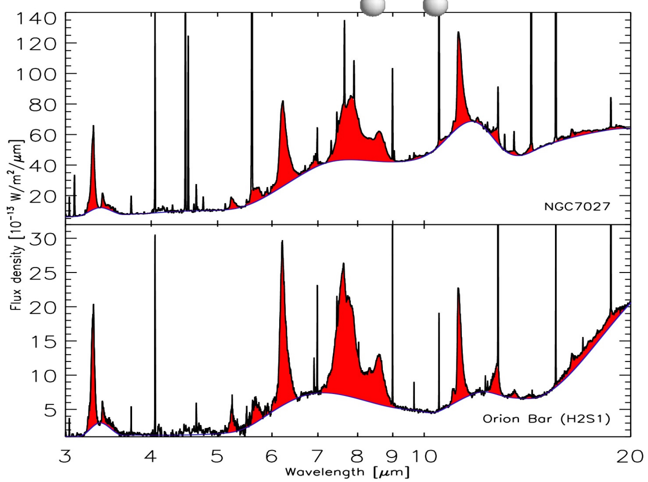


$+ H, H_2, C_2H_2$

Radiative cooling

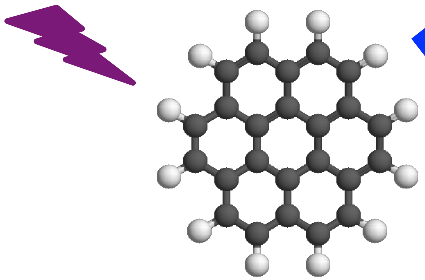
The Aromatic Infrared Bands

+ Recurrent Fluorescence



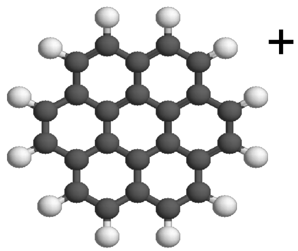
The key role of the interaction of PAHs with VUV photons

VUV photon



Ionization

Photoelectric effect/ Gas heating



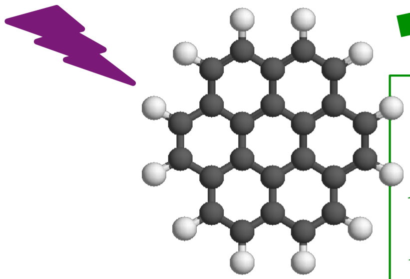
+ e⁻

Bakes and Tielens 1994, ApJ 427, 822

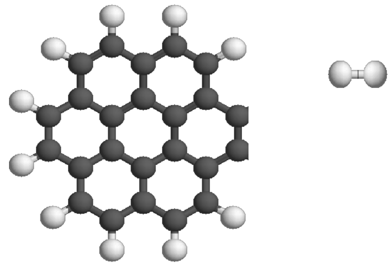
Bréchignac et al.

The key role of the interaction of PAHs with VUV photons

VUV photon



Photodissociation



+ **H, H_2, C_2H_2**

- PAH lifetime

Allain et al., 1996, A&A 305, 602
Le Page et al. 2001, ApJS 132, 233
Visser et al. 2007, A&A 466, 229
Montillaud et al. 2013, A&A 552, A15
Andrews et al. 2016, A&A 595, A23

→ Only large PAHs with N_C>50-60 can survive

- Formation of H_2

Habart et al., 2004, A&A 414, 531
Castellanos et al., 2018, A&A 616, A167

- Formation of small hydrocarbons

Pety et al., 2005, A&A 435, 885

- Deuteration

Draine 2004, Origin and Evolution of the Elements, Cambridge Univ. Press, p. 320
Peeters et al. 2004, ApJ 604, 252

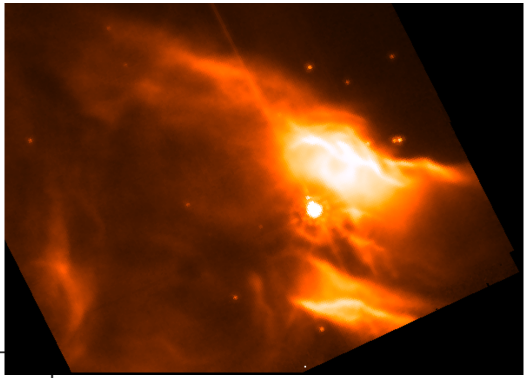
M. Tiwari, Knight et al.

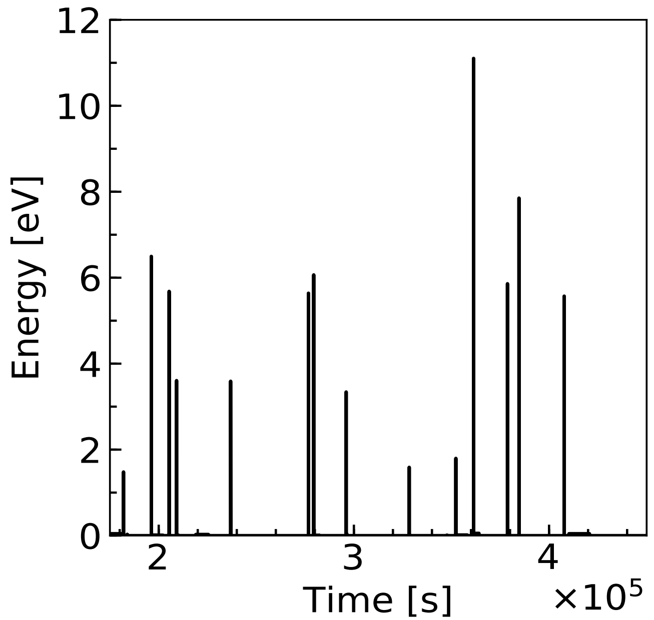
A. Petrignani

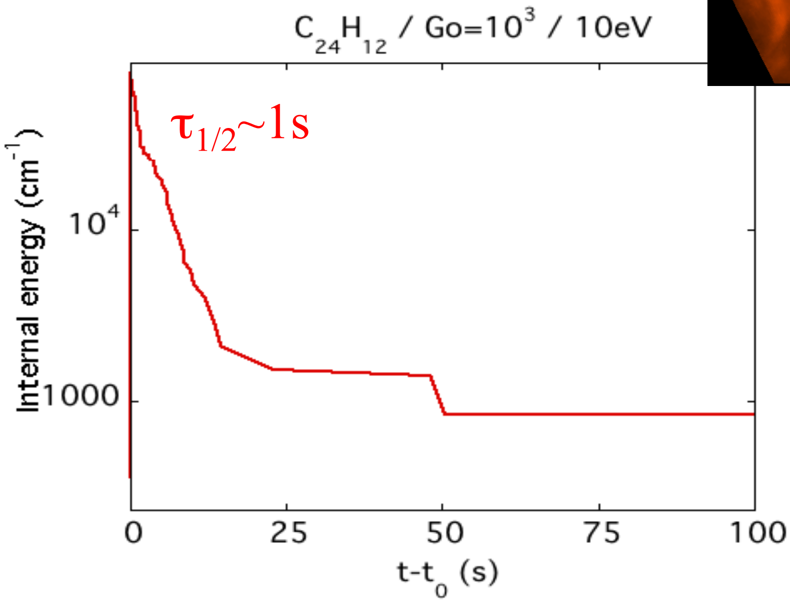
The extreme conditions of astrophysical environments

Kinetic Monte Carlo simulations

Mulas et al. 2006, A&A 456, 161; Joblin et al. 2002, Mol. Phys 100(22), 3595



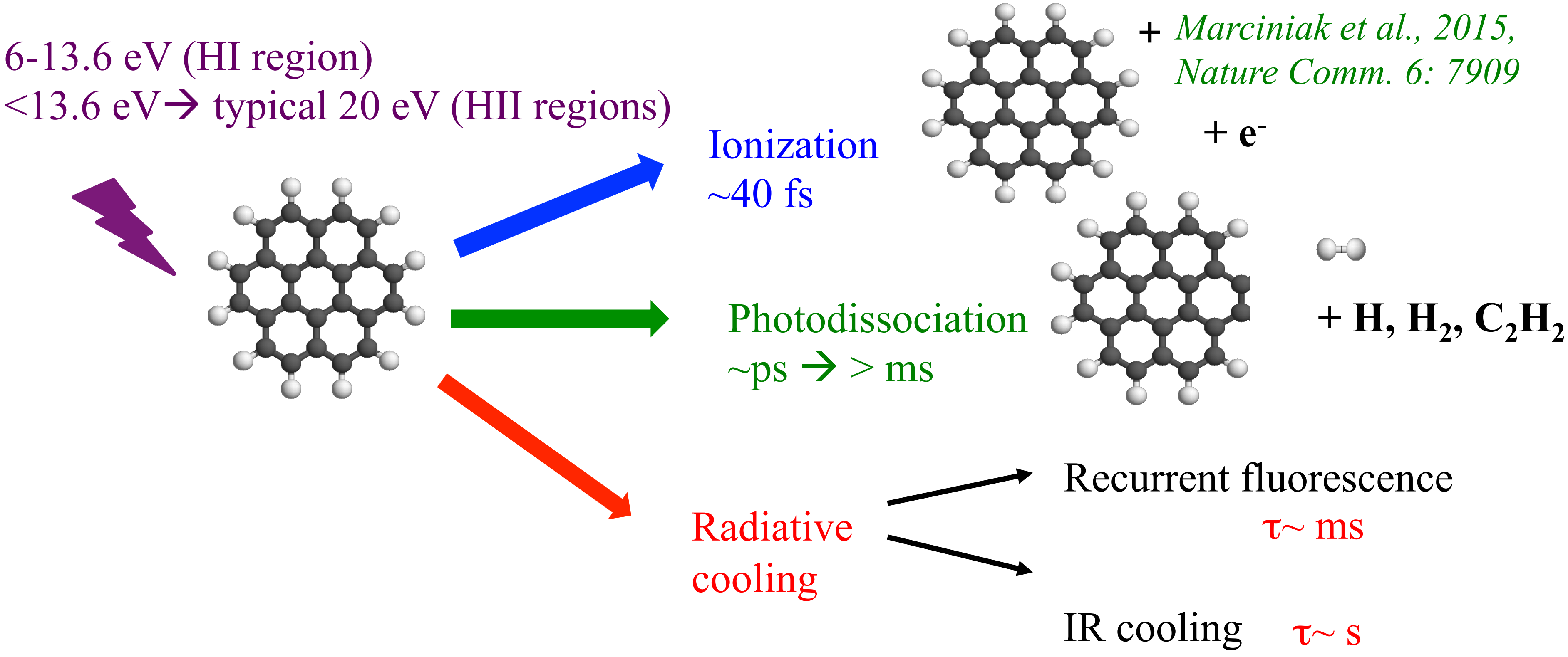




τ_{VUV} ~ few hours
τ_{coll} ~ 1 day

Slow infrared cooling

Molecular timescales

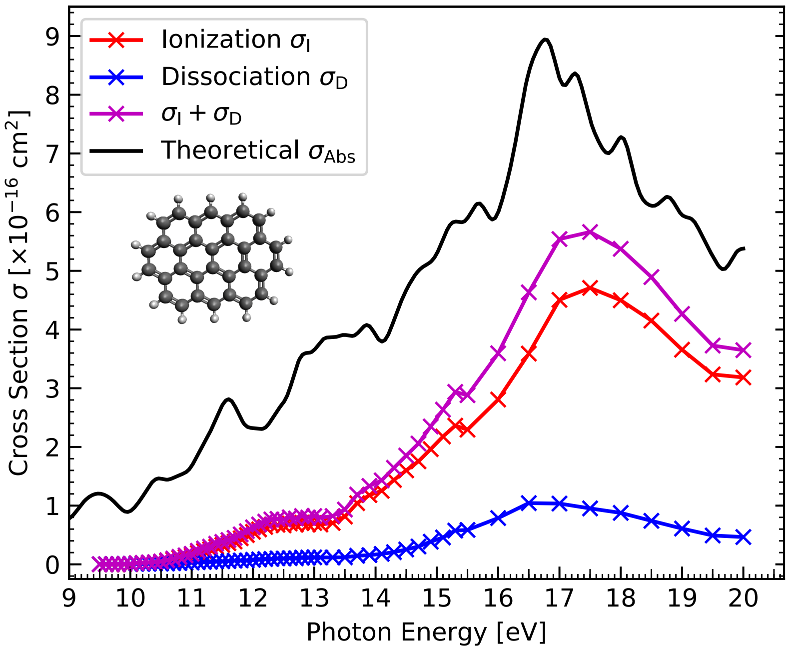


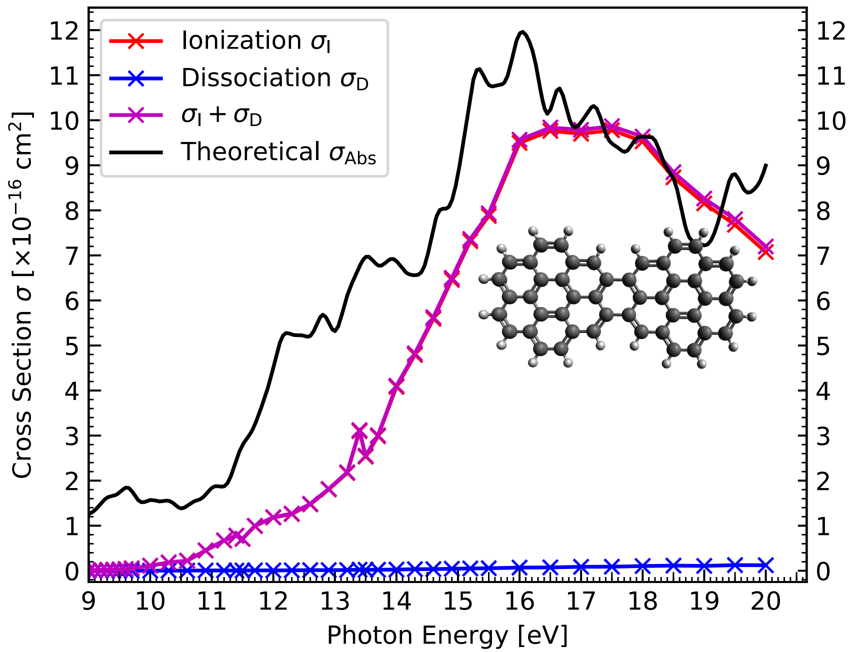
Martin et al. 2013, PRL 110, 063003

Competition between ionisation and fragmentation in ion traps

Leiden iPoP setup @ DESIRS beamline (SOLEIL)
Zhen et al. 2015, ApJL 804, L7

Linear ion trap @ DESIRS beamline (SOLEIL)
Wenzel et al. 2019, IAUS 350 proceedings & in prep.





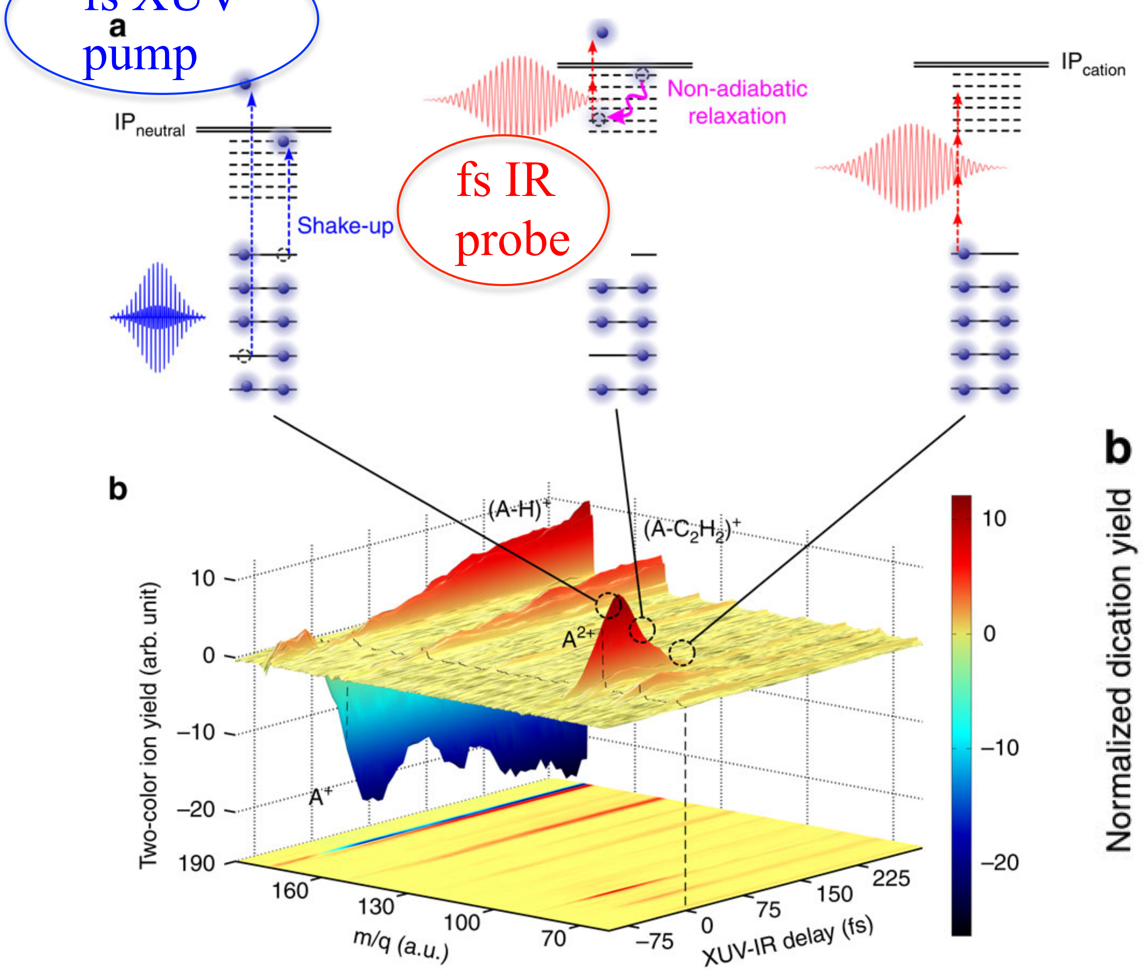
Increase N_C → Increase the ionisation yield and decrease the dissociation yield.

Dynamics in highly-excited states of PAHs probed with ultra-fast lasers

Fs pump-probe experiments @ Lyon University

fs XUV pump

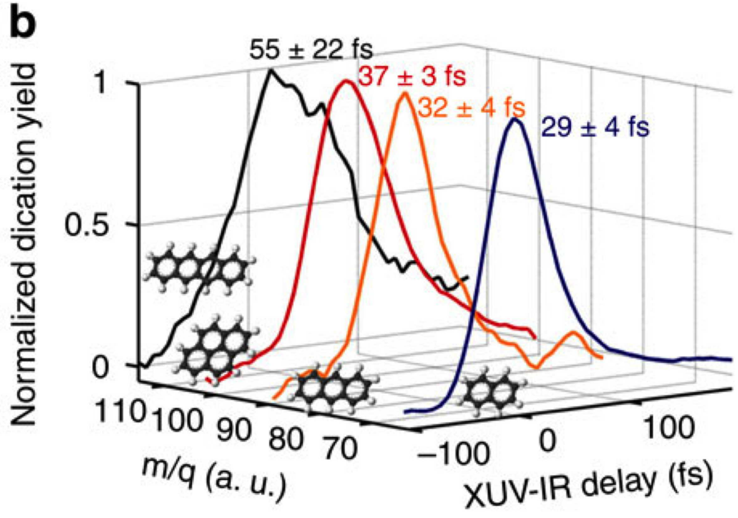
fs IR probe



Marciniak et al., 2015, Nature Comm. 6: 7909

→ Relaxation through internal conversion within a few tens of fs.

→ Dissociation of hot PAH$^+$ at t>100 fs

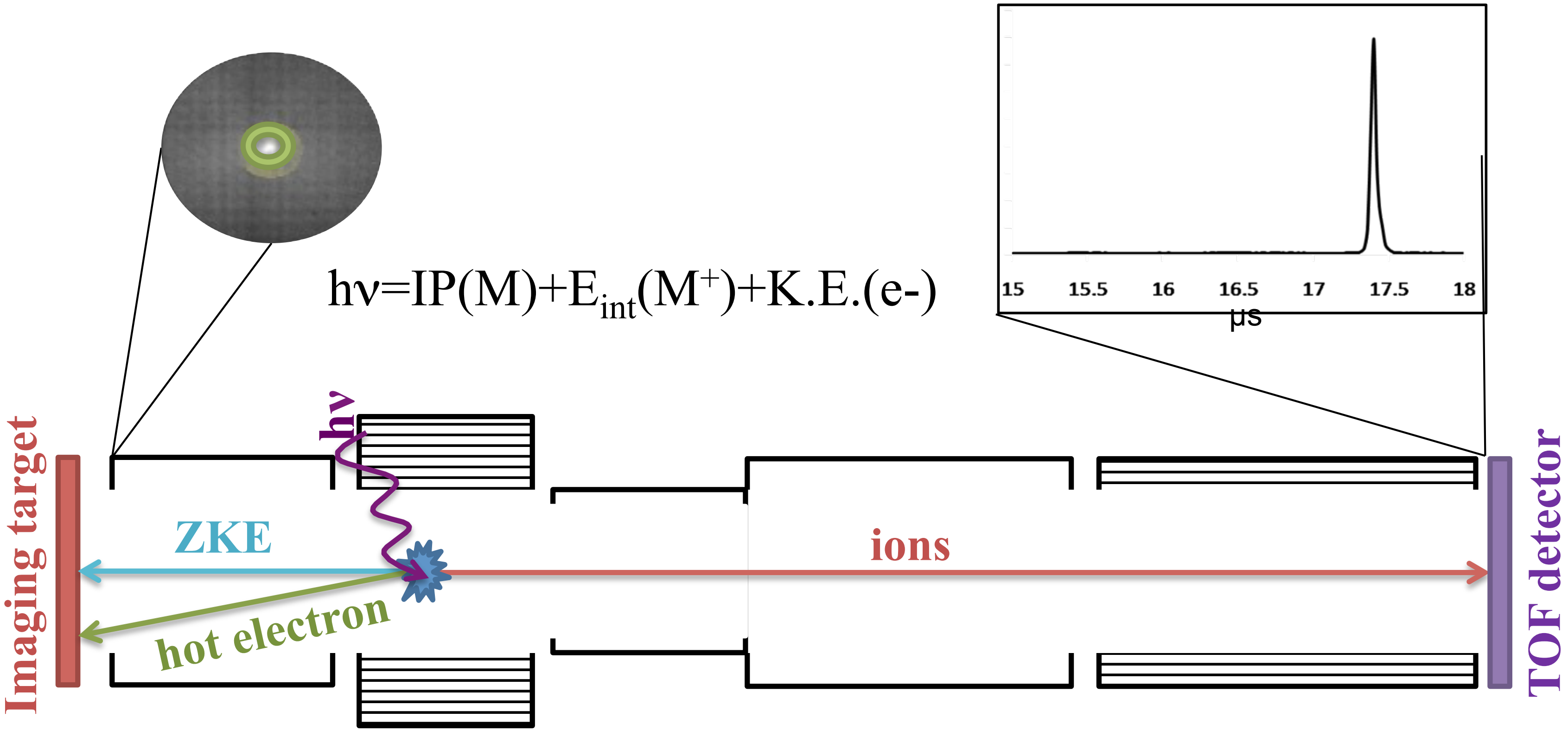


Photodissociation quantified in coincidence experiments

iPEPICO in molecular beam @ synchrotron VUV (Swiss Light Source)

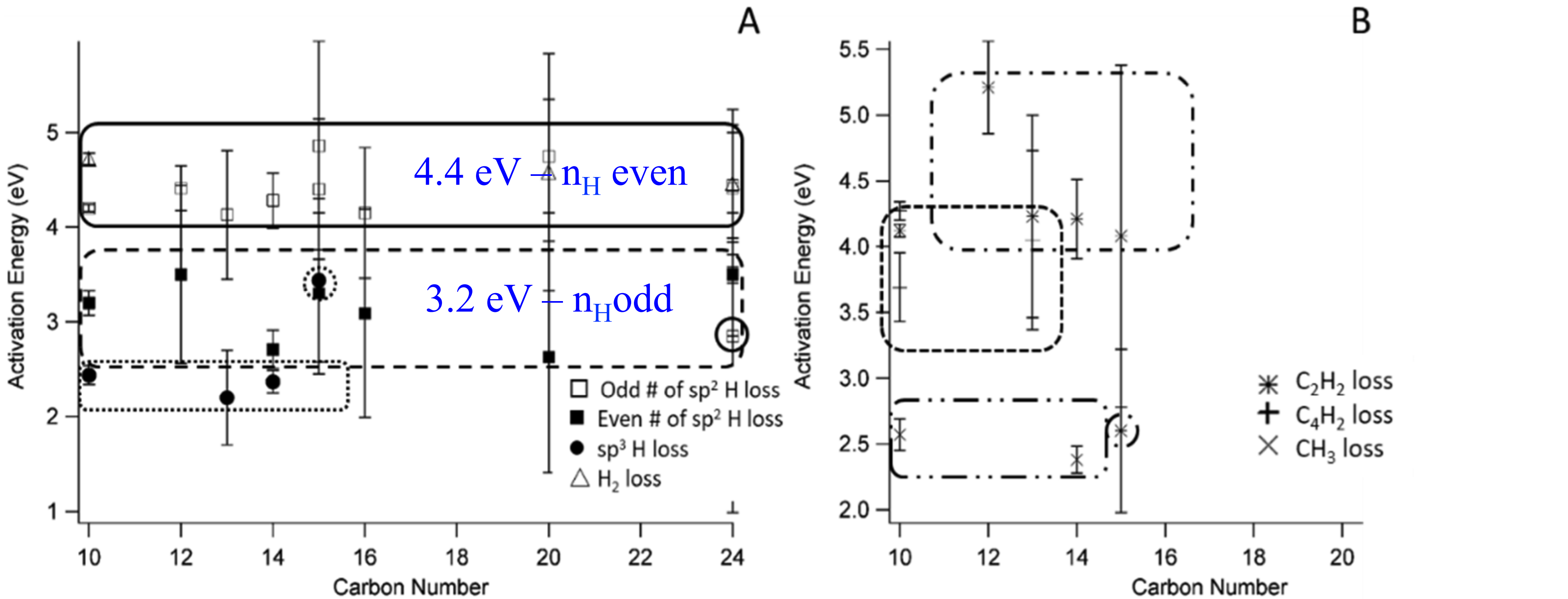
Imaging photoelectron photoion coincidence spectroscopy:
threshold electrons in coincidence with ions

$$h\nu = IP(M) + E_{int}(M^{+}) + K.E.(e-)$$



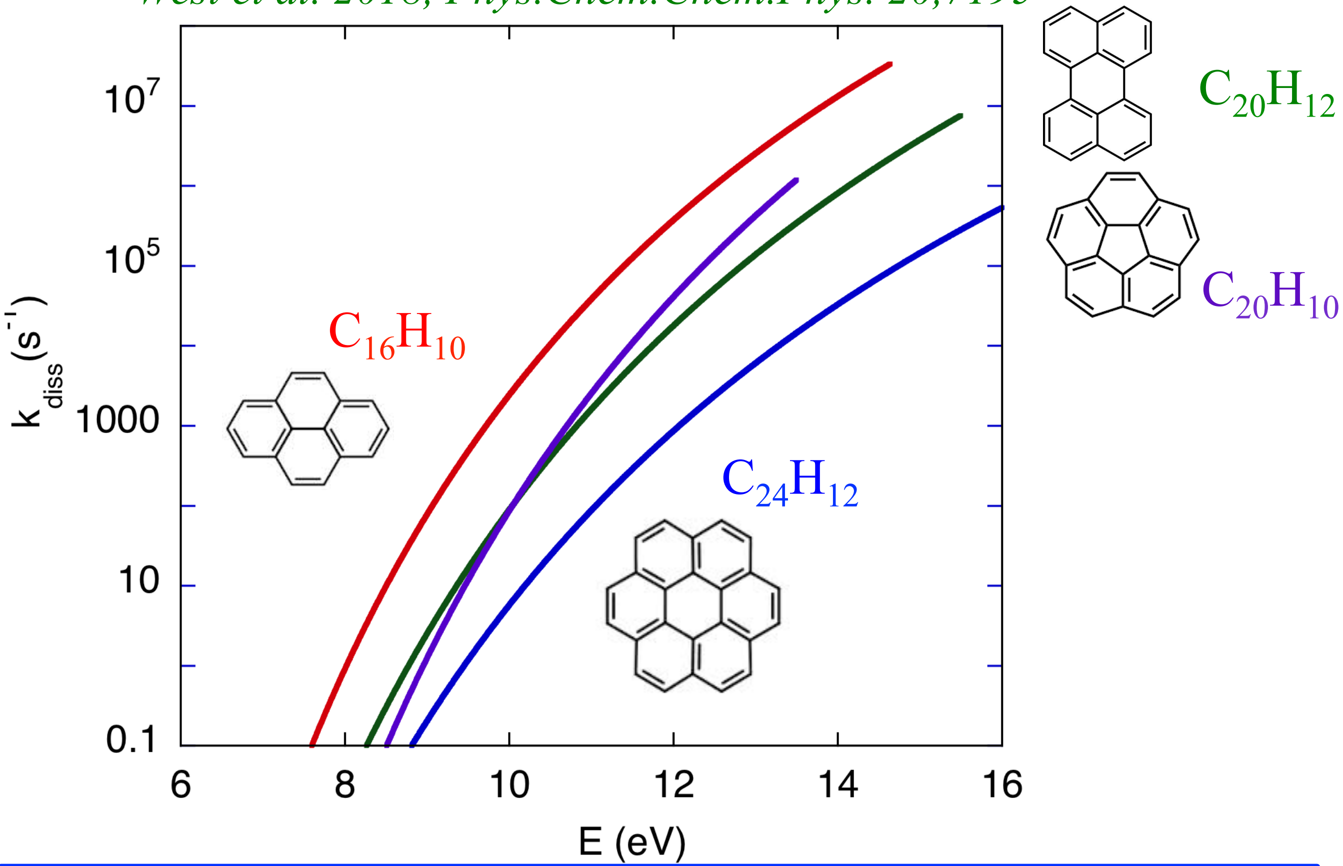
Unimolecular dissociation: Activation energies (E_0)

West et al. 2018, Phys.Chem.Chem.Phys. 20, 7195



Unimolecular dissociation rates (-H channel)

West et al. 2018, Phys.Chem.Chem.Phys. 20,7195

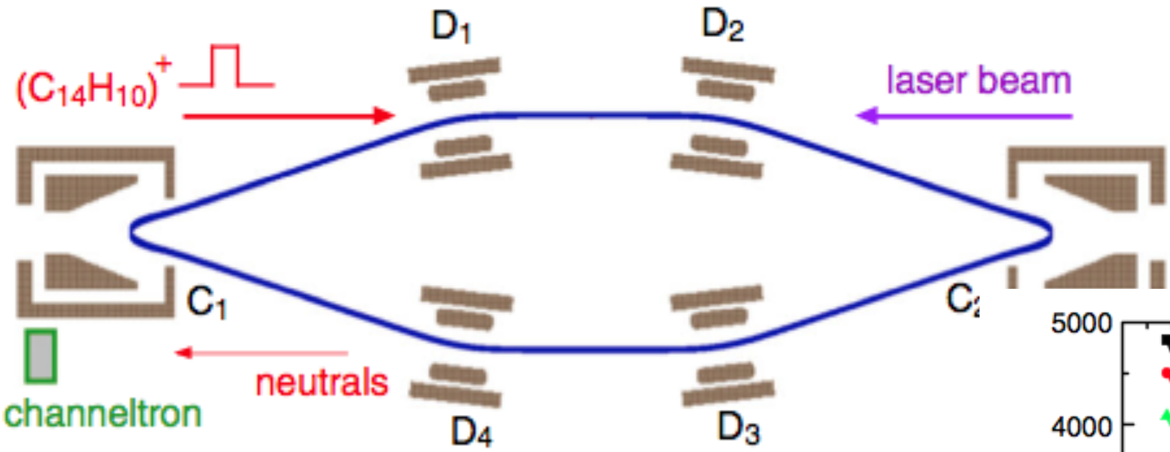


Kinetic shift observed with size in line with statistical theories

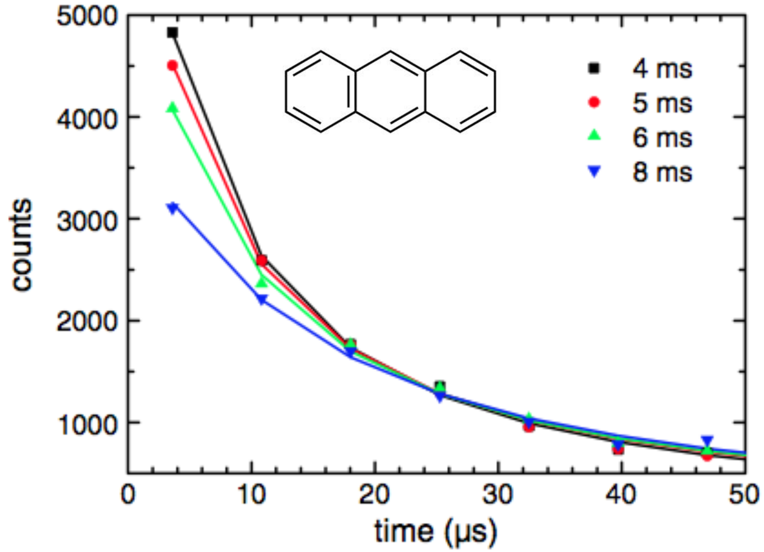
Radiative cooling in storage rings: from recurrent to IR fluorescence

Mini-ring storage ring + ECR source @ Lyon University

Martin et al. 2013, PRL 110, 063003; 2015, Phys. Rev. A 92, id.05342



Delay between injection of hot ions/ laser beam



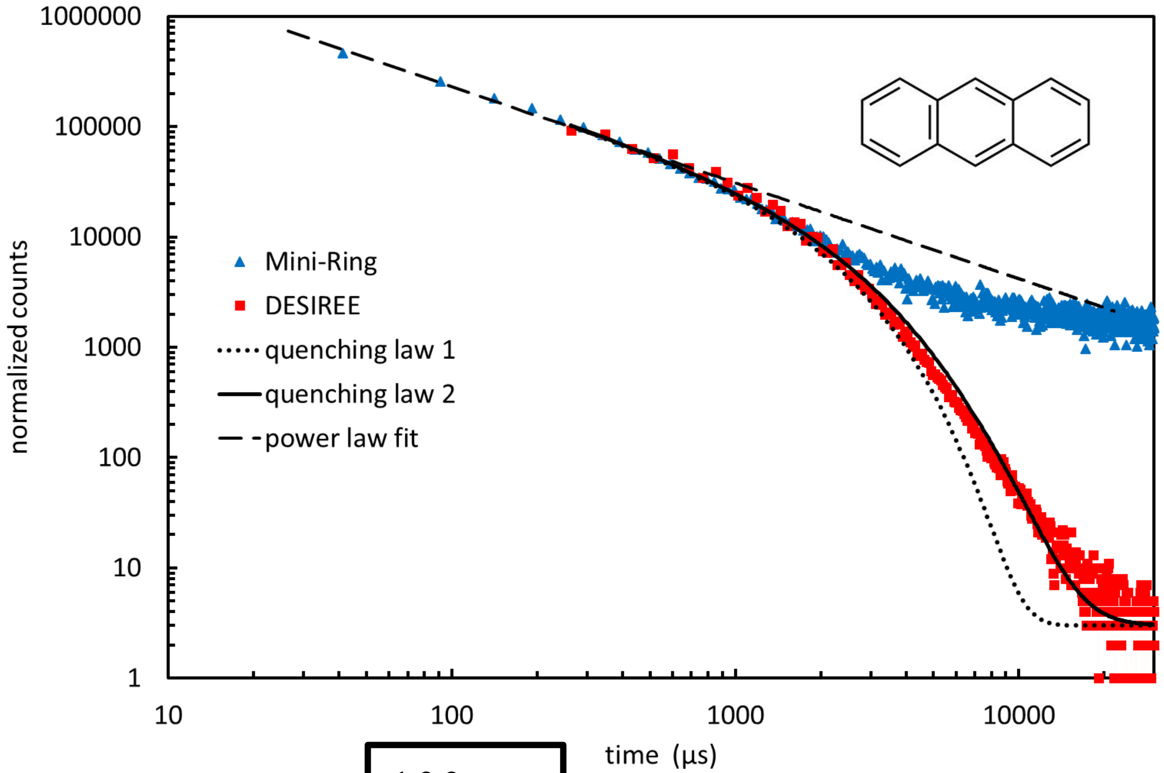
Evolution of the fragment count → k_{cool} =120-250 s^{-1} for E_{int}=6.6 to 6.8 eV

Faster than IR emission → fluorescence from thermally excited electrons

Dynamics of radiative cooling on long timescales (>s)

DESIREE cryogenic double ring facility @ Stockholm University

Bernard et al. 2019, in prep.

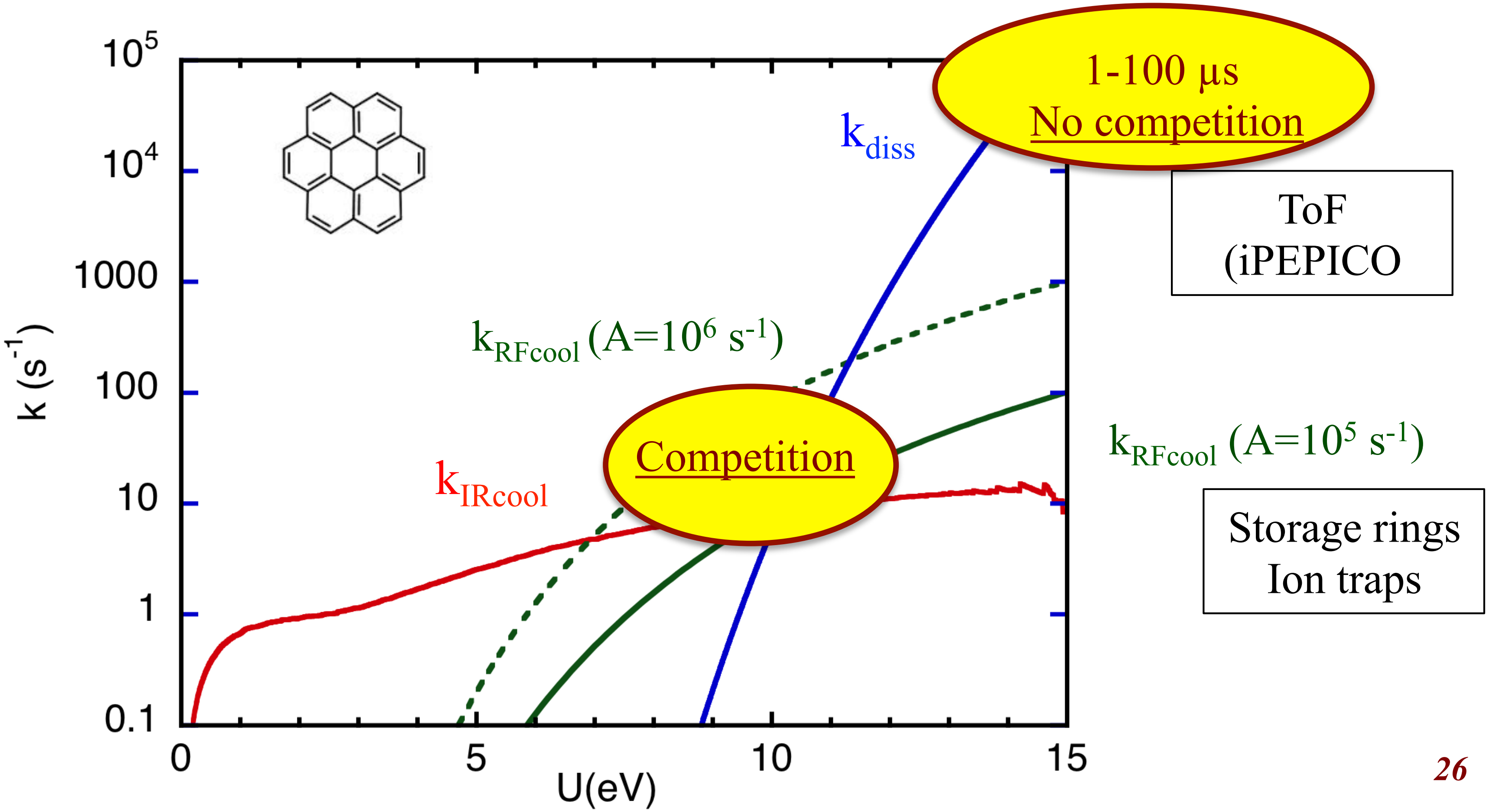


100 µs

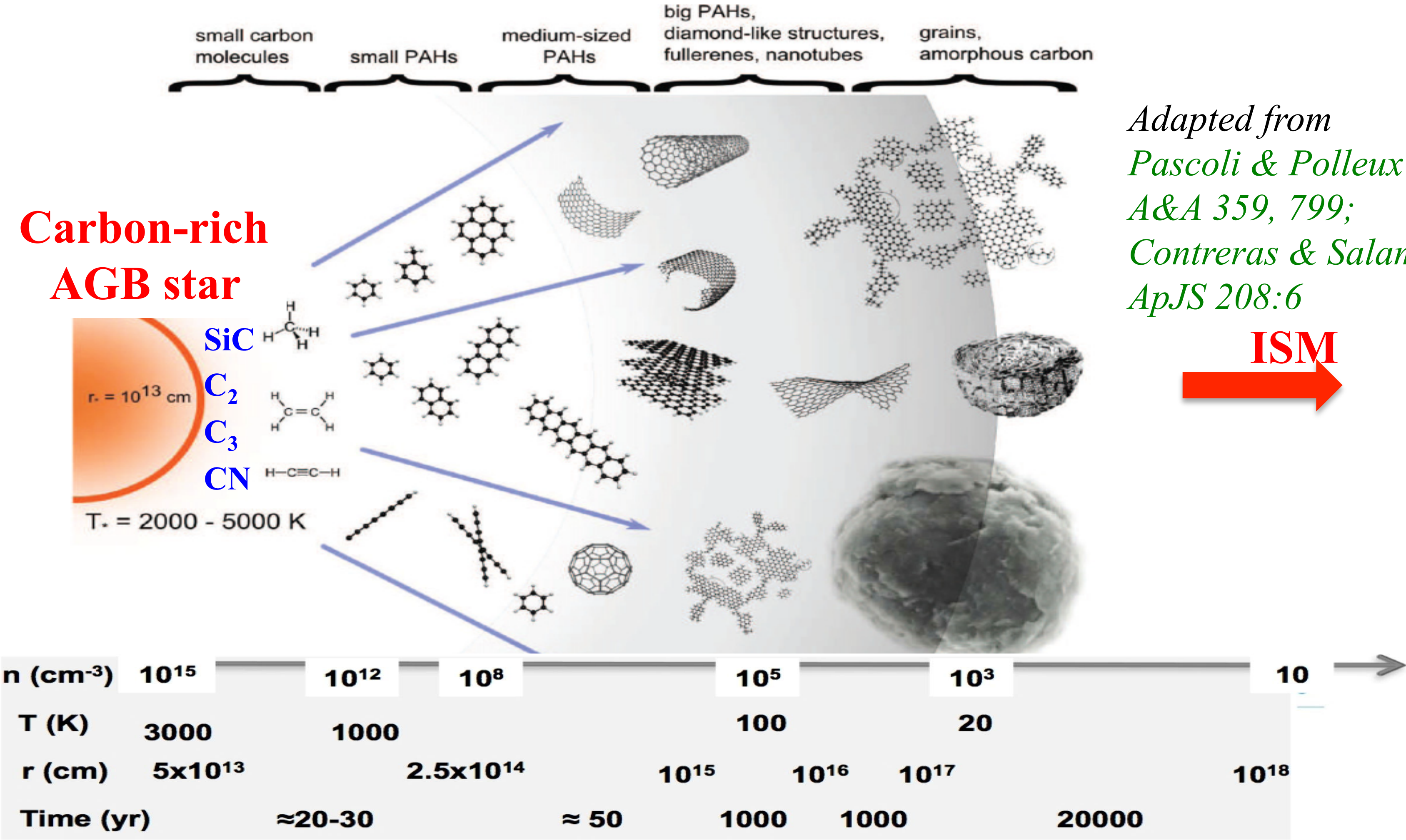
2 s

Competition between dissociation and radiative cooling

A key concept in astrophysical environments and laboratory experiments



Formation of C-dust in evolved stars: a schematic view



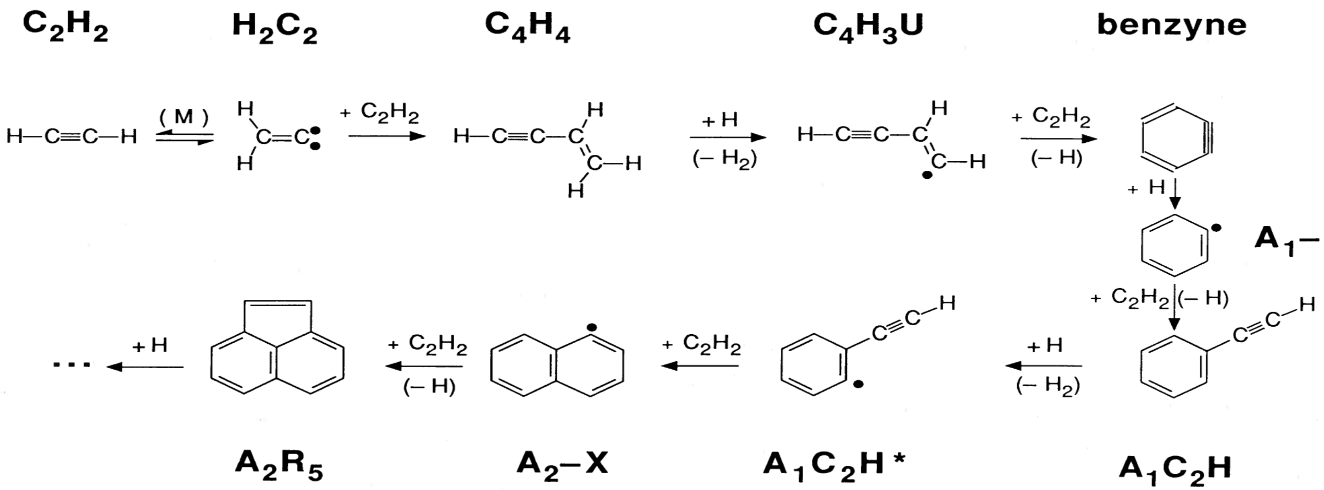
Adapted from
Pascoli & Polleux 2000, A&A 359, 799;
Contreras & Salama 2013, ApJS 208:6

ISM

Formation of PAHs in AGB stars

Models based on studies of soot production in hydrocarbon pyrolysis and combustion.

Frenklach & Feigelson 1989, ApJ 341, 372; Cherchneff, Barker, Tielens 1992, ApJ 401, 269



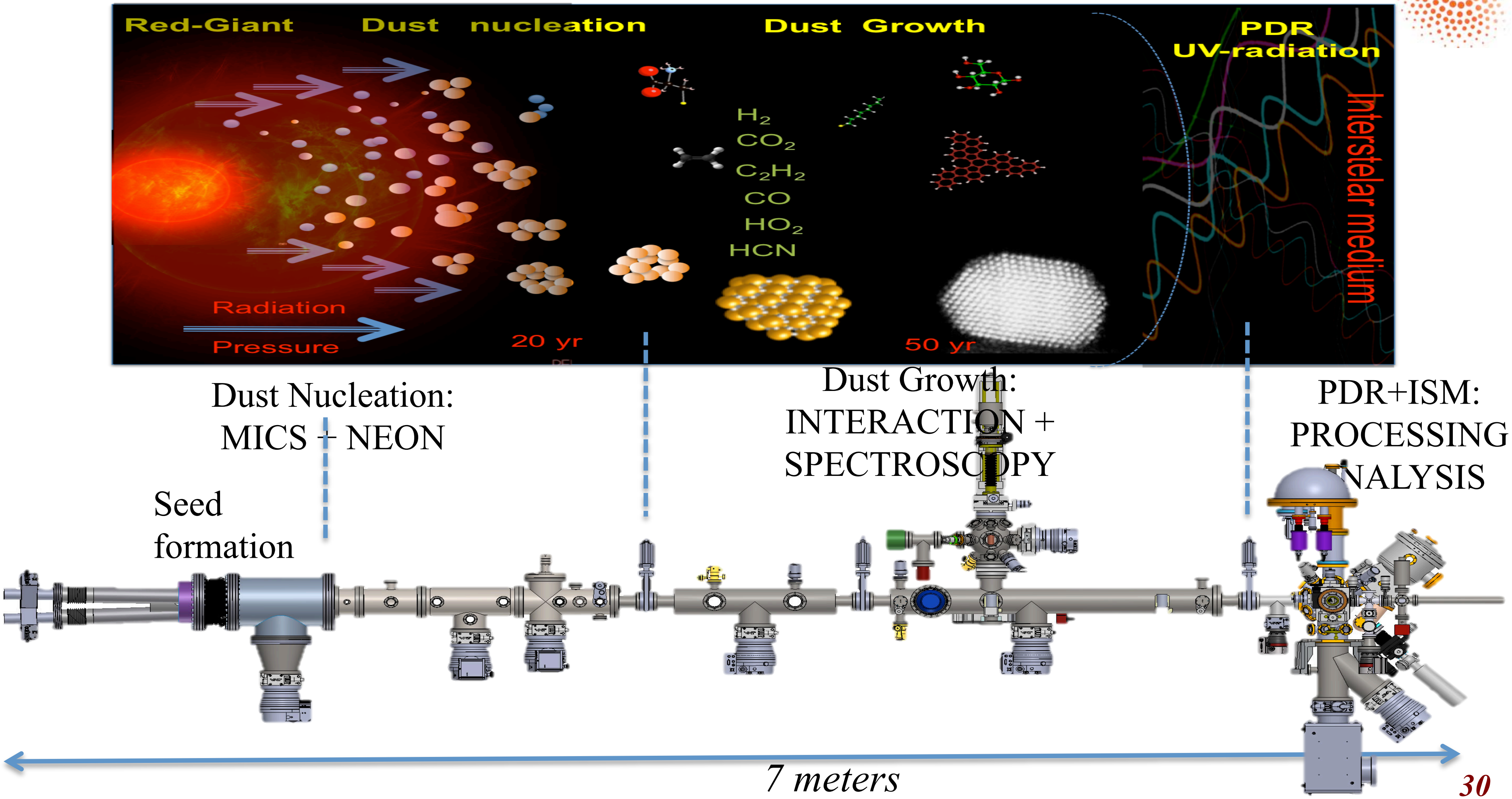
Models predict a low PAH yields in circumstellar envelopes but a lot of unknowns on the physical/ chemical conditions in evolved star shells.

Laboratory analogues of stardust

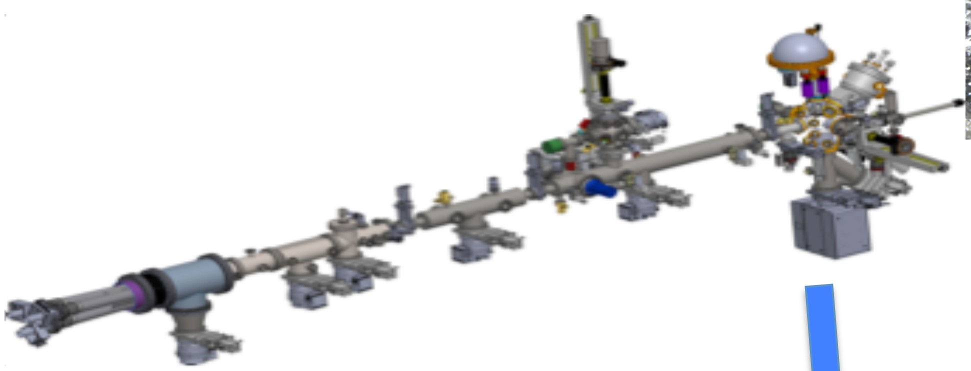
Technique	Precursors	T (K)	Ion chemistry	Wall effect	Refs
Laser ablation	Graphite +quenching gas	≥4000	yes	no	(1) (2)
Combustion/Flames	Hydrocarbons	1800-2500	weak	no	(3)
Pyrolysis (laser induced)	Hydrocarbons	1000-1700 ≥3500	no	depending on reactor	(4) (5)
Pyrolysis	Hydrocarbons	600-2000	no	depending on reactor	(6)
Dusty plasmas	Hydrocarbons	600-2000	weak	yes	(7) (8) (9)
Stardust machine	Graphite + gas (H_2,…)	<1000	weak/no	no	(10)

(1) Kroto et al. 1985, Nature 318, 162; (2) Jaeger et al. 2008, ApJ 689, 249 (3) Carpentier et al. 2012, A&A 548, A40; (4) Jaeger et al. 2006, ApJS 166, 557; (5) Jaeger et al. 2009, ApJ 696, 706; (6) Biennier et al. 2009, Carbon 47, 3295 ; (7) Kovacevic 2005, ApJ 623, 242; (8) Contreras & Salama 2013, ApJS 208: 6; (9) Maté et al. 2016, ApJ 831:51; (10) Martínez et al. 2019, subm.

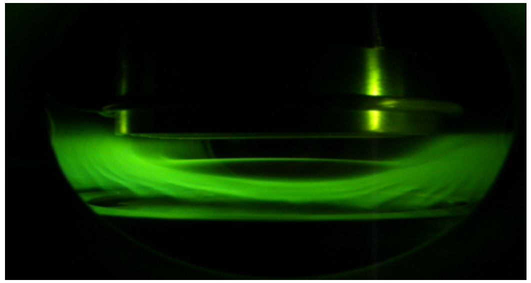
Nanocosmos: the Stardust machine



Molecular content of stardust analogues and meteorites



Meteorites
Natural stardust

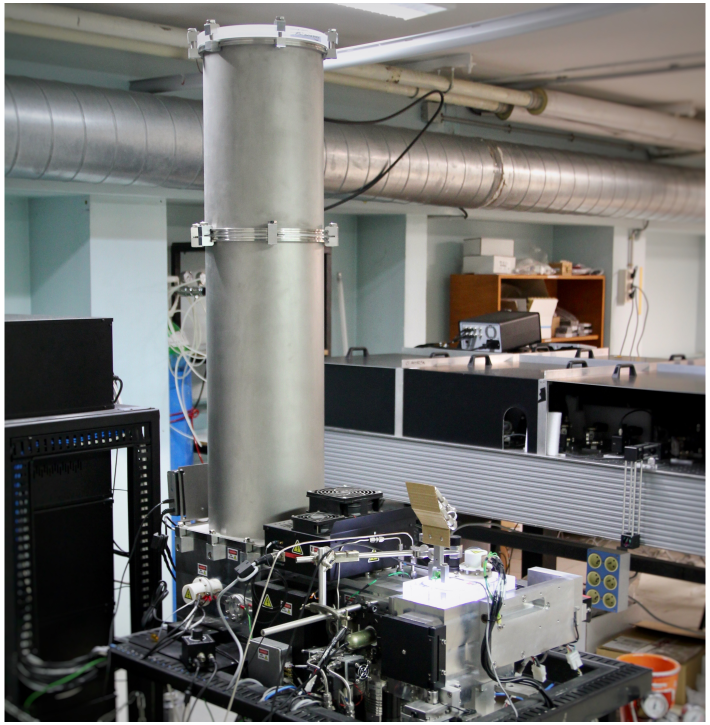


Stardust Machine
(ICMM)
Stardust lab. analogues

Plasma reactors
(LAPLACE/IEM)
Laser vaporisation source
Stardust laboratory analogues

Molecular analyzer
(IRAP/LCAR)
Molecular component of dust

Astrochemistry Research of Organics using a Molecular Analyzer



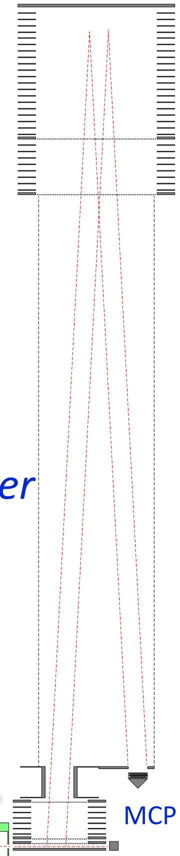
FasmaTech SCIENCE + TECHNOLOGY

Performances of AROMA:

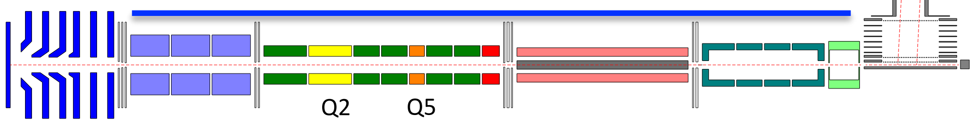
- Mass range : 20 to 10^4 amu
- Mass resolution: 8000 to 10000 @ 300 amu
- Mass accuracy : 10 ppm
- Isolation: 1 amu resolution
- MS/MS experiments
- Photodissociation and kinetics studies

Two stage reflectron

oTOF mass analyzer



Ion trap

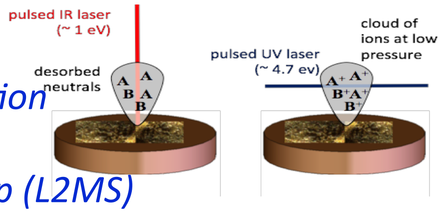


High Voltage Lens RF Octapole Injection

Segmented Linear QIT Isolation & Dipolar excitation

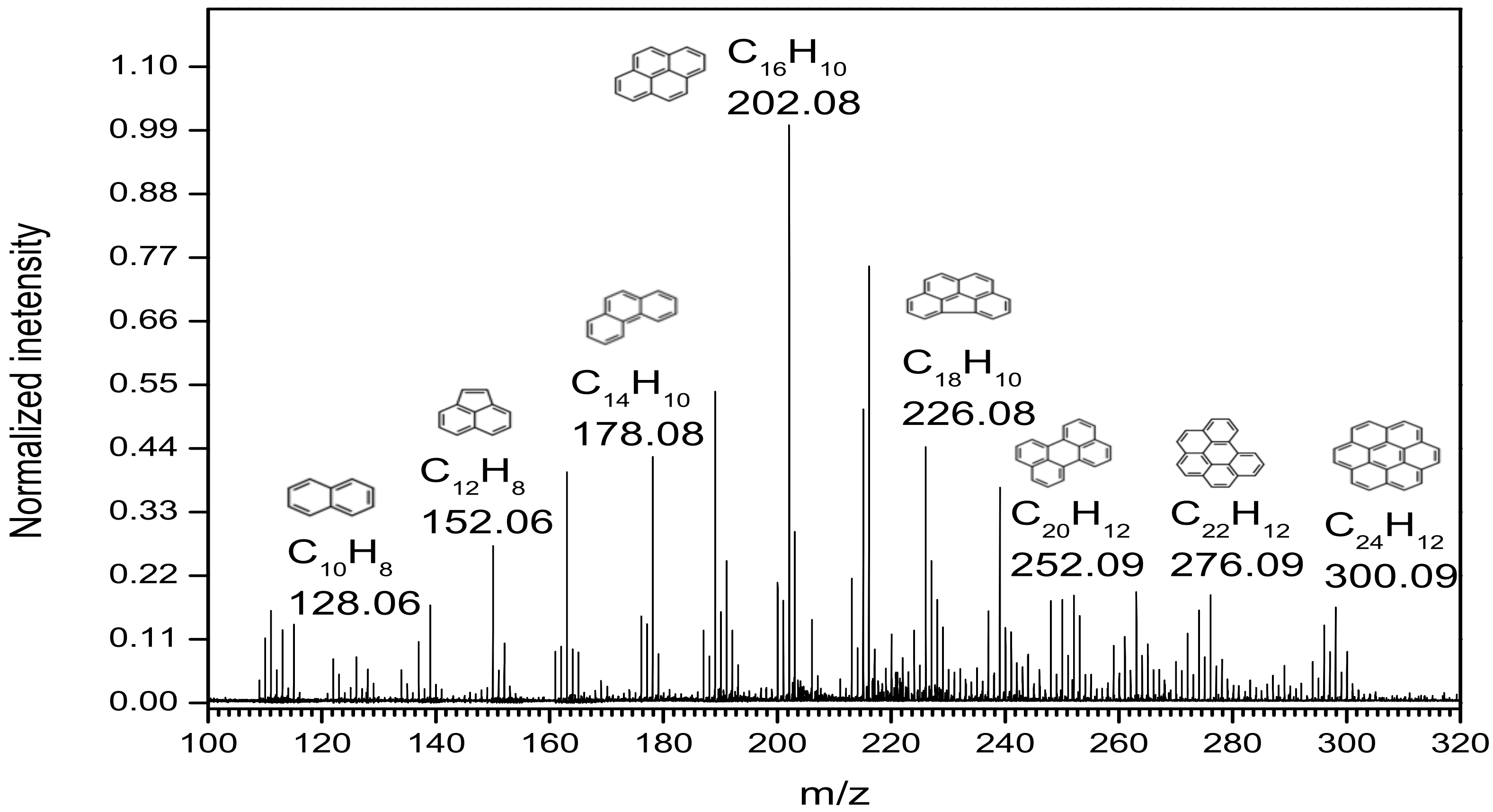
Ejection to oTOF, Hexapole and box KE ion optics

Laser desorption/ionization source:
In one (LDI) and two-step (L2MS)



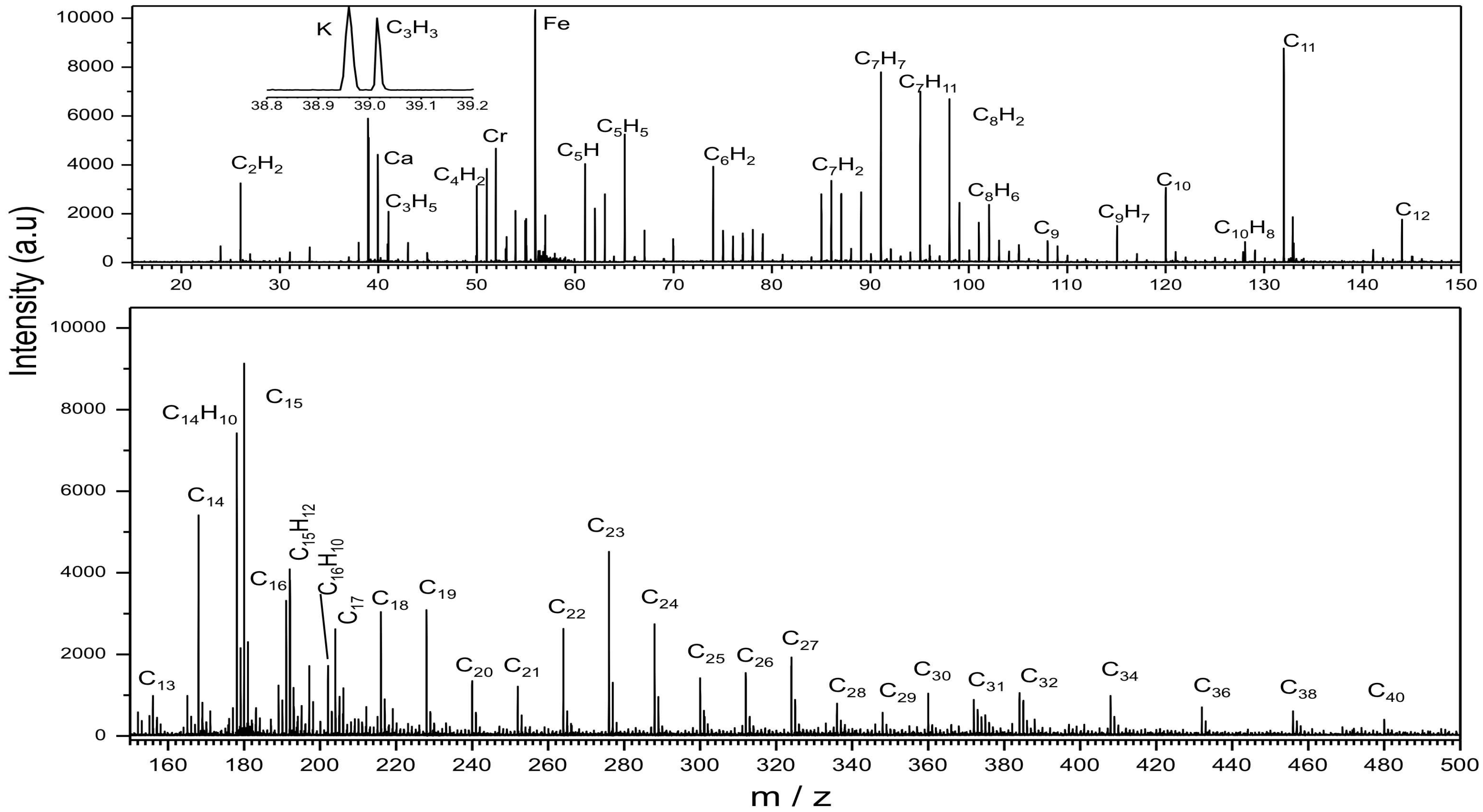
PAH distribution in the Murchison meteorite by AROMA

Sabbah et al., 2017, Astrophys. J. 843, id. 34



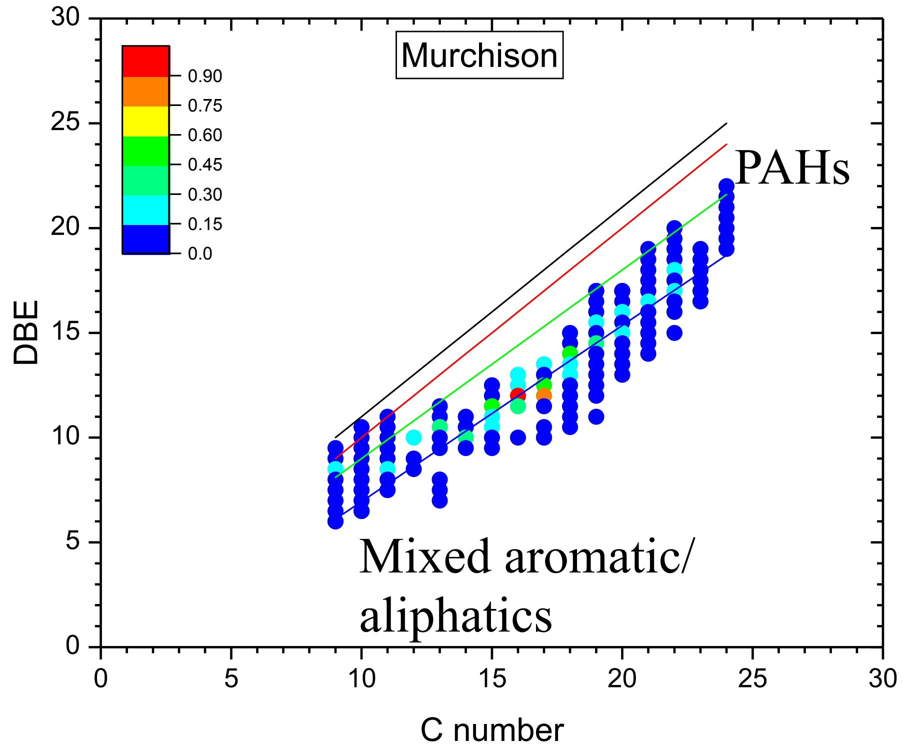
C_n and PAHs in the Almahata Sitta meteorite by AROMA

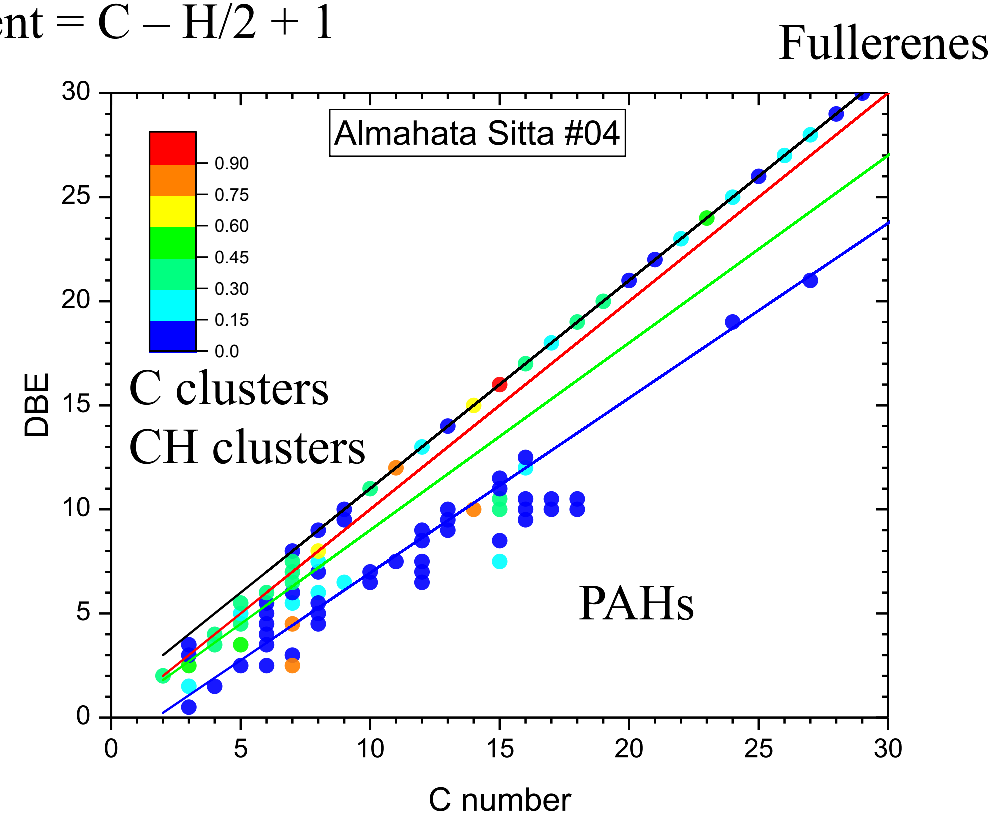
Sabbah et al., in prep.; collaboration P. Jenniskens (SETI Institute - ARC)



Meteorite samples: distribution of species (DBE)

Double Bond Equivalent = C – H/2 + 1

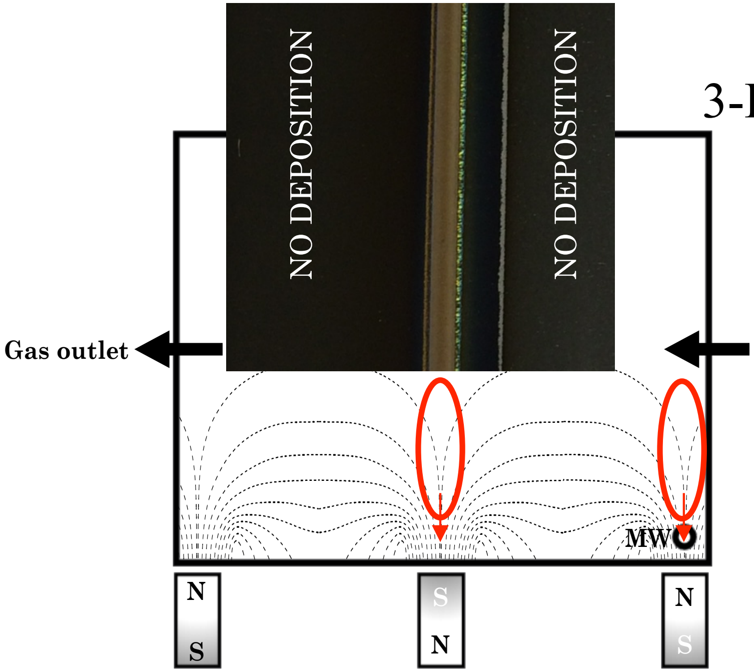




→ Different chemistries involved?

Very low-pressure nonthermal dusty plasma / C_2H_2

$P \sim 10^{-3}$ mbar



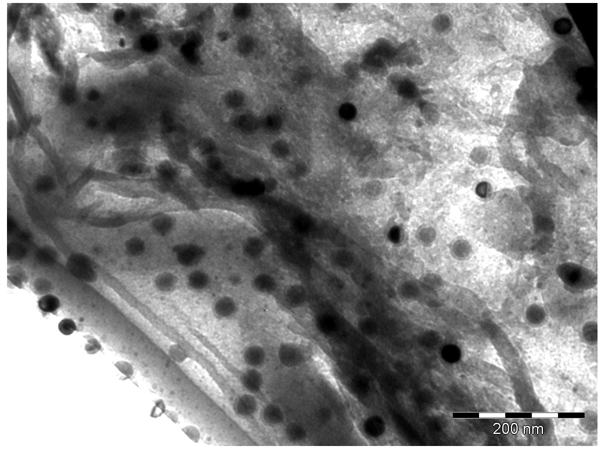
3-Deposition of dust particles

→ ex-situ analyses

C_2H_2 inlet

2-Dust particle growth
Magnetic confinement
→recombination in volume

1-Plasma production : Heating of electrons
<Te>=10 eV, $ne \sim 10^9$ cm^{-3}



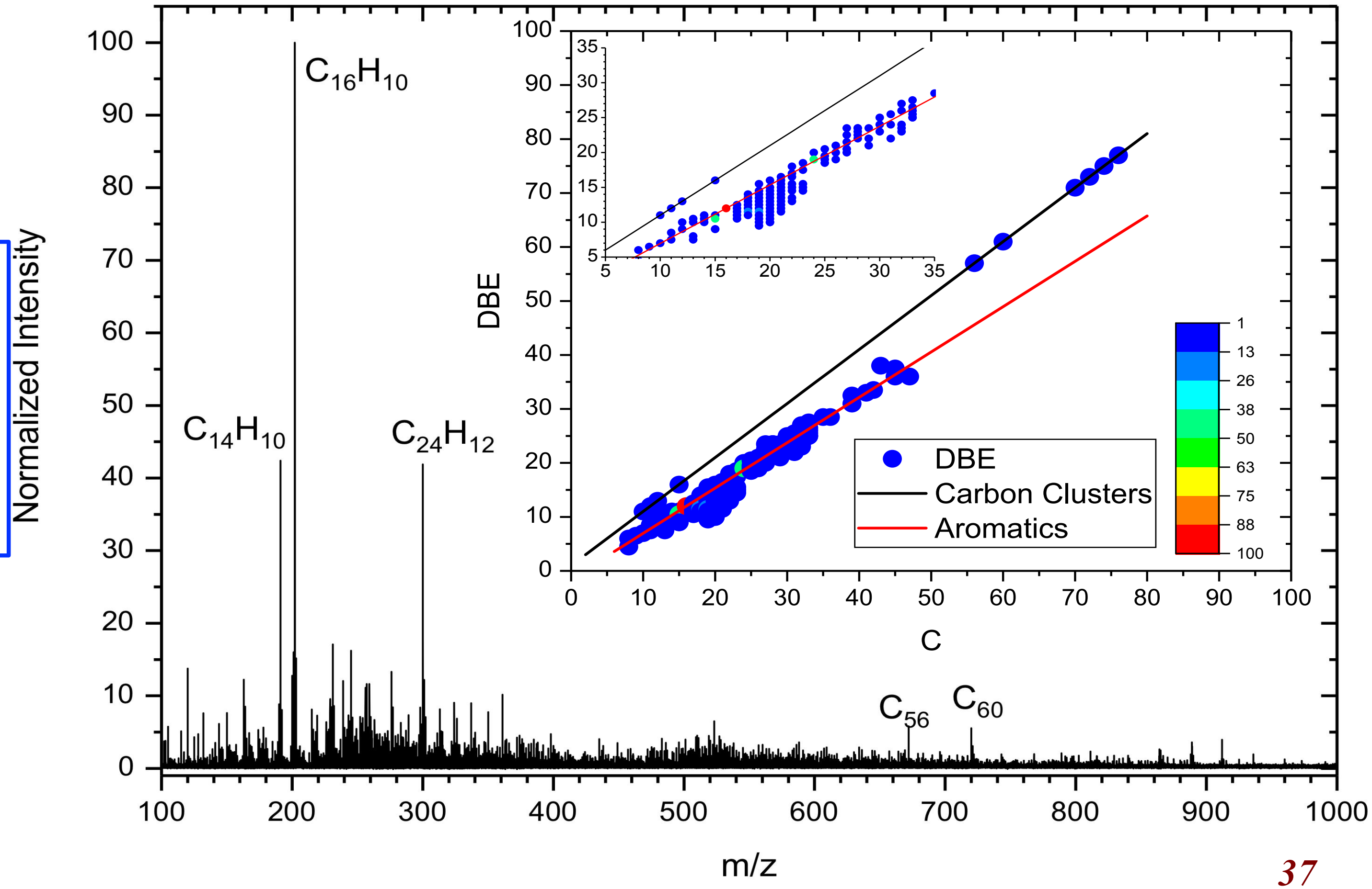
TEM analysis:
Average diameter of 20nm / 5min
Spherical → isotropic growth process

Very low-pressure nonthermal dusty plasma / C_2H_2

Clergereaux et al., in prep.

C_2H_2: 0.6 mTorr
Plasma: 5 min

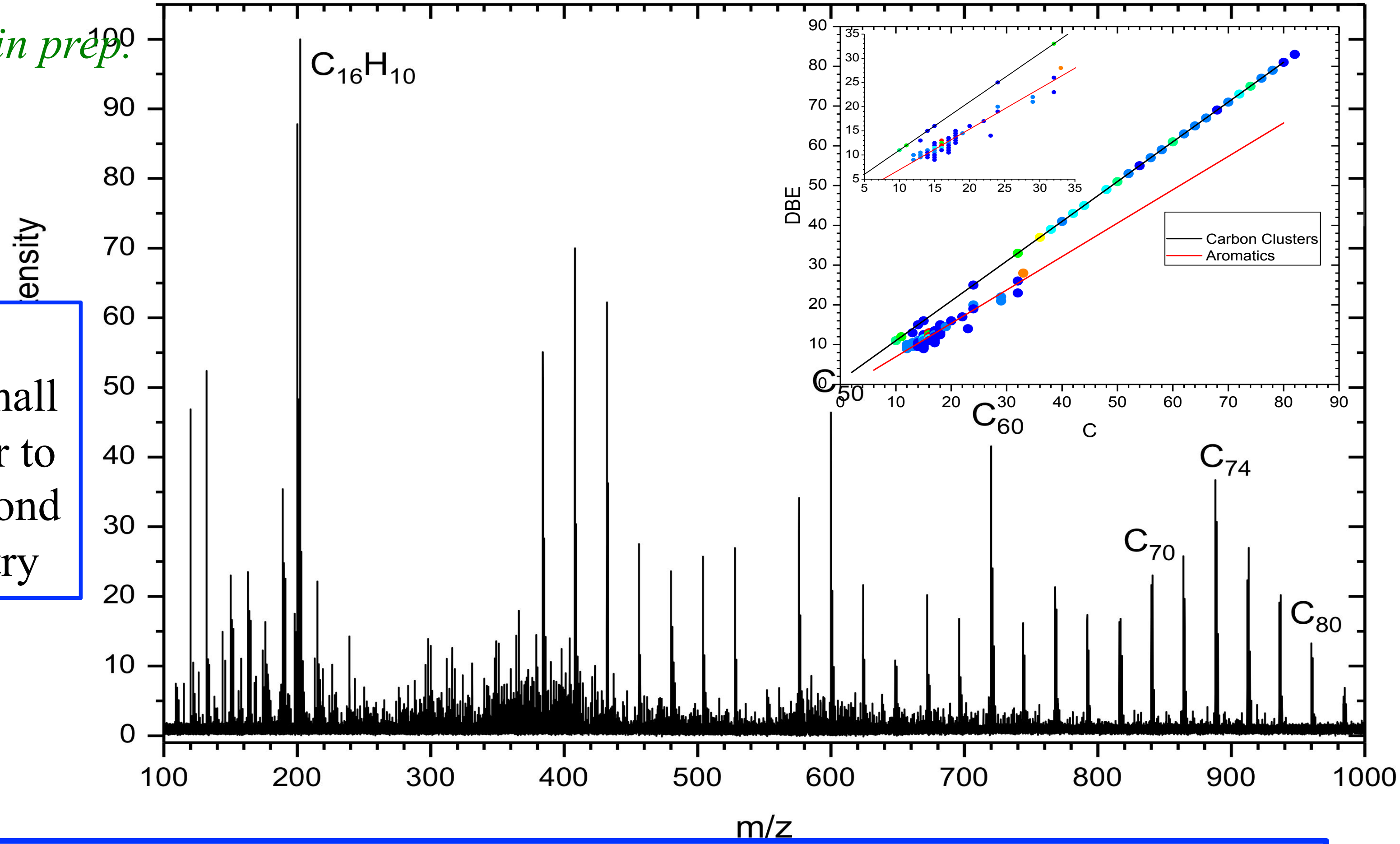
Formation of large molecules (PAHs and mixed aromatic/ aliphatics) despite the very low pressure



Very low-pressure nonthermal dusty plasma / C_2H_2

Clergereaux et al., in prep.

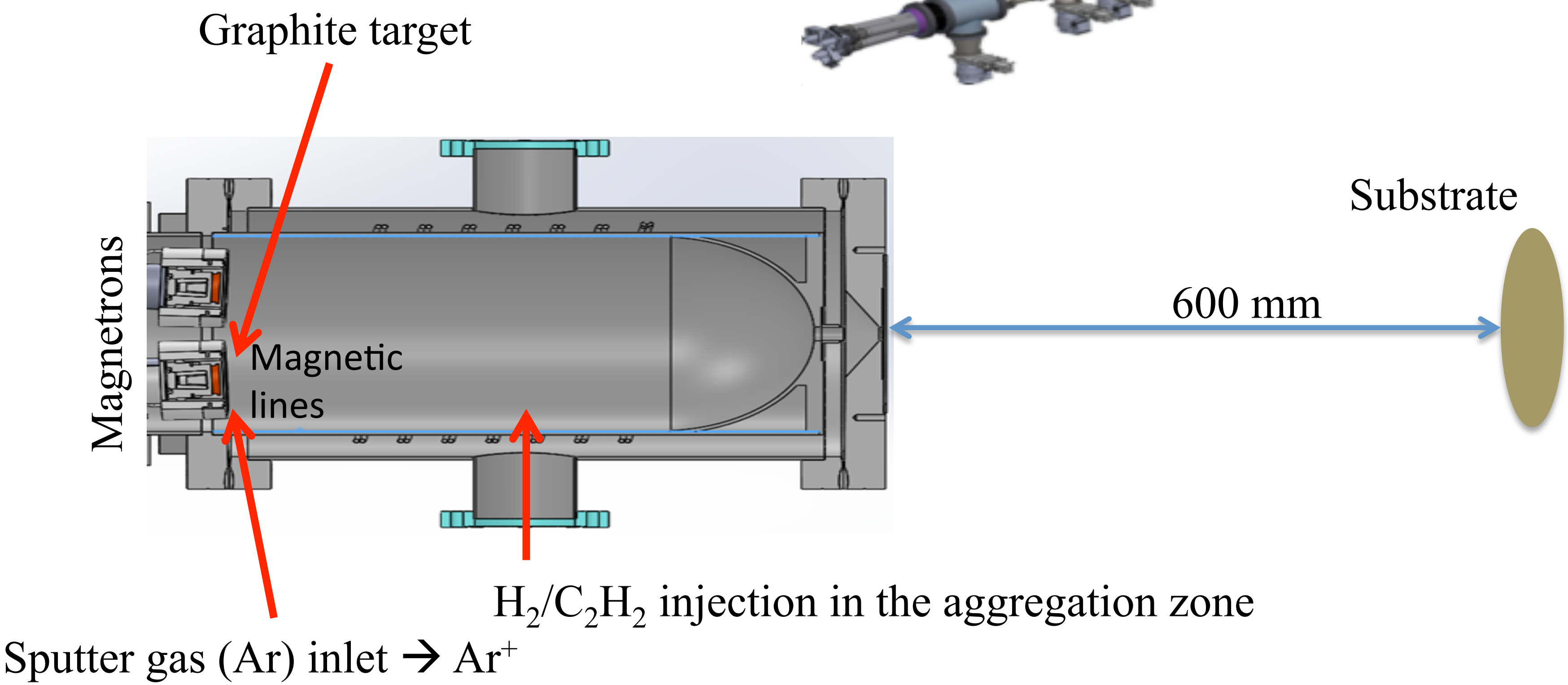
0.6 mtorr
C_2H_2/ 10 min



PAHs are formed first. C clusters (small +fullerenes) appear to be formed as a second generation chemistry

→ Possibility to form the populations in "controlled" conditions (pressure, time)

Experiments with the Stardust machine

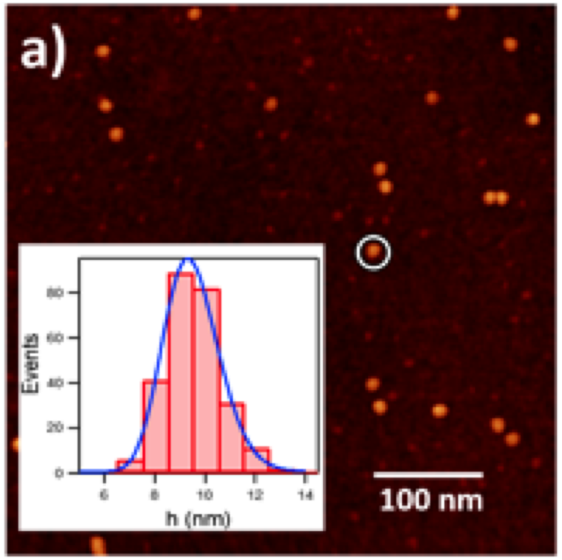


Martínez et al. 2018, Scientific reports 8:7250

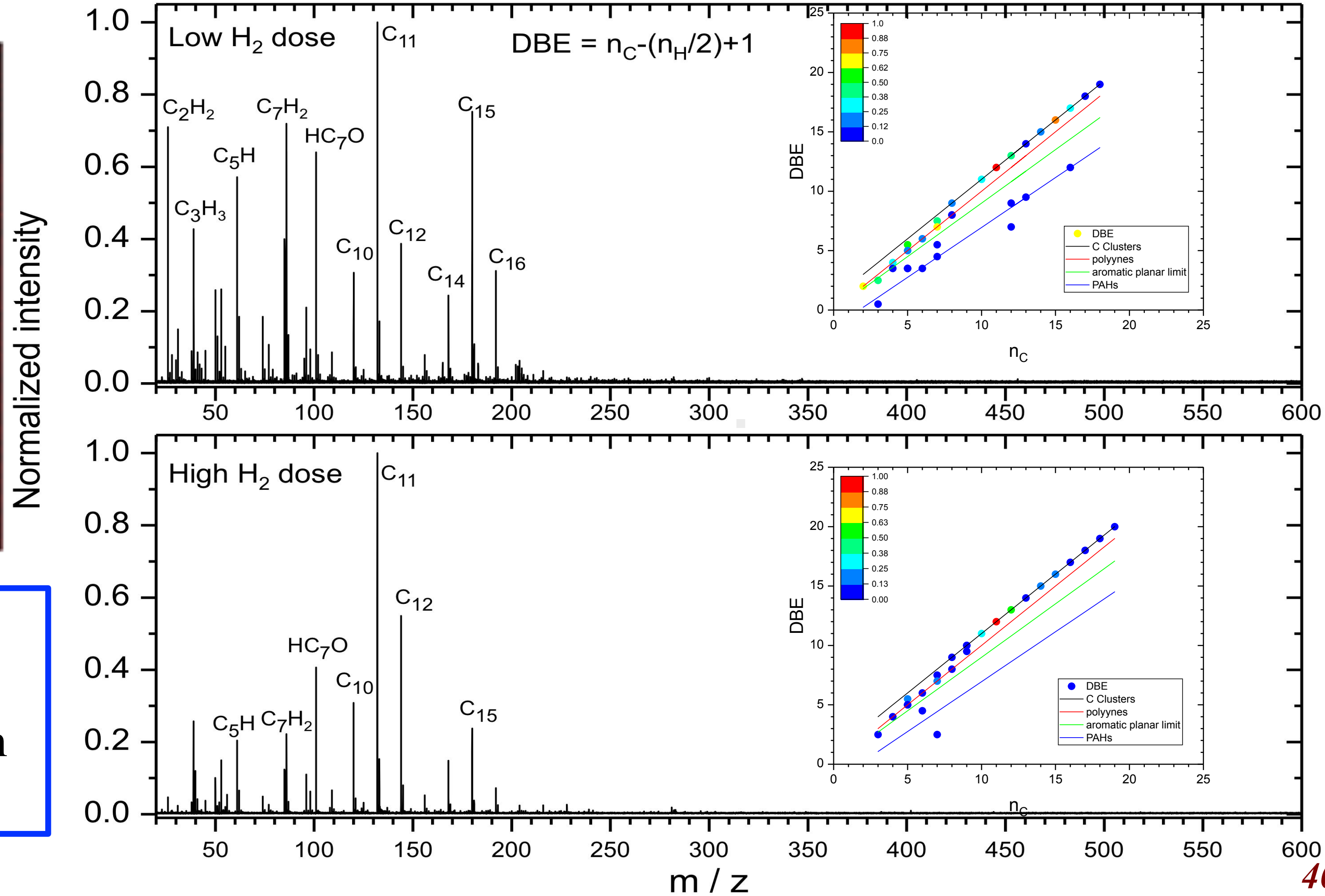
Stardust samples: C vs C+H_2

Martínez et al., 2019, in press

AFM image



Molecular analysis



Formation of C and HC clusters
Very low ion signal from aromatics <3%

Conclusion and perspectives

- Interstellar PAHs and fullerenes are in extreme environments.

→ Importance to study the competition between unimolecular dissociation and radiative cooling upon interaction with VUV photon.

- The formation mechanism(s) for (large) PAHs and fullerenes are not solved yet.

→ Part of the difficulty related to the still poorly characterized physical and chemical conditions by astronomical observations.

→ Interesting perspectives through the analysis of meteorites (identification of the stardust component).

→ Investigate formation pathways under controlled conditions.

More expected from coming experiments….

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