Today’s PAH Model: Four Not So Easy Pieces

Sombrero Galaxy
combined *Spitzer Hubble* Image

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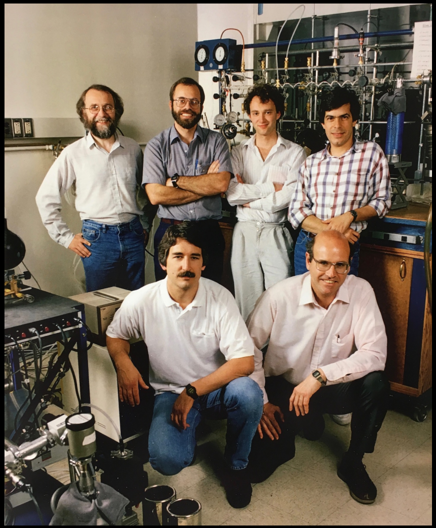
http://www.astrochem.org

THANK YOU XANDER

~1985 - Backyard BBQ, San Jose

~1990 – Kuiper Airborne Observatory (KAO)



~1988 – 1st Ames Astrochem Lab Group

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

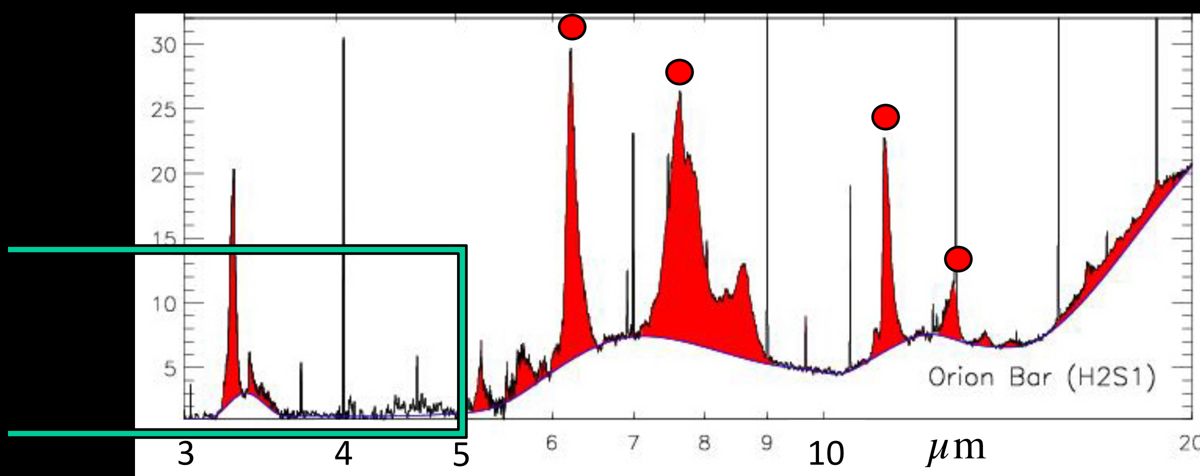


Fig courtesy Els peeters

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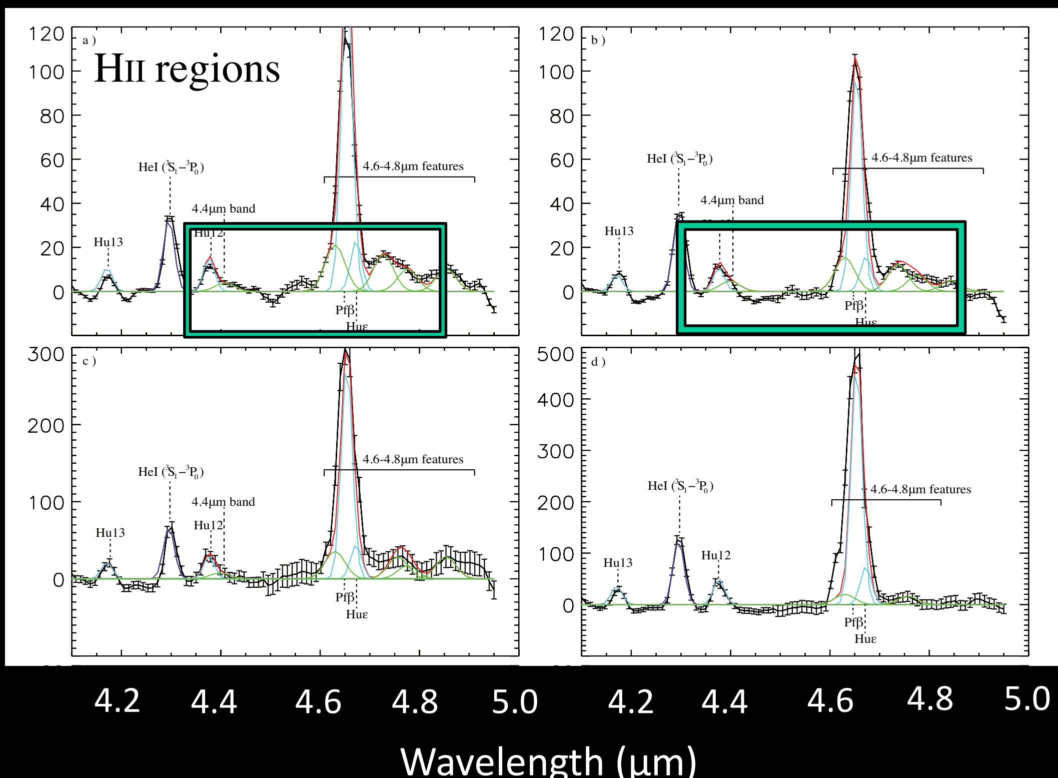
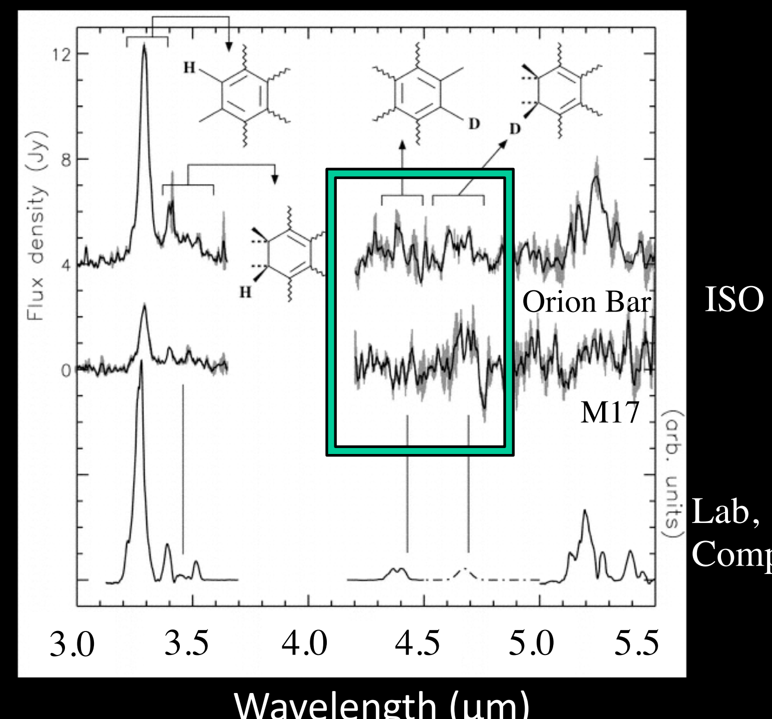
Vibration	Range in *µ*m
PAH CD stretch	4.3 - 4.5[a]
dPAH CD stretch	4.54 - 4.75[b]
PAH-nitrile C≡N stretch	4.46 - 4.5[c]

JWST DISCOVERY SPACE

Weak PAH bands are expected in the 3.8 – 5μm region



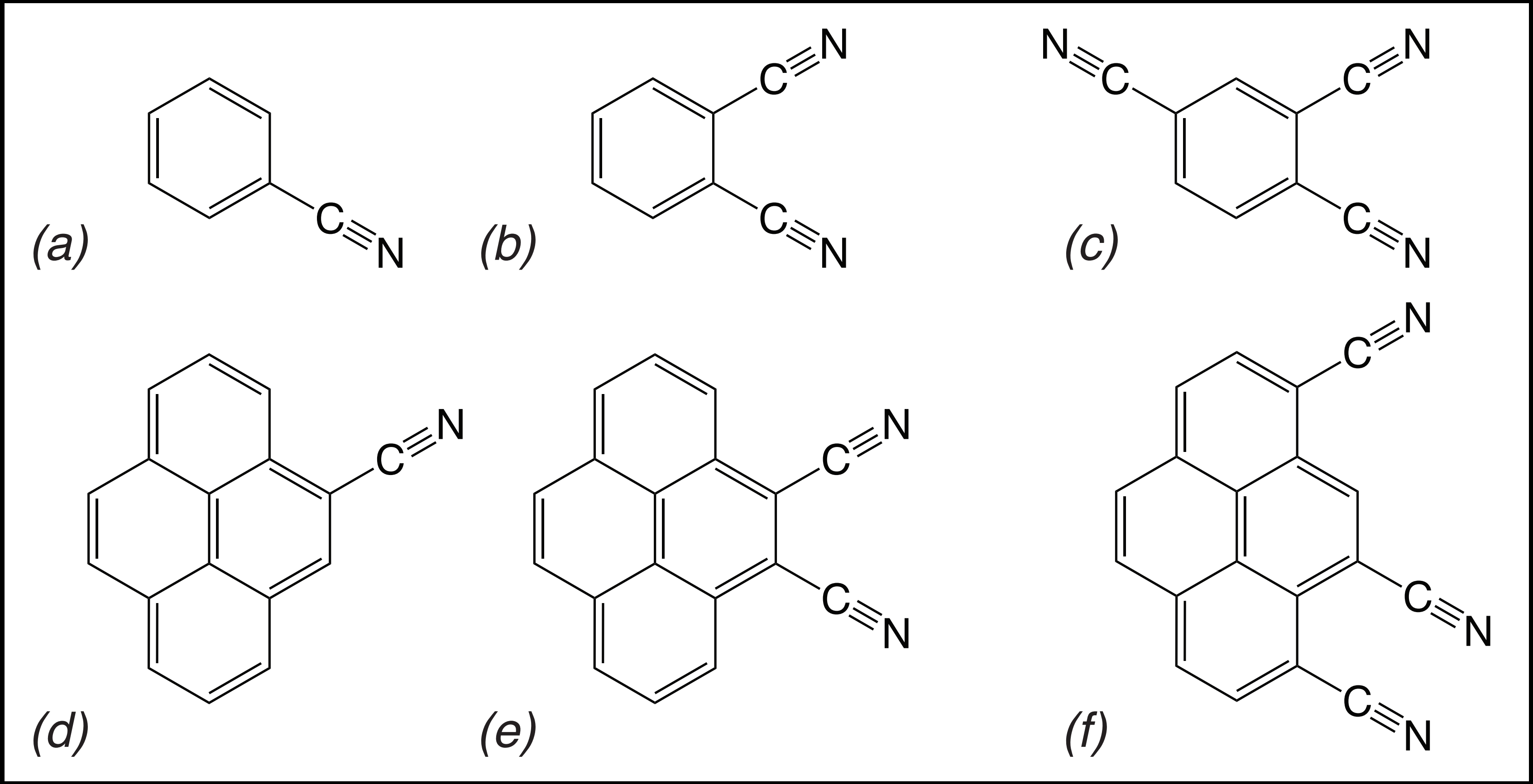
AKARI spectra
Doney et al. 2016, A&A, 586A,65D



ISO, experimental, and computational spectra
Peeters et al. 2004, ApJ 604, 252

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

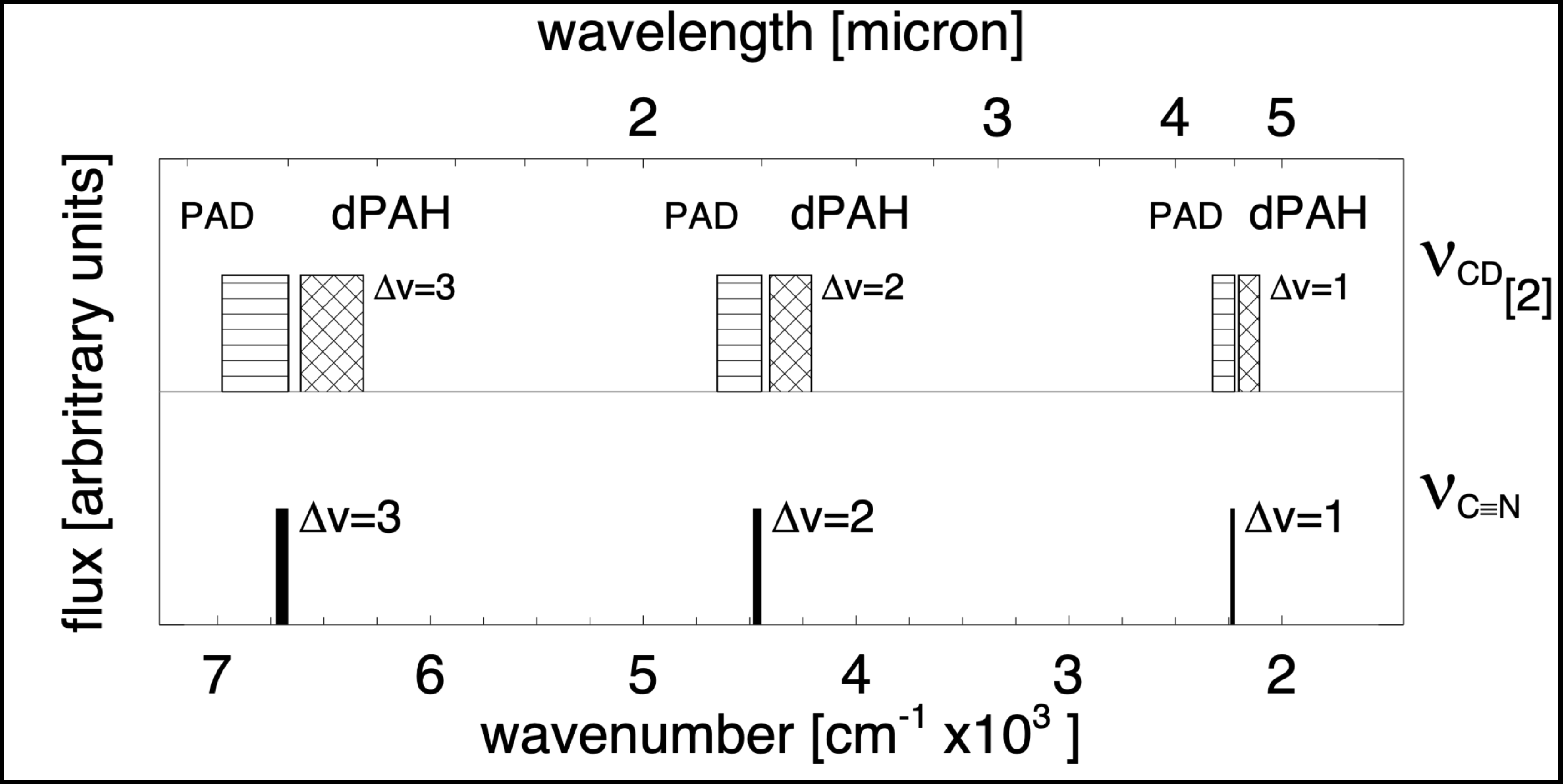
Benzo-dinitrile (b), Benzo-trinitrile (c) and some pyrene-nitriles (d-f).



*McGuire et al. *Science 359*, 202, 2018

Fig courtesy Christiaan Boersma

Fundamental and overtone band positions of the CD 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

Boersma et al. 2013, ApJS 211, 8; Bauschlicher et al. 2018, ApJS 234, 32

WHY 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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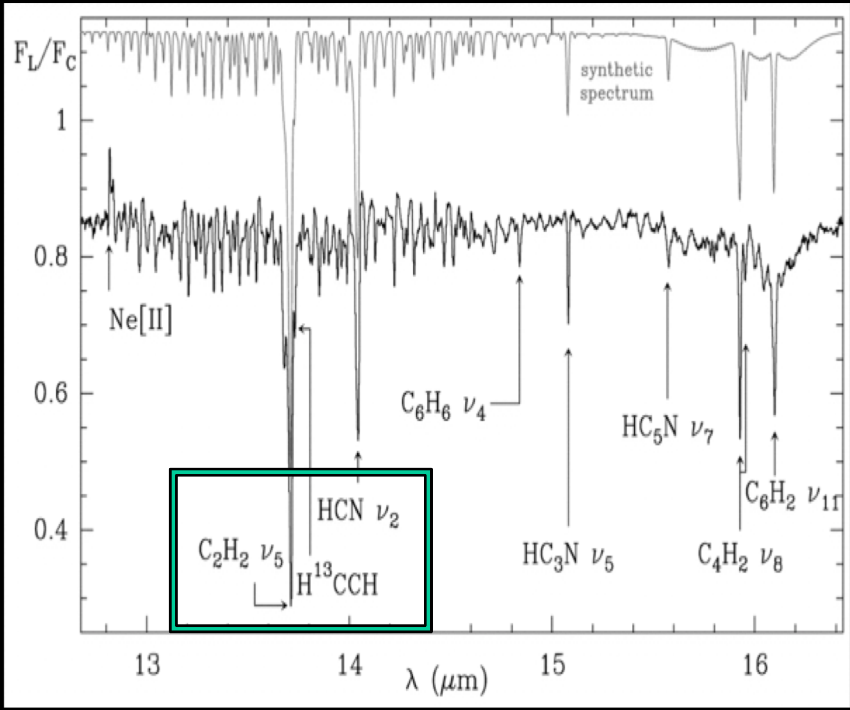
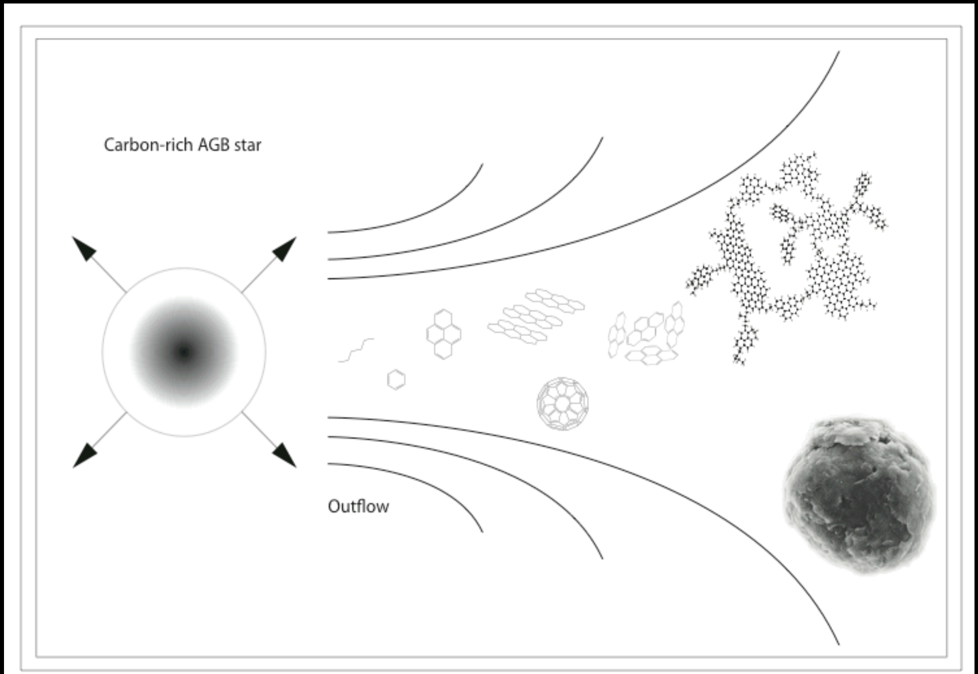
PAH Formation and Growth

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-C≡N …, the species that form carbon chains and PAHs



Cernicharo et al. 2001, ApJ 546, L123

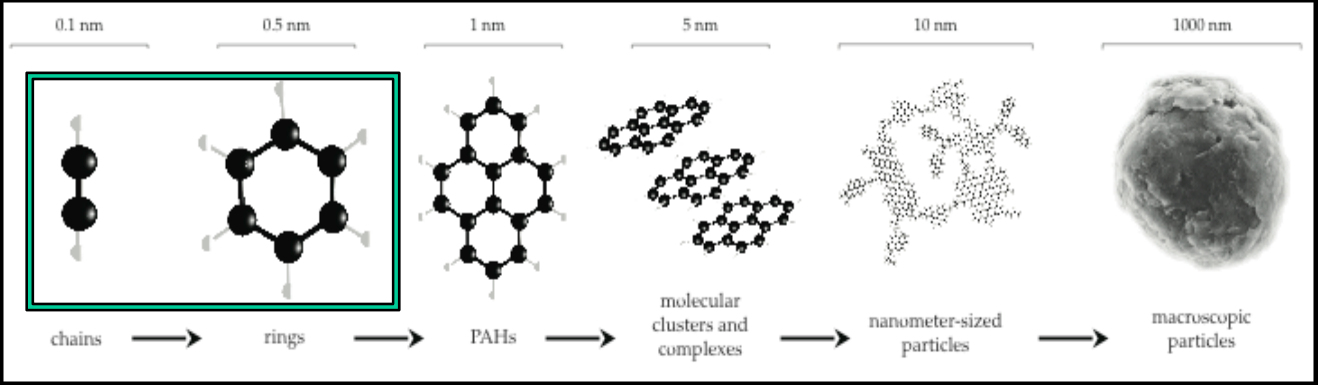


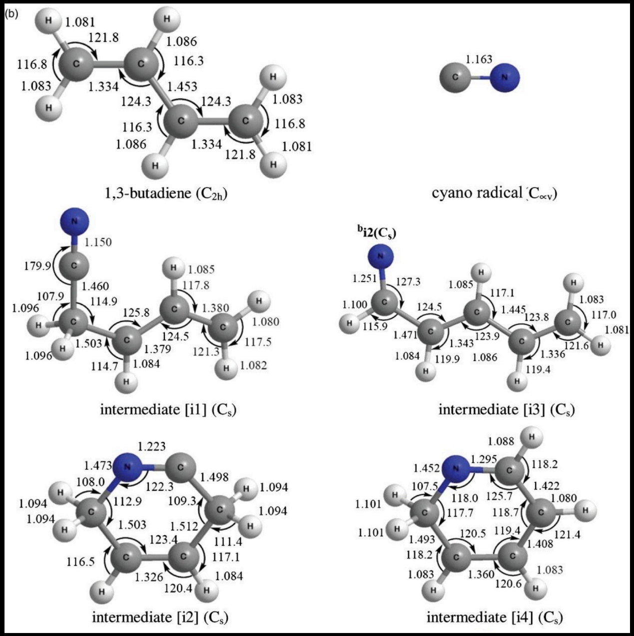
Formation of carbonaceous species in the outflow of carbon-rich AGB stars.

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.

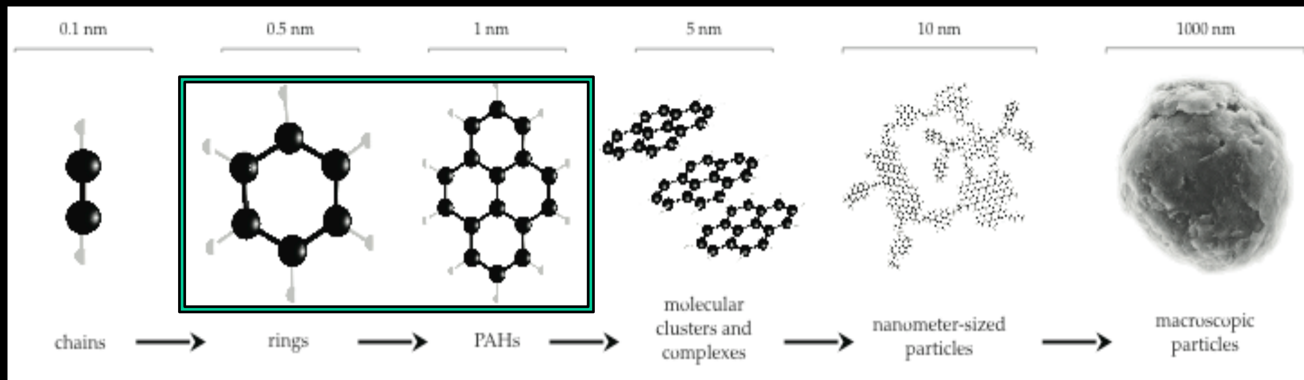
Further addition of HC≡CH, HC≡N and their reactive forms lead to ring formation and growth.

C≡N addition to $H_2C=CH-CH=CH_2$

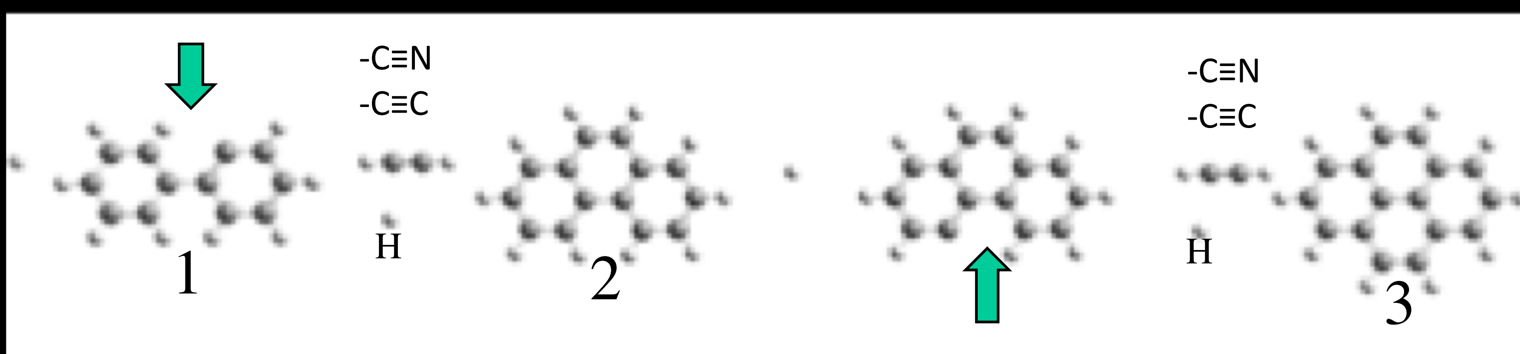
Morales et al. 2011, ApJ 742, 26

PAH Formation and Growth

From small PAHs to larger PAHs



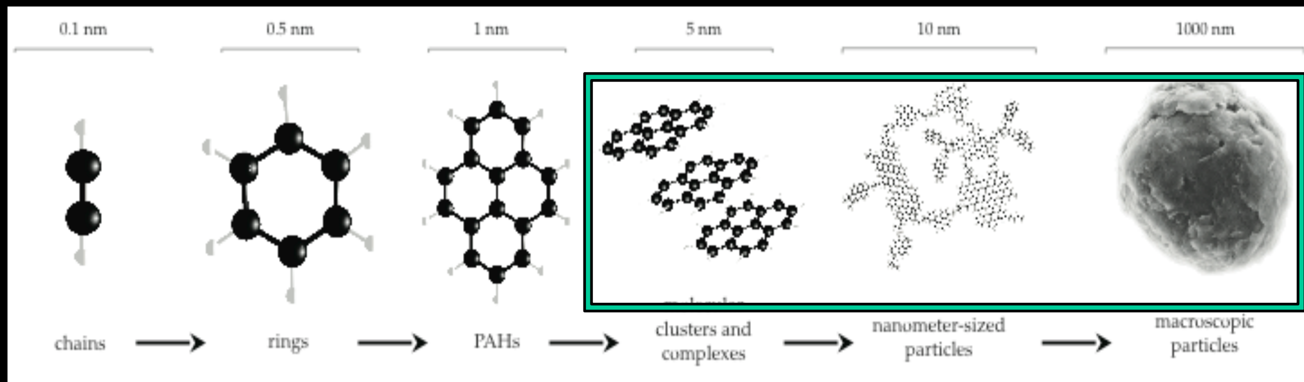
Small PAHs grow to large PAHs by sequential HC≡CH and HC≡N addition and insertion.



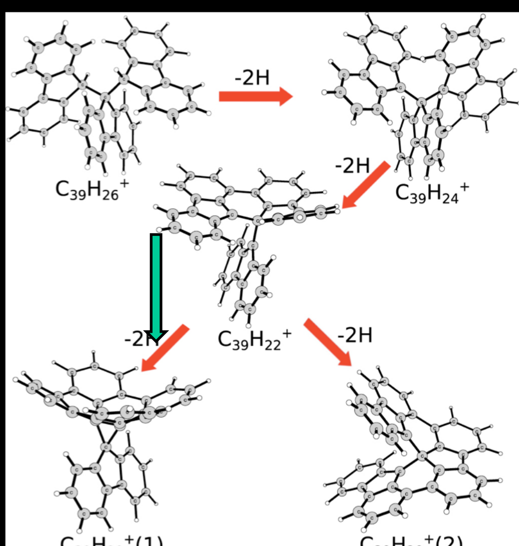
Zhao, Kaiser & Xu 2018, Nature Astronomy

PAH Formation and Growth

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



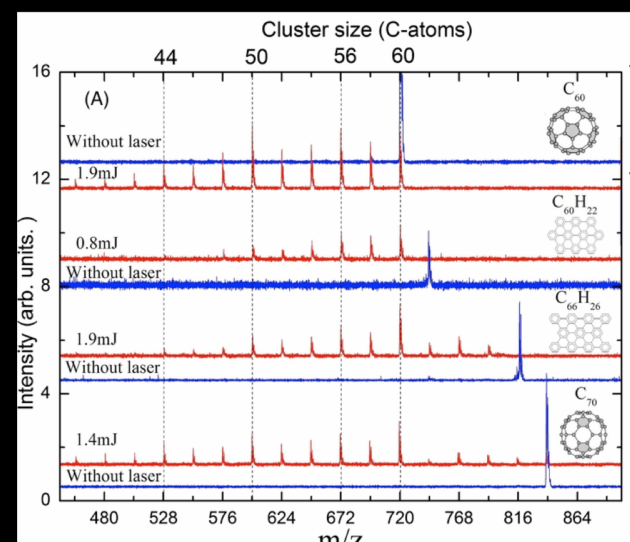
Small cluster isomerization



Zhang et al. 2019, ApJ 872:38

Experiments showing possible steps toward particle and fullerene growth.

Large PAH fragmentation



Zhen et al. 2014, ApJ 797:L30

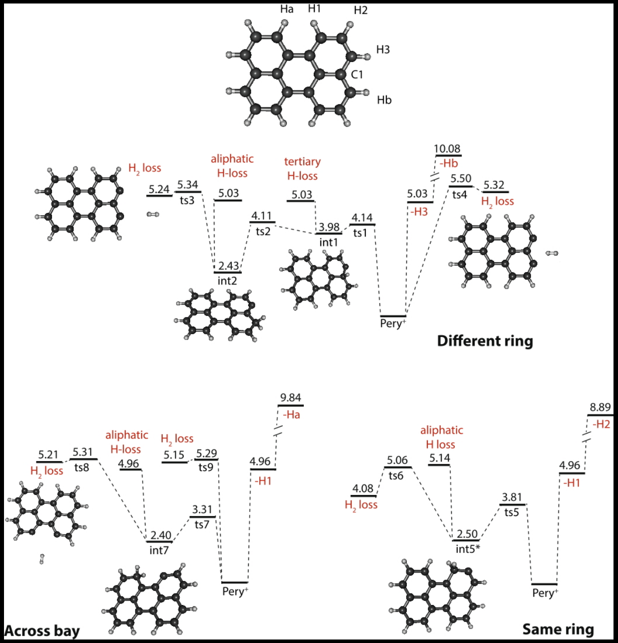
PAH Destruction

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

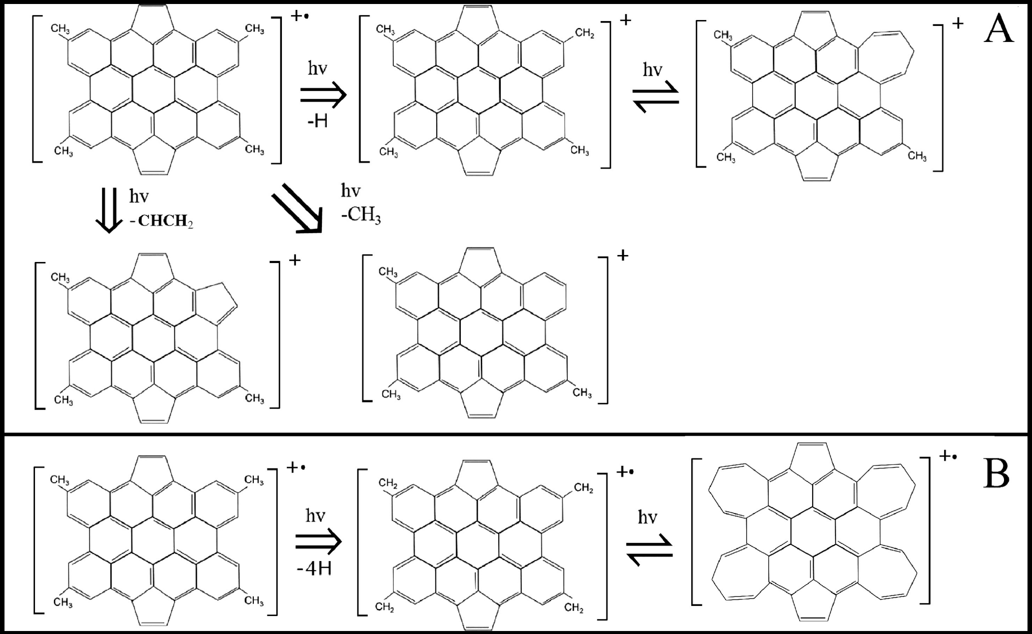


Castellanos et al., 2018, A&A 616, A 166

PAH^+ UV DRIVEN FRAGMENTATION

Site selective C_2/C_2H_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

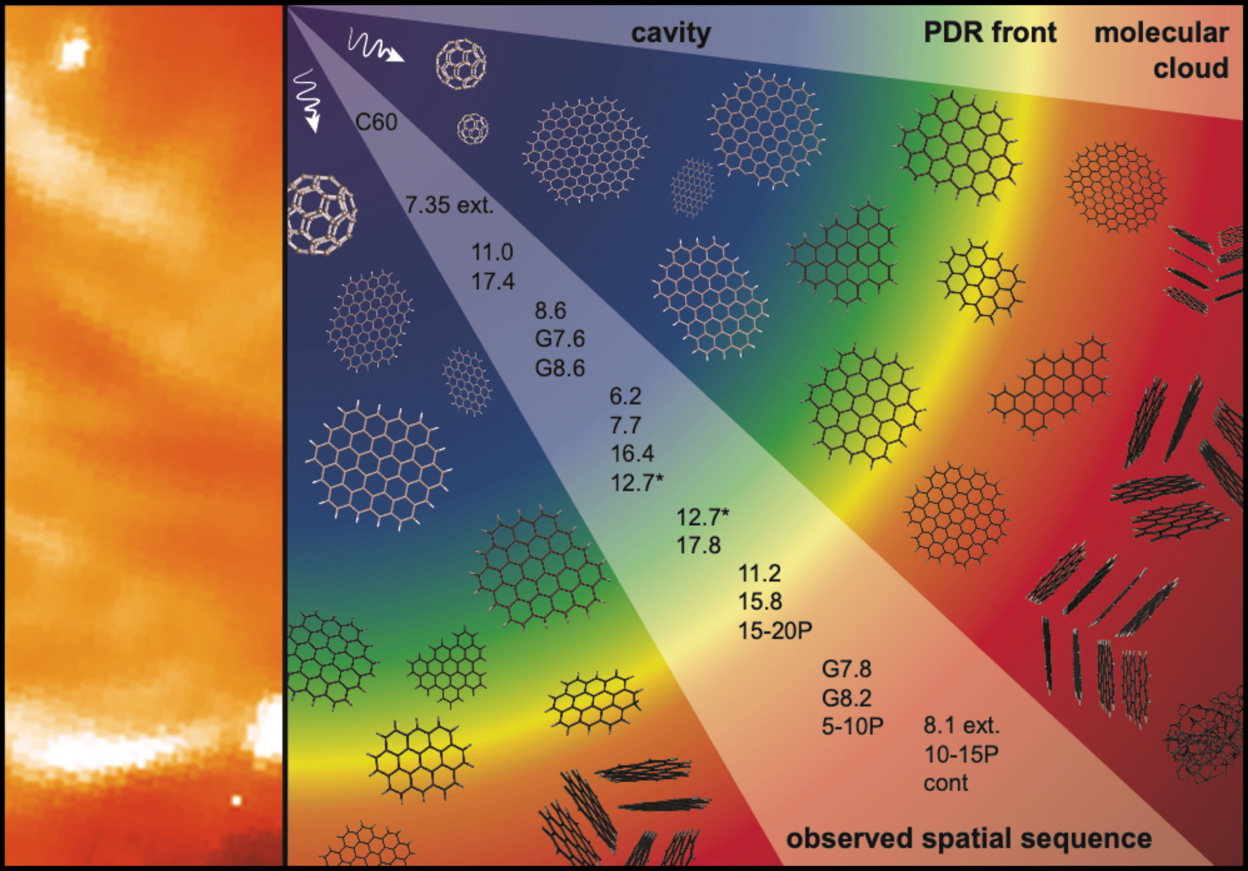


Zhen et al. 2016, Molecular Astrophys 5, 1

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



Peeters et al. 2017, ApJ 836:198

Andrews et al. 2015, ApJ 807, 99

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PAH H_2O Ice Chemistry

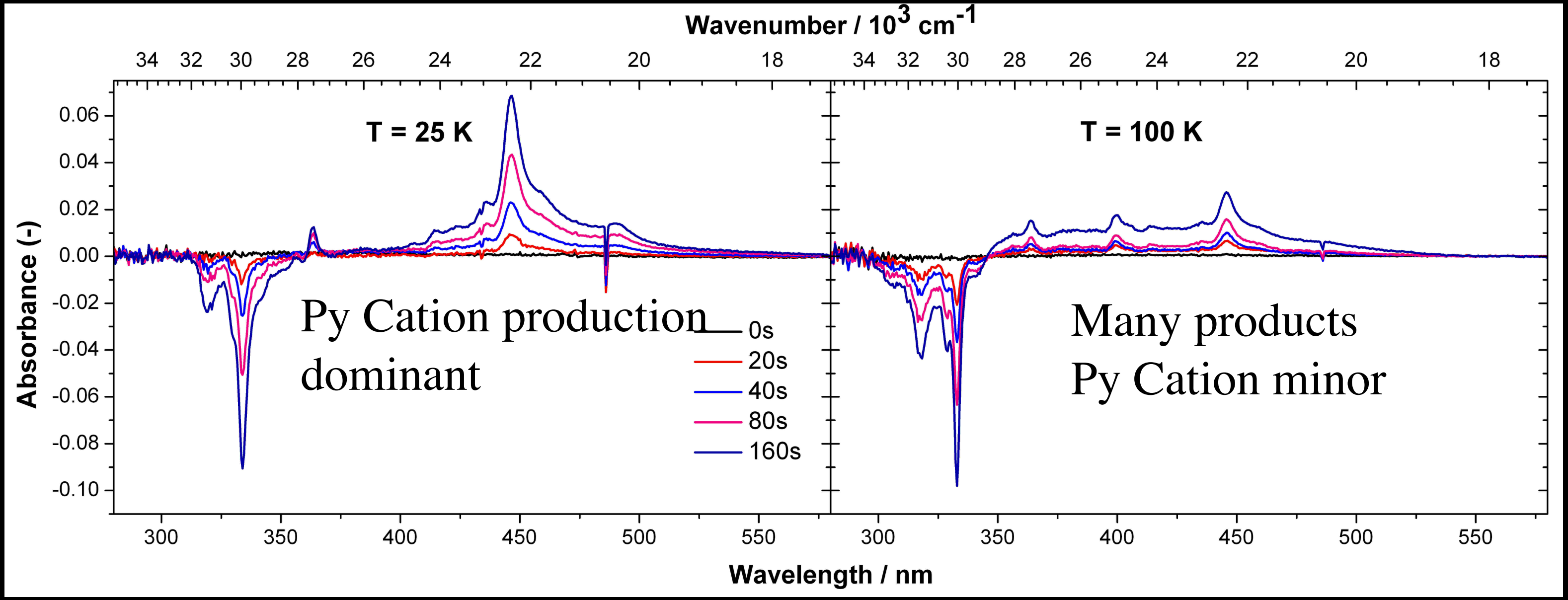
UV Photolysis studies of PAHs in low temperature ices show PAHs significantly alter the physical properties of the ice and chemical processes that occur within the ice.

- PAH ionization energy is lowered by 2 eV in H_2O Ice
- PAH cations are easily produced and remain trapped up to ice temperatures near 100K
- Hydrogenated (H_nPAHs) and oxidized PAHs (alcohols and ketones) are important photoproducts.

Bouwman et al. A&A 511, A33 (2010), Gudipati & Allamandola ApJ 596, L195 (2003)
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 : PAH/H_2O <1/10^3
- Radicals mediate the chemistry in ices above 50K and at high concentrations: PAH/H_2O >1/10^3

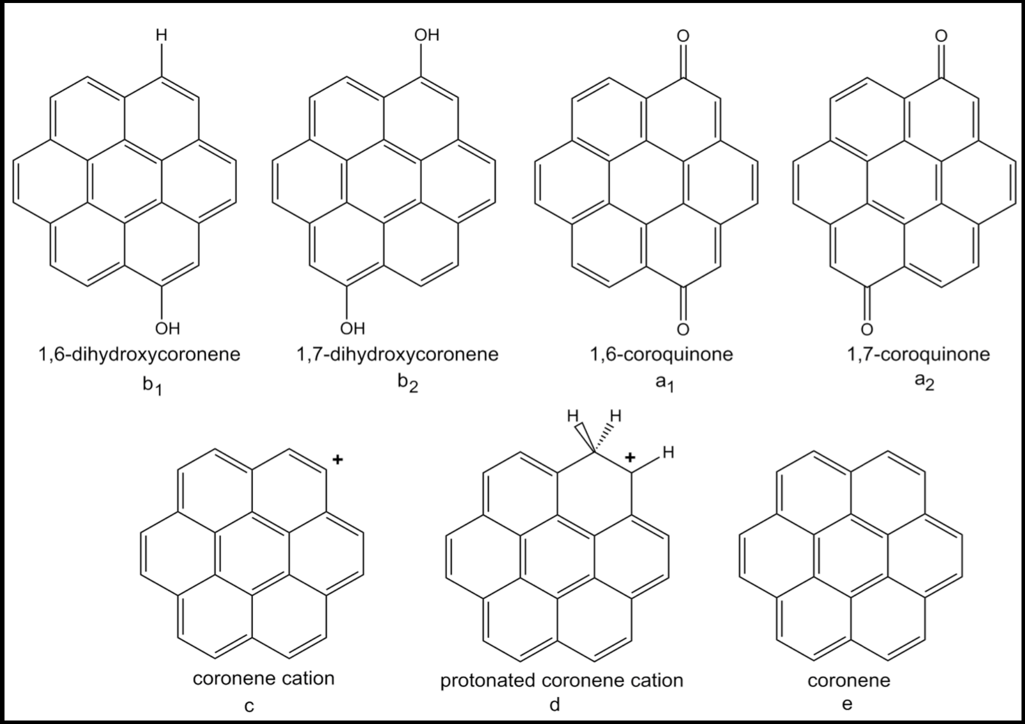


Bouwman et al. ApJ (2009), Bouwman et al. A&A (2010) Cuylle et al. A&A 562, A22 (2014)

PAH/H_2O Ice Photoproducts-

Cations (PAH^+), Hydrogenated (H_nPAHs) and Oxidized PAHs (alcohols and ketones)

Coronene and *identified* photoproducts



Guennoun, Aupetit, & Mascetti. 2011, PCCP 13, 730; Guennoun, Aupetit, & Mascetti. 2011, JPCA 115, 1844; Cook, Ricca, Mattioda et al. 2015, ApJ 799:14 (20pp); de Baros, Mattioda, Ricca et al. 2017, ApJ, 848, 112,

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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