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
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**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 $\mu$m
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 µm

• Bands near 3.4 µm typically attributed to anharmonic “hot bands” and overtone and combination modes

• Some post-AGB objects have abnormally large 3.4 µm 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 Hₙ-PAHs
• Characterize changes in the IR spectra of families of Hₙ-PAHs as a function of increasing hydrogenation
• Identify telltale spectral features of Hₙ-PAHs
• Compare laboratory derived spectra of Hₙ-PAHs to observational data
Methods

• Experiments conducted in the Ames Astrochemistry Lab using a cryovacuum chamber
  − ~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\textsubscript{n}-PAHs along with parent PAHs were collected

• Families of progressively more hydrogenated Hn-PAHs selected to demonstrate the changes in the spectrum

• All molecules in the study were fully cyclic (no terminal CH\textsubscript{3} groups)

• Special focus was paid to changes in the 3.2—3.6 \(\mu\text{m}\) region (C—H stretch) as well as the 6.9 (CH\textsubscript{2} scissoring) region of the IR spectrum
Experimental Setup

- PAH Sample
- ½” SS Cajon Fitting
- ½” Pyrex Tube
- Heating Wire
- Argon Deposition Line
- KBr Vacuum Window
- Infrared Beam Axis
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<sub>oop</sub> band

- DHN: Quartet + olefinic C-H<sub>oop</sub> band, growth of methylene scissoring bands

- THN: Quartet C-H<sub>oop</sub> band

- OHN/c-DHN/t-DHN: No C-H<sub>oop</sub> band
Other $H_n$-PAHs studied

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

- CH₂ 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 $\mu$m 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 $\mu$m feature, a methylene CH$_2$ scissoring mode must also appear near 6.9 $\mu$m

- The 6.9 $\mu$m 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 ~15 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 µm 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

Geballe et al. (1992)

Goto et al. (2007)

SOFIA Observations
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±0.005 µm (redshift)
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 CH$_2$ 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 μm features including the 6 μm region to identify and determine the precise positions of 6.9 μm 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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