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\textsubscript{60}

  * 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

Let’s celebrate Xander
NASA Ames 1993 - 1995

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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. Geballe2
Received 1995 April 6; accepted 1995 July 28

VARIATIONS OF THE 8.6 AND 11.3 μm EMISSION BANDS WITHIN NGC 1333: EVIDENCE FOR POLYCYCLIC AROMATIC HYDROCARBON CATIONS
C. Joblin,1,2 A. G. G. M. Tielens,1 T. R. Geballe,3 and D. H. Wooden1
Received 1995 December 6; accepted 1996 January 19
PAHs and the Universe: the 25th anniversary
Toulouse 31/05- 4/06 2010
And much more

- Herschel/HIFI – Preparatory work – key programs (from 1995)
- Molecular Astrophysics (Elsevier) since 2015
  Editor-in-chief: Xander Tielens
The Aromatic Infrared Bands (AIBs)

ISO SWS spectra

Infrared Space Observatory
ESA; 1995-1998

Spitzer Space Telescope
NASA; 2003-2009

AKARI
JAXA; 2006-2011

James Webb Space Telescope
NASA; 2021-2025?

Peeters et al., 2004, Astrophysics of Dust vol 309, p141
The Aromatic Infrared Bands (AIBs) \( \rightarrow \) The PAH model

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

CH and CC aromatic modes

- Stochastic heating – absorption of a single UV photon \( \rightarrow \) N~50 ; T~1000 K


- Candidates: PAH molecules

- Energetic budget: 10 to 20% of total C
\( \rightarrow \) ~ 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

<table>
<thead>
<tr>
<th>CH stretch</th>
<th>CC stretch, CH bend</th>
<th>CH out-of-plane bend</th>
</tr>
</thead>
</table>

- **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

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$_{60}$)

NGC 7023 reflection nebula (star-forming region)


Tc1 planetary nebula (evolved star)

Cami et al. 2010, Science 329, 1180
Chemical relation between PAHs and $C_{60}$?

Berné & Tielens 2012, PNAS 109, 401

NGC 7023 nebula

Herschel 70 µm

Spitzer 8.0 µm

Spitzer 3.6 µm
Photochemical evolution of $\text{C}_{66}\text{H}_{20}$ and formation of $\text{C}_{60}$

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

At 10'' from the star

Go $\sim 4 \times 10^4$

$n_H \sim 2000 \text{ cm}^{-3}$

**shrinking**

Age of NGC 7023

**dehydrogenation**  **folding**
The key role of the interaction of PAHs with VUV photons

- VUV photon
- Ionization
  - Photoelectric effect / Gas heating
- Photodissociation
  - PAH lifetime
- Radiative cooling
- The Aromatic Infrared Bands
  + Recurrent Fluorescence

+ $H$, $H_2$, $C_2H_2$
The key role of the interaction of PAHs with VUV photons


Bréchignac et al.
The key role of the interaction of PAHs with VUV photons

- PAH lifetime
  *Allain et al., 1996, A&A 305, 602*
  *Visser et al. 2007, A&A 466, 229*
  *Montillaud et al. 2013, A&A 552, A15*

→ 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*

*M. Tiwari, Knight et al.*

*A. Petrignani*
The extreme conditions of astrophysical environments

Kinetic Monte Carlo simulations


\[ \tau_{\text{VUV}} \sim \text{few hours} \]
\[ \tau_{\text{coll}} \sim 1 \text{ day} \]
Molecular timescales

6-13.6 eV (HI region)  
<13.6 eV $\rightarrow$ typical 20 eV (HII regions)  

Ionization  
$\sim$40 fs

Photodissociation  
$\sim$ps $\rightarrow$ $>$ ms

Radiative cooling

Recurrent fluorescence  
$\tau$ ~ ms

IR cooling  
$\tau$ ~ s

Martin et al. 2013, PRL 110, 063003  
Marciniak et al., 2015, Nature Comm. 6: 7909  

+ H, H$_2$, C$_2$H$_2$
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)

Increase $N_C \Rightarrow$ 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**

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

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

**Imaging target**

**TOF detector**

**hot electron**

**ZKE**

**ions**
Unimolecular dissociation: Activation energies ($E_0$)

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

4.4 eV $\Rightarrow n_H$ even

3.2 eV $\Rightarrow n_H$ odd
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

Evolution of the fragment count \( \rightarrow \)

\( k_{\text{cool}} = 120-250 \text{ s}^{-1} \) for \( E_{\text{int}} = 6.6 \) to 6.8 eV

Faster than IR emission \( \rightarrow \) fluorescence from thermally excited electrons

Delay between injection of hot ions/ laser beam

![Graph showing the evolution of fragment count over time with different lines representing different delay times.](image)
Dynamics of radiative cooling on long timescales (>s)

DESIREE cryogenic double ring facility @ Stockholm University

Bernard et al. 2019, in prep.
Competition between dissociation and radiative cooling

A key concept in astrophysical environments and laboratory experiments

1-100 µs
No competition

ToF
(iPEPICO)

Storage rings
Ion traps
Formation of C-dust in evolved stars: a schematic view

Formation of PAHs in AGB stars

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


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

<table>
<thead>
<tr>
<th>Technique</th>
<th>Precursors</th>
<th>T (K)</th>
<th>Ion chemistry</th>
<th>Wall effect</th>
<th>Wall effect</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser ablation</td>
<td>Graphite + quenching gas</td>
<td>≥4000</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>(1) (2)</td>
</tr>
<tr>
<td>Combustion/Flames</td>
<td>Hydrocarbons</td>
<td>1800-2500</td>
<td>weak</td>
<td>no</td>
<td>(3)</td>
<td></td>
</tr>
<tr>
<td>Pyrolysis (laser induced)</td>
<td>Hydrocarbons</td>
<td>1000-1700</td>
<td>no</td>
<td>depending on reactor</td>
<td>(4) (5)</td>
<td></td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>Hydrocarbons</td>
<td>≥3500</td>
<td>weak</td>
<td>no</td>
<td>(6)</td>
<td></td>
</tr>
<tr>
<td>Dusty plasmas</td>
<td>Hydrocarbons</td>
<td>600-2000</td>
<td>no</td>
<td>depending on reactor</td>
<td>(7) (8)</td>
<td></td>
</tr>
<tr>
<td>Stardust machine</td>
<td>Graphite + gas (H₂,…)</td>
<td>&lt;1000</td>
<td>weak/no</td>
<td>no</td>
<td>(9) (10)</td>
<td></td>
</tr>
</tbody>
</table>

Nanocosmos: the Stardust machine

Dust Nucleation:
MICS + NEON

Dust Growth:
INTERACTION + SPECTROSCOPY

PDR+ISM:
PROCESSING ANALYSIS

Seed formation

7 meters
Molecular content of stardust analogues and meteorites

Meteorites
Natural stardust

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

Stardust Machine
(ICMM)
Stardust lab. analogues

Molecular analyzer
(IRAP/LCAR)
Molecular component of dust
Astrochemistry Research of Organics using a Molecular Analyzer

**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

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\textsubscript{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 / $C_2H_2$

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

3-Deposition of dust particles
$\Rightarrow$ ex-situ analyses

2-Dust particle growth
Magnetic confinement
$\Rightarrow$ recombination in volume

1-Plasma production: Heating of electrons
$\langle Te \rangle = 10$ eV, $n_e \approx 10^9$ cm$^{-3}$

TEM analysis:
Average diameter of 20nm / 5min
Spherical $\Rightarrow$ 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$_2$H$_2$

Clergereaux et al., in prep.

0.6 mtorr
C$_2$H$_2$/ 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

Graphite target

Magnetrons

Magnetic lines

Sputter gas (Ar) inlet $\rightarrow$ Ar$^+$

H$_2$/C$_2$H$_2$ injection in the aggregation zone

Martínez et al. 2018, Scientific reports 8:7250
Stardust samples: C vs C+H\textsubscript{2}

Molecular analysis

Martínez et al., 2019, in press

AFM image

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….
Acknowledgments and special thanks

IRAP (UPS/CNRS, Toulouse) H. Sabbah, G. Wenzel
LAPLACE (UPS/CNRS, Toulouse) R. Clergereaux
Dept Chem. & Bio Sci. (Univ. Ottawa) P. Mayer, B. West
Synchrotron SOLEIL A. Giuliani, L. Nahon
ILM (Univ. Lyon1) J. Bernard, S. Martin

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

NANOCOSMOS ERC SYNERGY
J. Cernicharo (IFF, Madrid)

J. A. Martín-Gago and the Stardust team L. Martínez, G. Santoro, P. Merino (ICMM, Madrid)