Evidence for interstellar ice

Sombrero Galaxy
combined Spitzer Hubble Image

Today’s PAH Model: Four Not So Easy Pieces

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Sombrero Galaxy
combined Spitzer Hubble Image
THANK YOU XANDER

~1985 - Backyard BBQ, San Jose

~1988 – 1st Ames Astrochem Lab Group

~1990 – Kuiper Airborne Observatory (KAO)

1988 - Interstellar Dust Proceedings IAU Symp 135
Today’s PAH Model: Four Not So Easy Pieces

Outline

1. Spectroscopy between 1 -5 μm and JWST
2. Formation and Growth
3. Destruction
4. Ice Chemistry
PAH Spectroscopy between 1 - 5 µm and JWST

The Near Infrared Spectrograph (NIRSpec) on JWST will measure spectra across the 1-5 µm range with significantly greater sensitivity and resolving power than previously possible.

This opens up the study of weak, but important and unique, PAH transitions that are spread across this region.

PAH Overtone, Combination, and Hot bands;
CD stretching bands in deuterated PAHs and
C≡N stretching bands in PAH nitriles

Fig courtesy Els peeters
PAH Spectroscopy between 1 -5 µm and JWST

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<table>
<thead>
<tr>
<th>Vibration</th>
<th>Range in µm</th>
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<tbody>
<tr>
<td>PAH CD stretch</td>
<td>4.3 - 4.5</td>
</tr>
<tr>
<td>dPAH CD stretch</td>
<td>4.54 - 4.75</td>
</tr>
<tr>
<td>PAH-nitrile C≡N stretch</td>
<td>4.46 - 4.5</td>
</tr>
</tbody>
</table>
Weak PAH bands are expected in the 3.8 – 5µm region

ISO, experimental, and computational spectra

AKARI spectra
PAH-nitrile structures suggested by the detection of Benzonitrile (a) in TMC-1

Benzo-dinitrile (b), Benzo-trinitrile (c) and some pyrene-nitriles (d-f).

*McGuire et al. Science 359, 202, 2018
Fig courtesy Christiaan Boersma
Fundamental and overtone band positions of the CD$_8^+$ stretch in deuterated PAHs and the C≡N stretch in PAH-nitriles between 1 and 5 µm.

Overtone band positions not corrected for anharmonicity

Fig courtesy Christiaan Boersma
The NASA Ames PAH IR Spectroscopic Database

PAHdb

a Website, PAH spectroscopic library, IDL and Python suites

www.astrochem.org/pahdb

Spectroscopic assignments are based on spectra of actual aromatic molecules in specific charge states, structures, sizes and so on. This allows the analysis of the spectra without the need of an ad-hoc interpretation of the state of the PAH population since the average synthesized spectra can be traced back to the fully characterized individual PAH molecules.
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IR spectra of late type stars (here CRL 618) show a wealth of lines from molecular intermediaries such as HC≡CH, HC≡N, HC≡C-C≡C≡N ..., the species that form carbon chains and PAHs.


Fig courtesy Christiaan Boersma
PAH Formation and Growth

From carbon chains to rings

Carbon chains grow by sequential HC≡CH and HC≡N addition.

When long enough (~6-12 C atoms), chains cyclize.

Further addition of HC≡CH, HC≡N and their reactive forms lead to ring formation and growth.

C≡N addition to H₂C=CH-CH=CH₂

PAH Formation and Growth

From small PAHs to larger PAHs

Small PAHs grow to large PAHs by sequential HC≡CH and HC≡N addition and insertion.

Zhao, Kaiser & Xu 2018, Nature Astronomy
PAH Formation and Growth

From PAH clusters and large PAHs to particles and fullerenes...

Small cluster isomerization

Large PAH fragmentation

Experiments showing possible steps toward particle and fullerene growth.


PAH Destruction

**PAH^0 UV DRIVEN FRAGMENTATION**

H and H\(_2\) loss are the first steps

PAH edge shape influences odd to even H atom loss.
H\(_2\) loss dominates in larger PAHs

**PAH^+ UV DRIVEN FRAGMENTATION**

Site selective C\(_2\)/C\(_2\)H\(_2\) loss and stepwise H loss

UV driven fragmentation of substituted PAHs may contribute to formation of smaller species normally considered to form by merging atoms and molecules

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Castellanos et al., 2018, A&A 616, A 166

Zhen et al. 2016, Molecular Astrophys 5, 1
Putting it all Together

Schematic of PAH population changes with distance from the exciting star in the Reflection Nebula, NGC 2023.

PAH structures inferred from the fundamental PAH band groupings and ratios

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   1. Destruction
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PAH H$_2$O Ice Chemistry

UV Photolysis studies of PAHs in low temperature ices show PAHs significantly alter the physical properties of the ice and chemical processes that occur within the ice.

- PAH ionization energy is lowered by 2 eV in H$_2$O Ice
- PAH cations are easily produced and remain trapped up to ice temperatures near 100K
- Hydrogenated (H$_n$PAHs) and oxidized PAHs (alcohols and ketones) are important photoproducts.

Bernstein, Sandford et al. Science 283, 1135 (1999)
PAH/Ice photochemistry depends on ice temperature and PAH concentration

- Ions mediate the chemistry in ices below 50K, and at low concentrations: $\text{PAH}/\text{H}_2\text{O} < 1/10^3$

- Radicals mediate the chemistry in ices above 50K and at high concentrations: $\text{PAH}/\text{H}_2\text{O} > 1/10^3$

PAH/H$_2$O Ice Photoproducts-
Cations (PAH$^+$), Hydrogenated ($H_n$PAHs) and Oxidized PAHs (alcohols and ketones)

Coronene and *identified* photoproducts

Conclusions

1. JWST’s unprecedented sensitivity, spectroscopic resolution and bandwidth will open the 1-5 µm region

2. The experimental, theoretical and computational tools that have been developed over the past few years are revealing a detailed and surprising picture of how PAHs grow and evolve. This information will guide model development, clarify, and enable quantification of the many roles PAHs play in astrophysics.

3. PAH/ice chemistry and spectroscopy should be considered in astrochemical models.
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