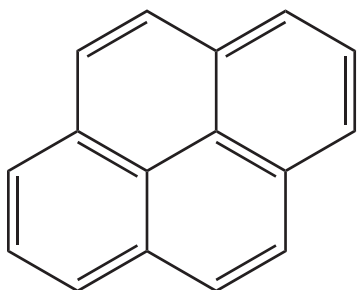
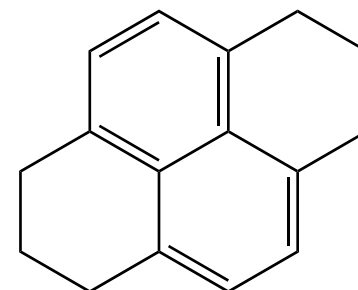


Could polycyclic aromatic hydrocarbons with excess peripheral H atoms (H_n -PAHs) be responsible for anomalous 3.4 μm emission bands in protoplanetary nebulae?

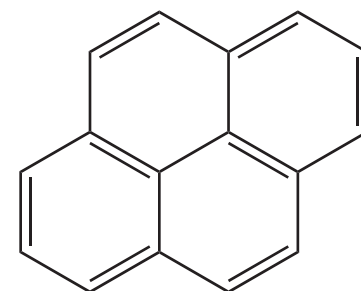
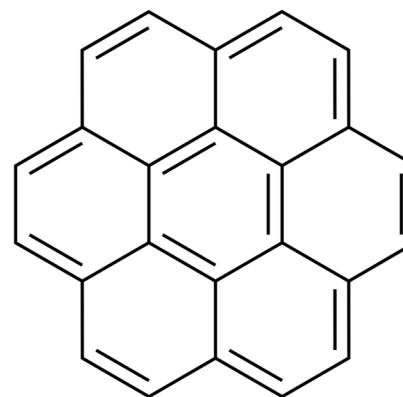


SOFIA tele-talk
Dr. Christopher Materese
Dr. Scott Sandford, Dr. Jesse Bregman,
Dr. Max Bernstein
December 19, 2018



Background: Polycyclic Aromatic Hydrocarbons

- Polycyclic Aromatic Hydrocarbons (PAHs) are multi-ringed organic compounds
- Alternating single and double bonds delocalize e^- density and increases resistance to radiolysis
- PAHs, their ions, and derivatives are thought to be ubiquitous in space
- Key infrared (IR) bands: 3.3, 6.2, 7.7, 8.7, 11.3, and 12.7 μm



PAHs in Post-Asymptotic Giant Branch Objects

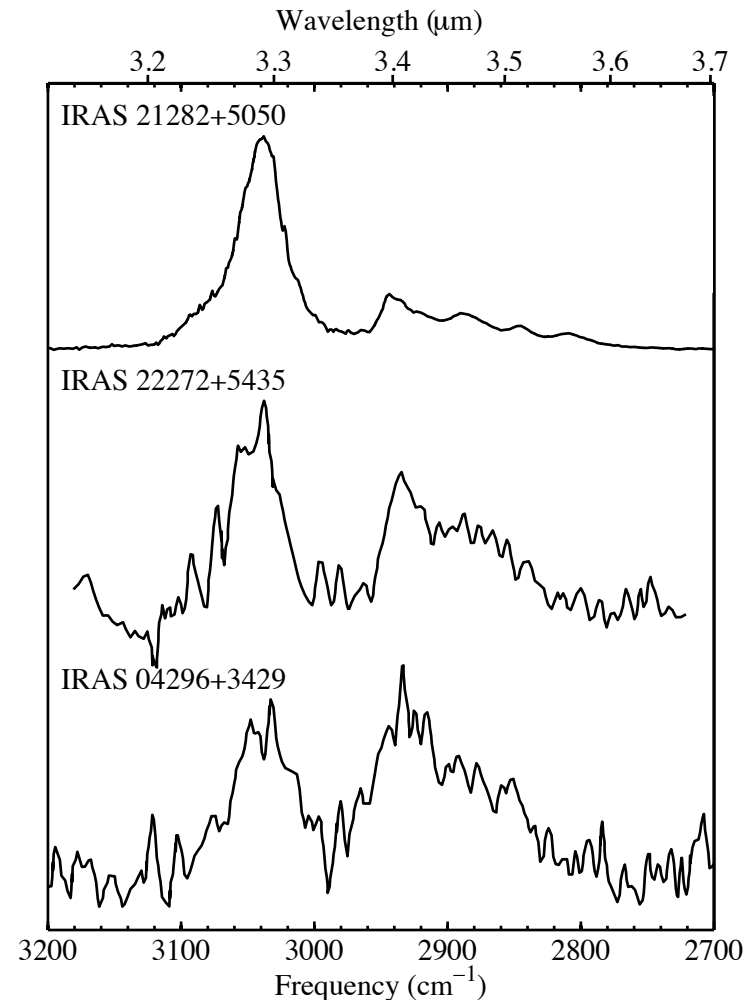


HST image of PPN IRAS 22272+5435
(False color)

Credit Toshiya Ueta, Margaret
Meixner, and Matthew Bobrowsky

Motivation

- Typical post-AGB objects have strong PAH emission bands at $3.3 \mu\text{m}$
- Bands near $3.4 \mu\text{m}$ typically attributed to anharmonic “hot bands” and overtone and combination modes
- Some post-AGB objects have abnormally large $3.4 \mu\text{m}$ features possibly linked to the presence of aliphatics



IRAS 21282+5050 from Jourdain de Muizon et al. (1986)

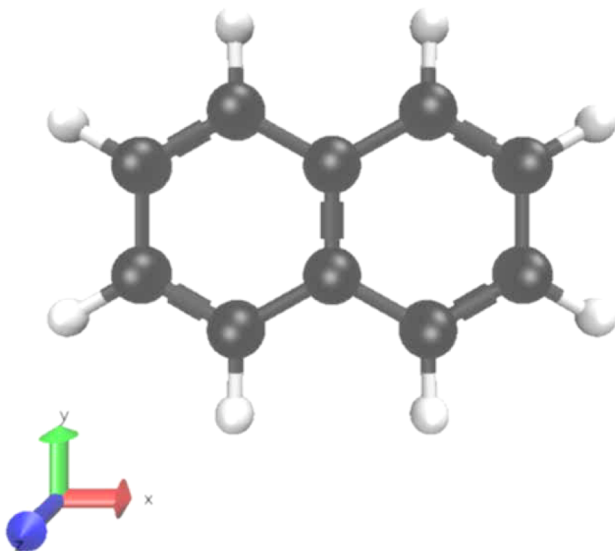
IRAS 22272+5435 and IRAS 04296+3429 from Geballe et al. (1992)

Hypothesis:

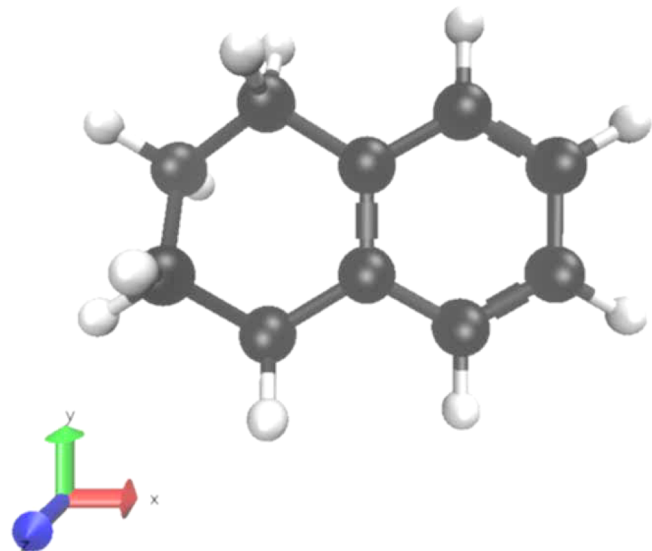
Aliphatic groups (moieties) from PAH derivatives with excess peripheral hydrogen (H_n -PAHs) may significantly contribute to the abnormally large 3.4 μm emission band in some post-AGB objects

What is an H_n -PAH?

Naphthalene
(PAH)



1,2,3,4-
tetrahydronaphthalene
(H_n -PAH)

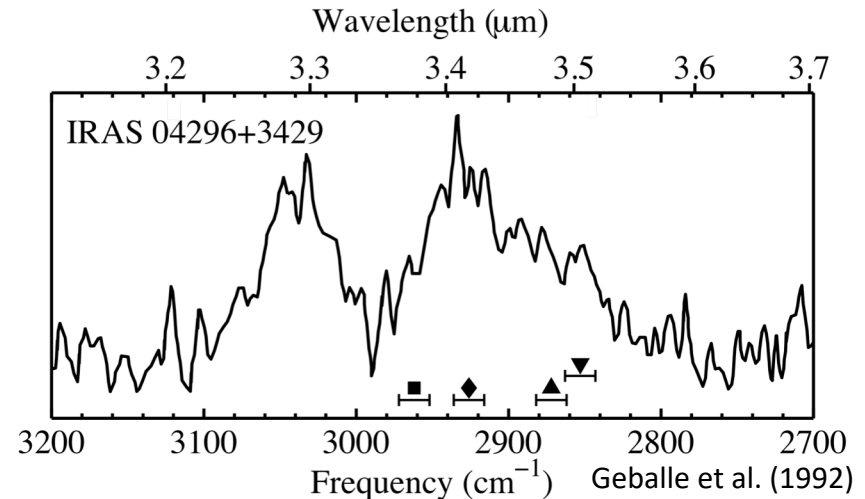
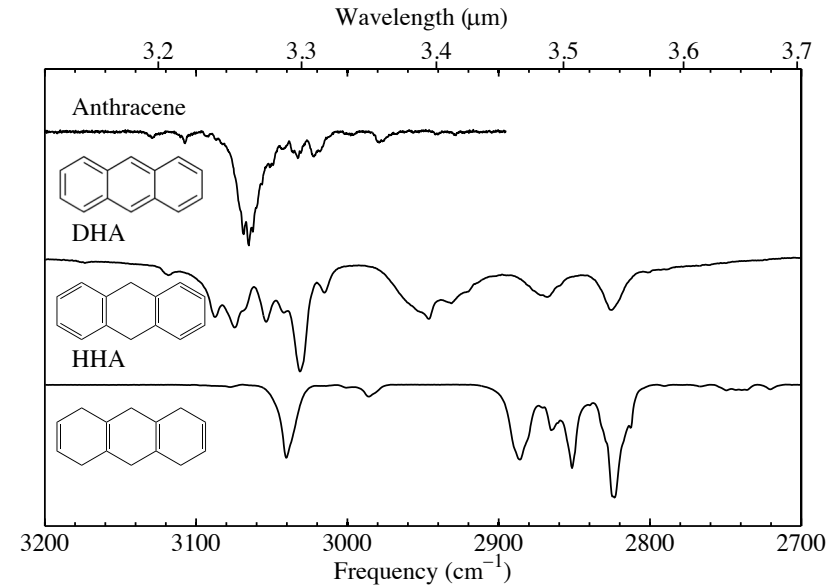


Consequences of excess peripheral hydrogen in H_n-PAHs

- Aromatic and aliphatic will moieties exist within the same molecule, reducing that molecule's resistance to radiolysis because of some loss of e- delocalization
- Adjacent planar (SP²) bond hybridization (aromatic) and tetrahedral (SP³) bond hybridization (aliphatic) leads to ring strain near their interface
- This strain causes spectroscopically observable changes that can be measured in laboratory experiments

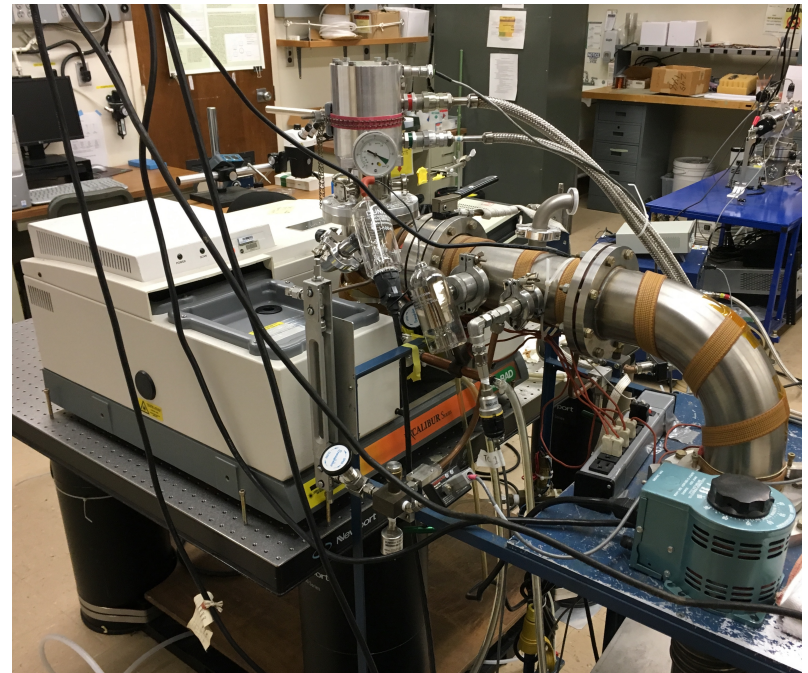
Goals

- Obtain IR spectra of H_n -PAHs
- Characterize changes in the IR spectra of families of H_n -PAHs as a function of increasing hydrogenation
- Identify telltale spectral features of H_n -PAHs
- Compare laboratory derived spectra of H_n -PAHs to observational data



Methods

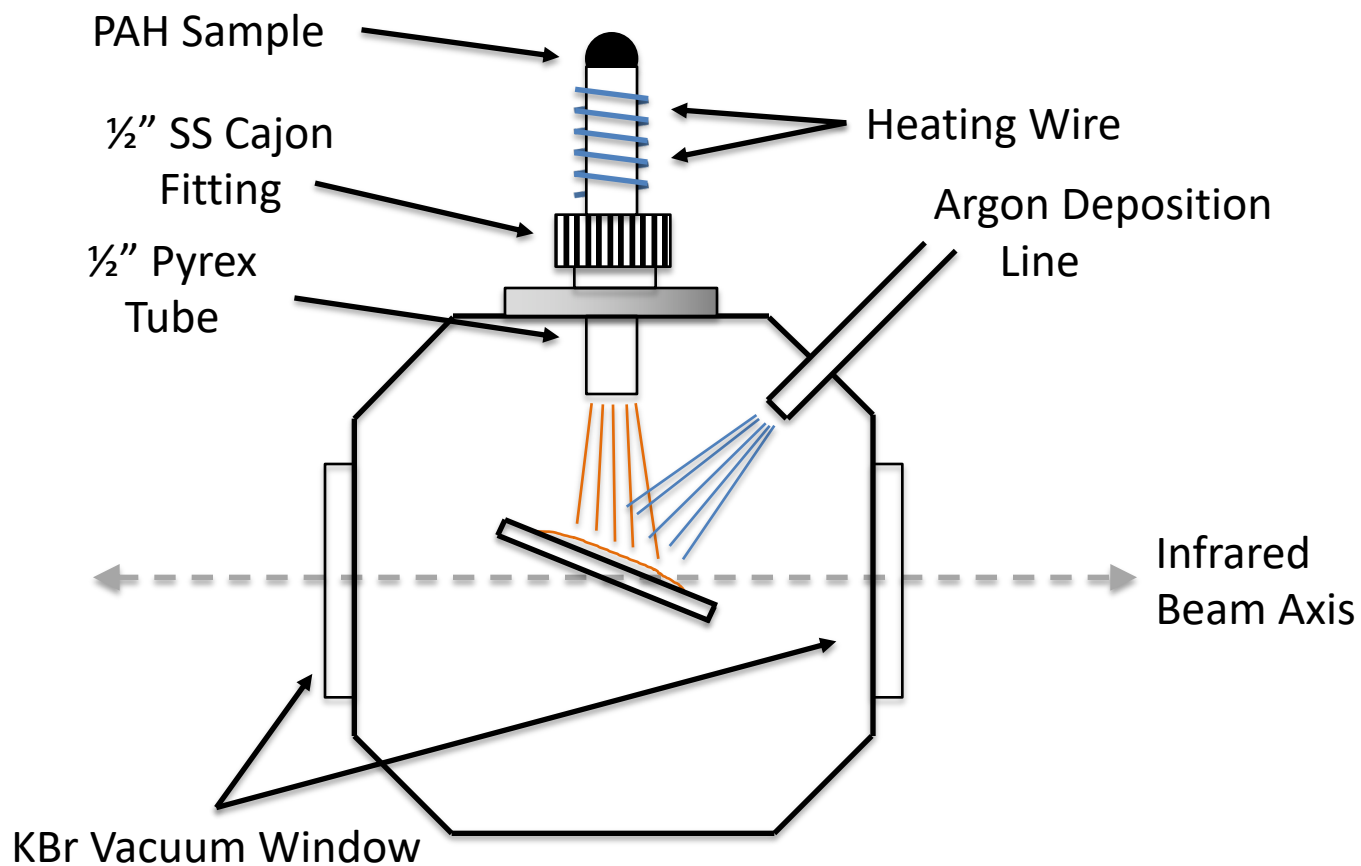
- Experiments conducted in the Ames Astrochemistry Lab using a cryovacuum chamber
 - $\sim 10^{-8}$ torr at 15K
- All sample PAHs/ H_n -PAHs were diluted in an argon matrix with Ar/PAH > 1000/1 to reduce intermolecular interactions and simulate vacuum
- Vacuum chamber is placed in the beamline of the IR spectrometer allowing *in situ* measurements



Methods Continued

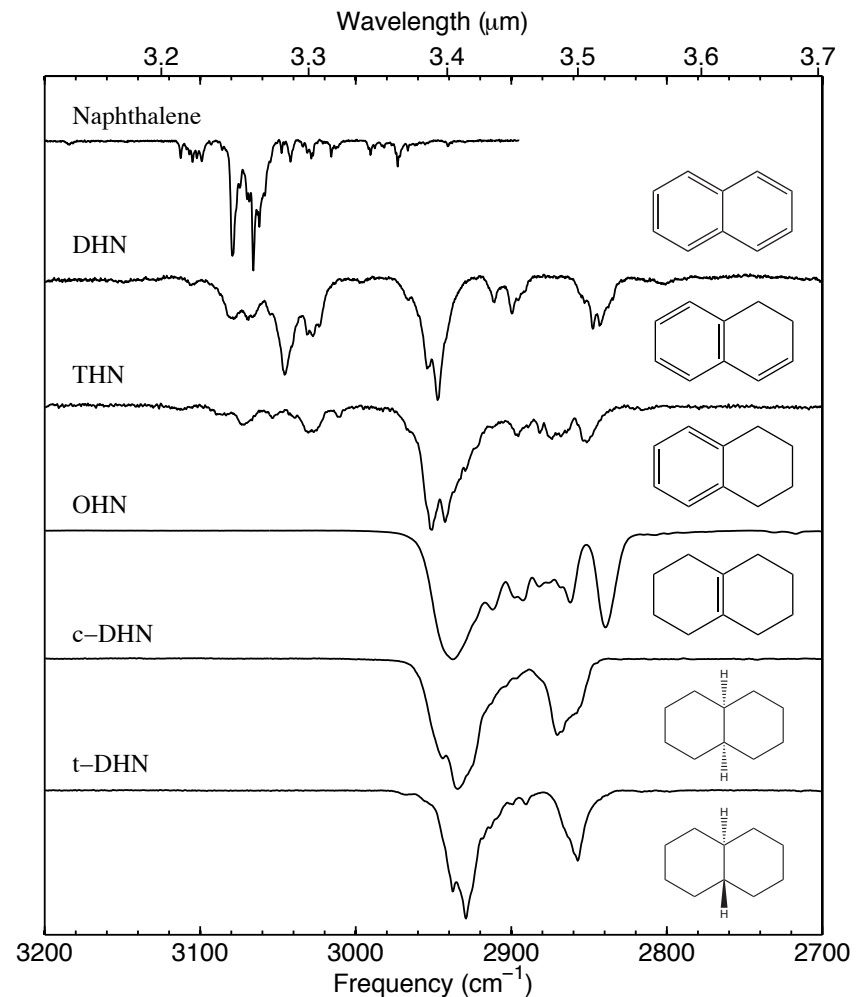
- Mid-IR spectra of 23 H_n-PAHs along with parent PAHs were collected
- Families of progressively more hydrogenated H_n-PAHs selected to demonstrate the changes in the spectrum
- All molecules in the study were fully cyclic (no terminal CH₃ groups)
- Special focus was paid to changes in the 3.2—3.6 μm region (C—H stretch) as well as the 6.9 (CH₂ scissoring) region of the IR spectrum

Experimental Setup



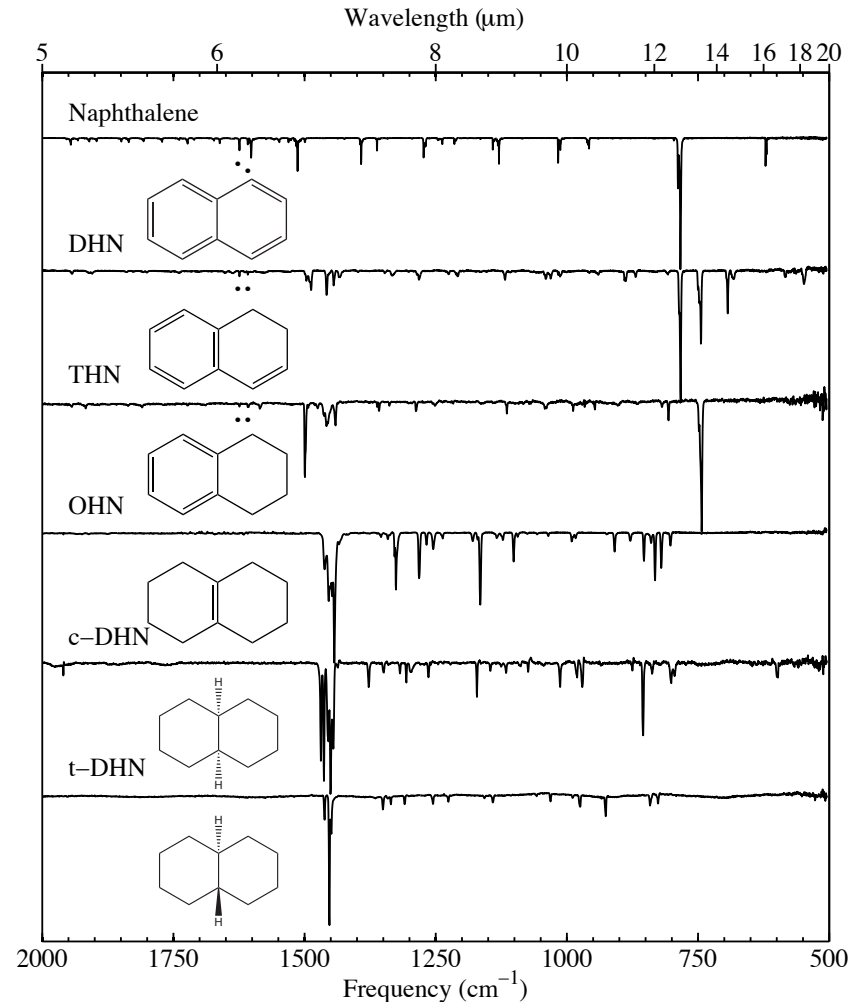
Naphthalenes (3 μm region)

- Naphthalene: Only aromatic C-H stretch
- DHN/THN: Growth of aliphatic features
- OHN: Loss of aromatic/olefinic features
- c-DHN/t-DHN: Fully aliphatic



Naphthalenes (5-20 μm region)

- Naphthalene: Quartet C-H_{oop} band
- DHN: Quartet + olefinic C-H_{oop} band, growth of methylene scissoring bands
- THN: Quartet C-H_{oop} band
- OHN/c-DHN/t-DHN: No C-H_{oop} band



Other H_n-PAHs studied

Table 1
The H_n-PAHs Examined in this Study

Series	H _n -PAH Name	Abbreviation	Formula	Structure
B	9,10-dihydroanthracene (Aldrich)	DHA	C ₁₄ H ₁₂	
B	1,4,5,8,9,10-hexahydroanthracene (Aldrich)	HHA	C ₁₄ H ₁₆	
C	9,10-dihydrophenanthrene (Aldrich)	DHPH	C ₁₄ H ₁₂	
C	Dibenzosuberane (Aldrich)	DBS	C ₁₅ H ₁₄	
C	<i>trans</i> -perhydrofluorene (Aldrich)	<i>t</i> -PHF	C ₁₃ H ₂₂	
D	4,5-dihdropyrene (TRC)	DHP	C ₁₆ H ₁₂	
D	1,2,3,6,7,8-hexahdropyrene (Aldrich)	HHP	C ₁₆ H ₁₆	
E	7,8,9,10-tetrahydrobenzo[a]pyrene (TRC)	THB[a]P	C ₂₀ H ₁₆	
E	9H-cyclopenta[a]pyrene (TRC)	9H-Cp[a]P	C ₁₉ H ₁₂	
E	4,5,7,8,10,11-hexahydro-9H-cyclopenta[a]pyrene (TRC)	HHCp[a]P	C ₁₉ H ₁₈	
F	Dodecahydrotriphenylene (Aldrich)	DDHTP	C ₁₈ H ₂₄	

Table 1
(Continued)

Series	H _n -PAH Name	Abbreviation	Formula	Structure
F	Perhydrocoronene (JCF)	PHC	C ₂₄ H ₂₄	
G	5,6-dihydro-4H-benzo[de]anthracene (TRC)	DHB[de]A	C ₁₇ H ₁₄	
G	4H-cyclopenta[def]phenanthrene (Aldrich)	Cp[def]Ph	C ₁₅ H ₁₀	
G	11H-benzo[b]fluorene (Aldrich)	11HB[b]F	C ₁₇ H ₁₂	
H	7,14-dihydrodibenz[ah]anthracene (TRC)	DHDB[ah]A	C ₂₂ H ₁₆	
H	9,10-dihydrobenzo[e]pyrene (TRC)	DHB[e]P	C ₂₀ H ₁₄	
H	Triptycene (Aldrich)	TRIP	C ₂₀ H ₁₄	

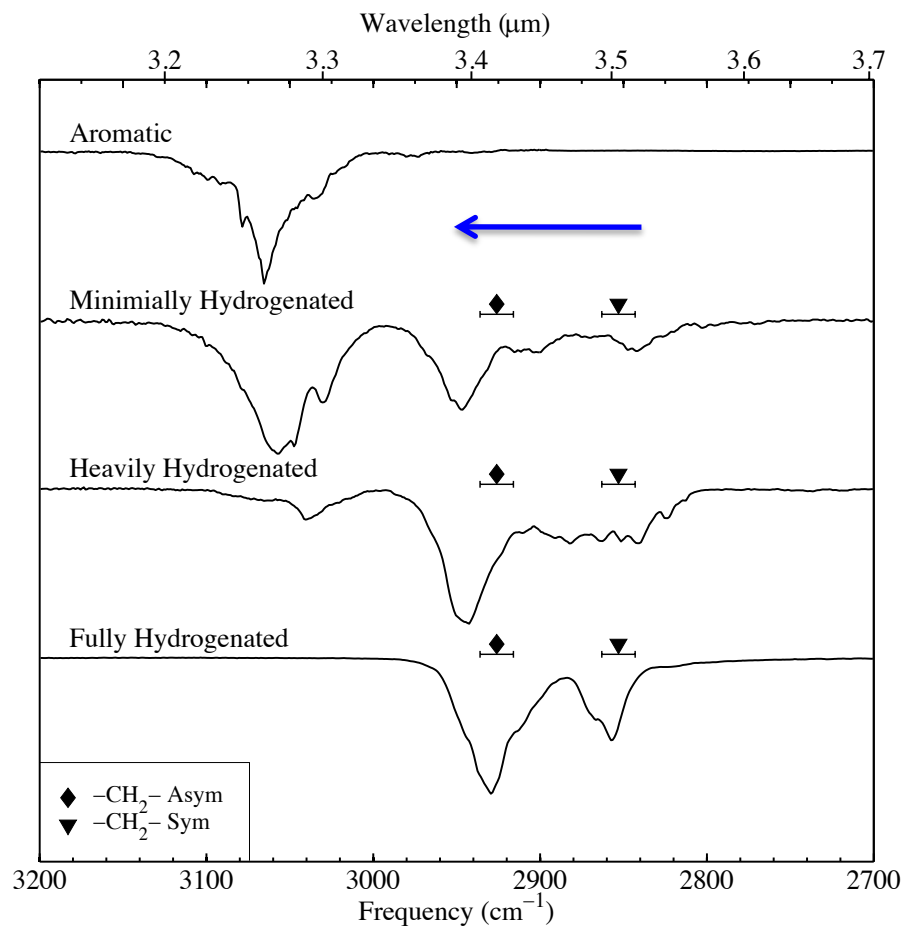
Sandford et al. (2013) ApJS.

H_n-PAHs by degree of hydrogenation

- To learn more about how increasing levels of hydrogenation change the spectra of PAHs, we grouped all molecules in the study into 4 categories:
 - Aromatic
 - Minimally hydrogenated
 - Heavily Hydrogenated
 - Aliphatic
- In general, for **Minimally hydrogenated molecules** the average *aliphatic moiety* in a molecule is **more** strained because it is more likely to be adjacent to aromatic moieties
- In general, for **Heavily hydrogenated molecules** the average *aliphatic moiety* in a molecule is **less** strained because it more likely to be adjacent to other aliphatic moieties

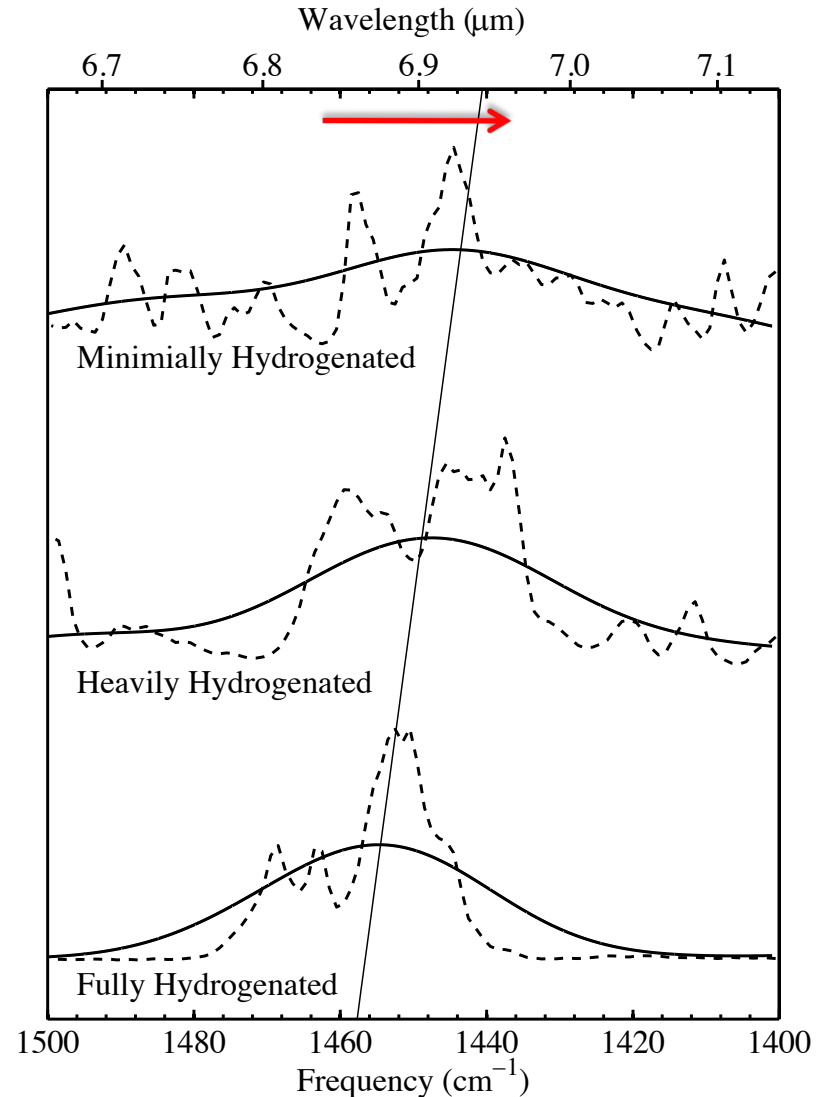
Co-added spectra: 3.2-3.6 μm region

- Rapid growth of aliphatic/slow loss of aromatic bands
- Cyclic aliphatics are strained compared to linear aliphatics
- Strain causes a blueshift in aliphatic C-H modes
- Adjacent aromatic/aliphatic increases strain
- In general, minimal hydrogenation leads to more strain



Co-added spectra: 6.9 μm band

- CH_2 scissoring mode grows with more hydrogenation
- Strain causes a **redshift** in aliphatic C-H modes
- Adjacent aromatic/aliphatic further increases strain
- In general, minimal hydrogenation leads to more strain



Summary of Laboratory Results

- As hydrogenation increases, the aromatic C-H stretch band strength decreases and aliphatic bands grow in their place
- As hydrogenation increases, methylene scissoring bands grow
- C-H out-of-plane bending modes are changed or eliminated by hydrogenation
- Strain from adjacent aliphatic and aromatic moieties shifts the band position of the aliphatic C-H stretch (blueshift) and the CH₂ scissoring modes (redshift)

Hypothesis:

H_n-PAHs significantly contribute to the abnormally large 3.4 μm features observed around some protoplanetary nebulae

- There should be little to no emission from methyl C-H stretch modes
- C-H stretch features should be **blueshifted** relative to canonical positions for linear aliphatics because of both ring strain and strain caused by adjacent aromatic/aliphatic moieties
- If methylene C-H stretch modes are responsible for the 3.4 μm feature, a methylene CH₂ scissoring mode must also appear near 6.9 μm
- The 6.9 μm feature should be **redshifted** relative to canonical positions for linear aliphatics because of both ring strain and strain caused by adjacent aromatic/aliphatic moieties

Complication

- It is known that the process of emission can cause a redshift of $\sim 15 \text{ cm}^{-1}$ in PAH bands (relative to their absorption spectra)
- If methylene bending modes behave similarly, this could potentially explain some redshifting in the $6.9 \mu\text{m}$ band
- No directly relevant laboratory data exist to address this
- A better understanding of how much the methylene scissoring mode may shift is needed

New Observations:

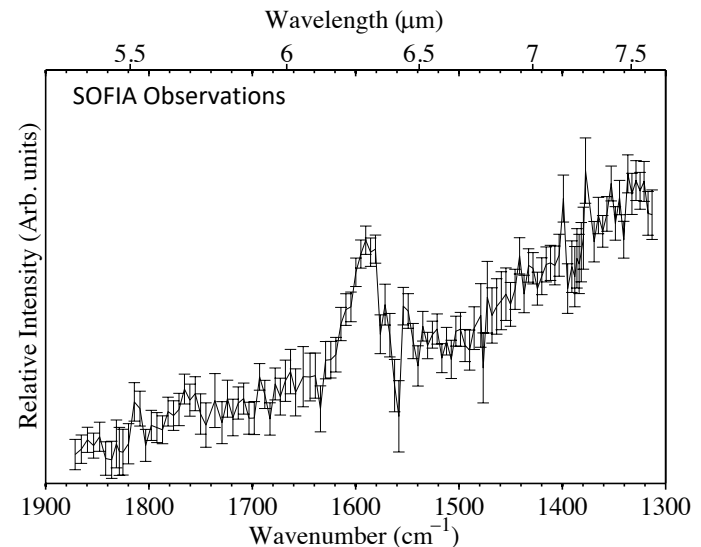
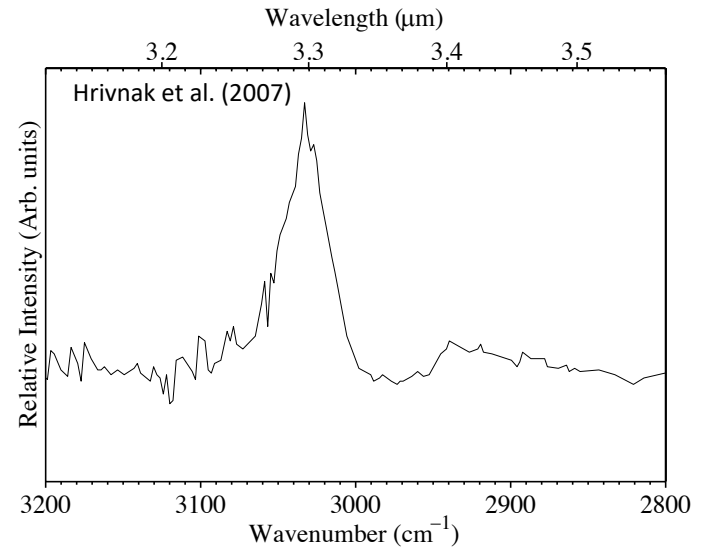
- New observations using the Stratospheric Observatory for Infrared Astronomy (SOFIA)
- FORCAST instrument (Herter et al. 2012) in cross-dispersed grism mode (FOR_XG063)
- Data collected for 4 protoplanetary nebulae:
 - Normal PAH emitter
 - IRAS 20000+3239
 - Abnormally large 3.4 μm emission features
 - IRAS 22272+5435
 - IRAS 04296+3429
 - IRAS 05341+0852



Image credit: NASA / Jim Ross

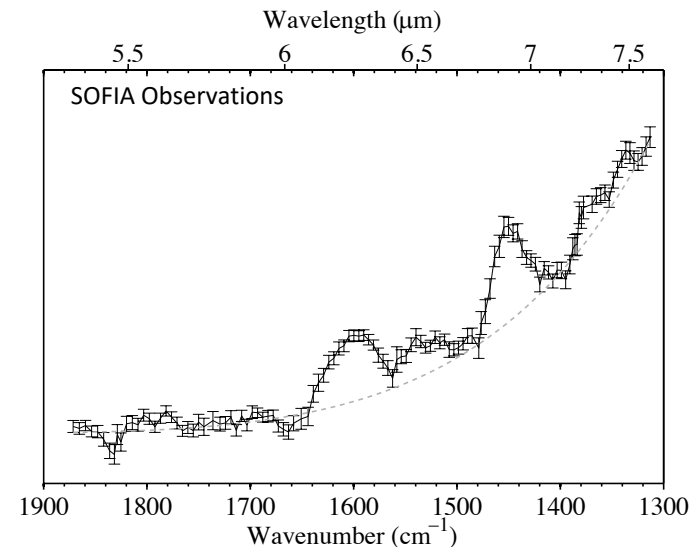
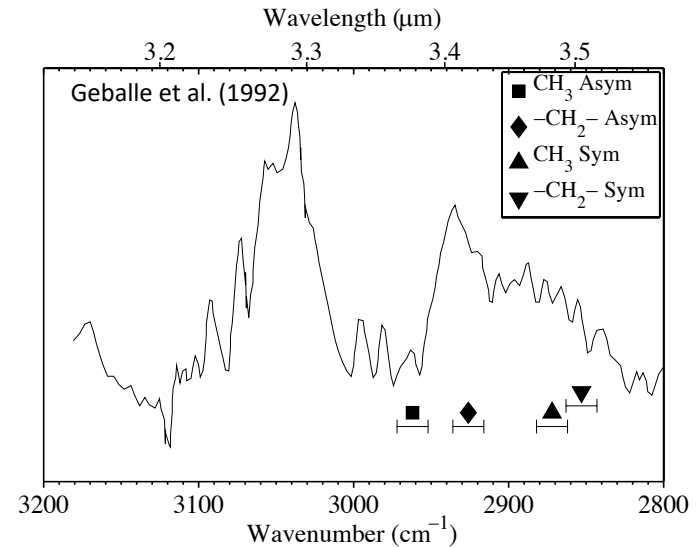
Normal PAH emitter IRAS 20000+3239

- Strong 3.3 μm PAH emission band (aromatic)
- Normal 3.4 μm features
- Normal 6.2 μm PAH band observed
- No detectable 6.9 μm band



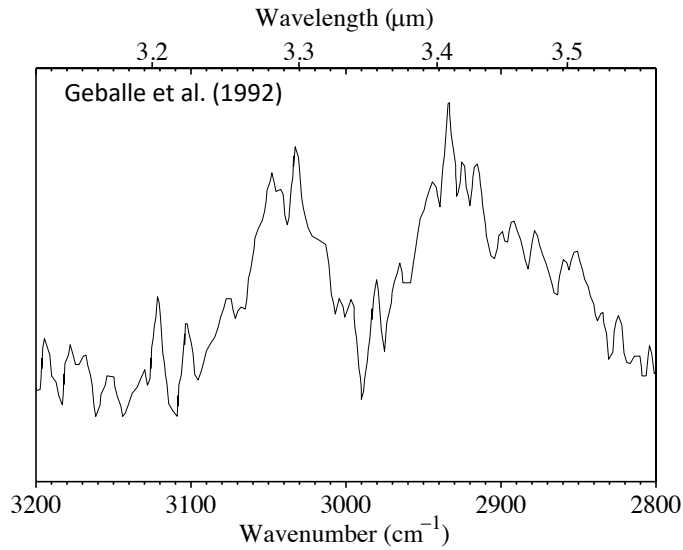
Abnormal 3.4 μm emitter IRAS 22272+5435

- Little to no apparent emission from CH_3 stretch
- Slight **blueshift** from canonical methylene CH stretch modes
- Methylene scissoring mode readily apparent near 6.9 μm

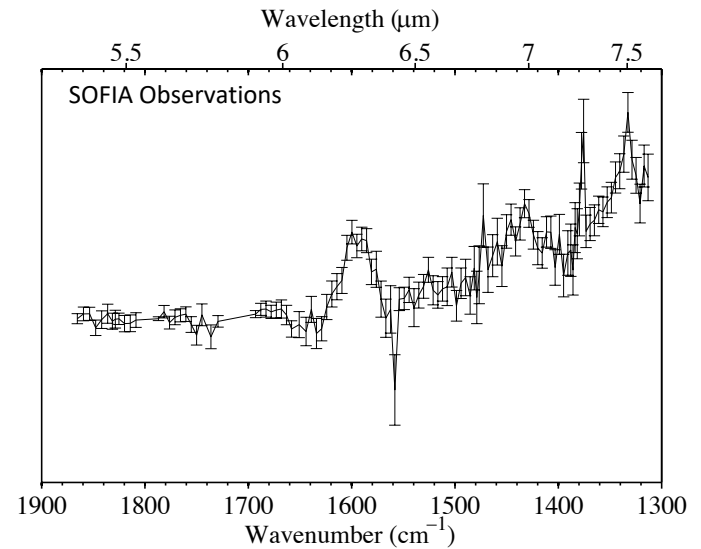
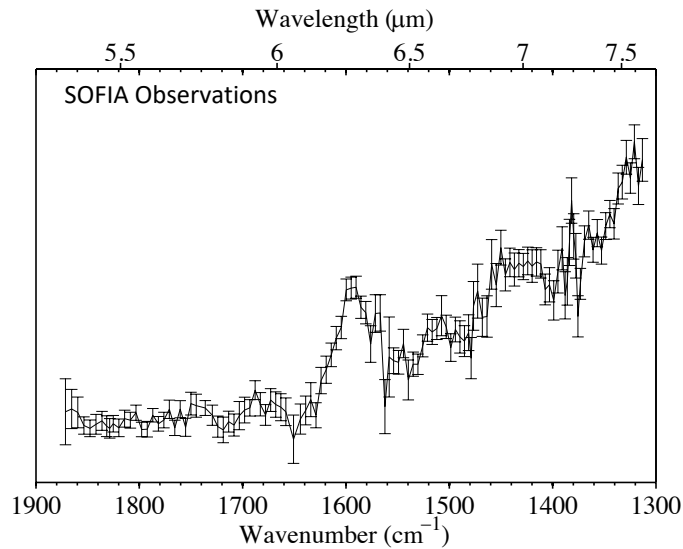
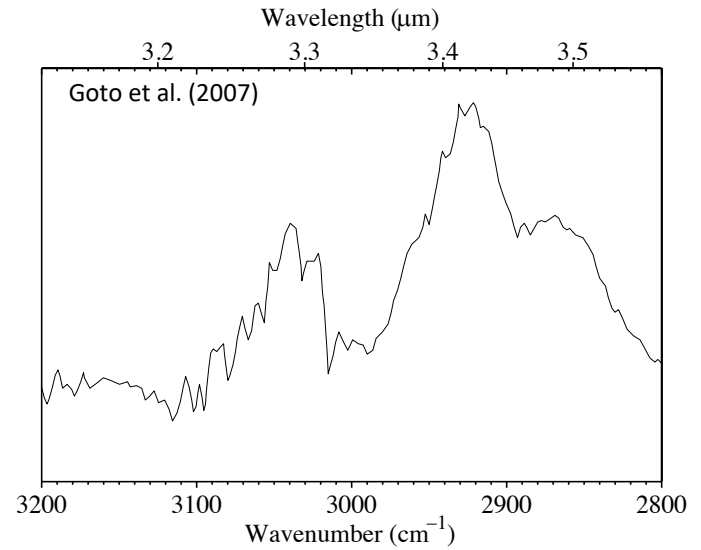


Abnormal 3.4 μm PAH emitters

IRAS 04296+3429

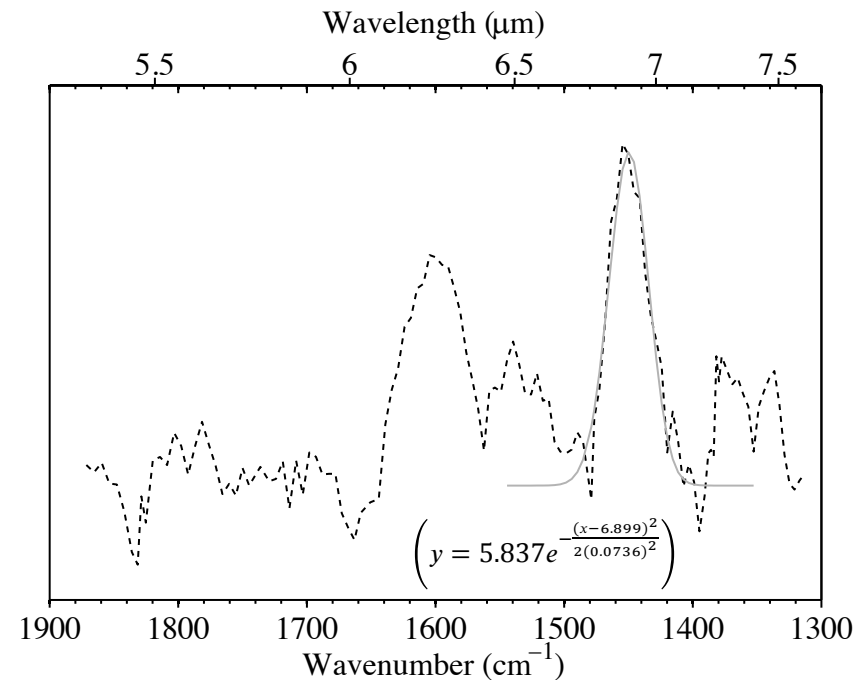


IRAS 05342+0852



Position of 6.9 μm feature for IRAS 22272+5435

- Canonical band positions for methylene scissoring modes:
 - Linear aliphatic: 6.811 μm
 - Minimally strained cyclic aliphatic: 6.887 μm
- Baseline correction + Gaussian fitting to the spectrum of IRAS 222872+5435
- Band position of 6.9 μm feature: $6.899 \pm 0.005 \mu\text{m}$ (redshift)



Summary:

The protoplanetary nebulae spectra are consistent with the presence of H_n-PAHs

- ✓ Little to no emission from methyl C-H stretch modes
- ✓ C-H stretch features are **blueshifted** relative to canonical positions for linear aliphatics
- ✓ A band consistent with a methylene CH₂ scissoring mode appears near 6.9 μm
- ✓ The 6.9 μm feature is **redshifted** relative to canonical positions for linear aliphatics

Future directions

- A study of more post-AGB objects with abnormally large $3.4\ \mu\text{m}$ features including the $6\ \mu\text{m}$ region to identify and determine the precise positions of $6.9\ \mu\text{m}$ bands if present
 - These objects tend to be dim
 - We have observed the brightest known objects already
 - An instrument with better S/N will be required
- Laboratory studies that characterize the expected shift in the band position of the methylene scissoring mode in emission vs absorption

Conclusions:

- Normal PAH emitters with weak features at 3.4 μm possess no clearly detectable emission features at 6.9 μm
- Post-AGB objects with abnormally large 3.4 μm features also possess detectable emission features at 6.9 μm , consistent with aliphatic methylene scissoring modes
- The abnormally large 3.4 μm emission features suggest that methylene groups are far more abundant than methyl groups
- H_n -PAHs are an attractive candidate family of molecules that could contribute to both aromatic and aliphatic features in abnormal PAH emitters
- H_n -PAHs are also attractive because their rings contain a high ratio of methylene to methyl moieties
- The positions of the 3.4 and 6.9 μm features may provide additional support for the H_n -PAH hypothesis

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