Theoretical Studies on the Complex Organic Molecules Origin of the Mid Infrared UIE bands in Planetary Nebulae

SeyedAbdolreza Sadjadi

Dec 12th, 2017

Laboratory for Space Research (LSR)

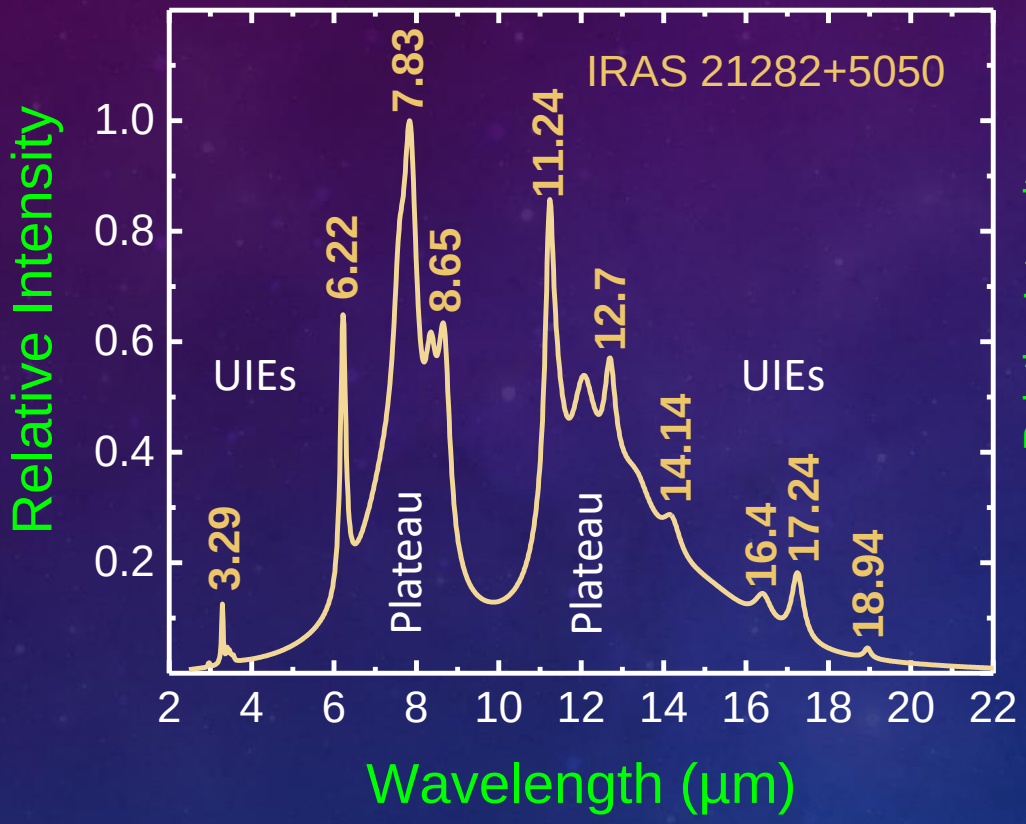
The University of Hong Kong

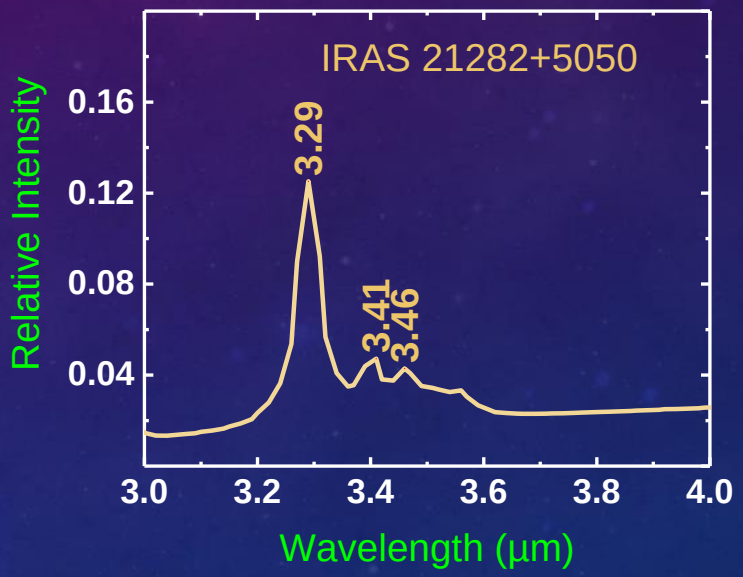
ssadjadi@hku.hk

http://www.lsr.hku.hk/abdi/abdi.html

UIE Bands in Young PN

Understanding the Deep Space Chemistry





Despite their harsh environments, PNs can be the host of complex organic molecules

Sun Kwok, Astrophys Space Sci, 319:5 (2009)

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What Do UIE Bands and Plateaus Tell Us

Origin — UIE bands are broad

- Collection of atoms in forms of clusters or molecules

Size — Plateau features

- UIEs sit on top of the very broad plateau features. By assuming the same source for both UIEs and plateaus, we can estimate the size of more than 100 atoms for UIE carrier

Bonds — UIE bands are discrete

- If the UIE carrier is one big molecules or group of molecules, they should composed of just a few types of bonds. Usually the wavelength range of 3-10 μm is the bond type control region, wavelength longer than 10 μm is stereochemistry control region.

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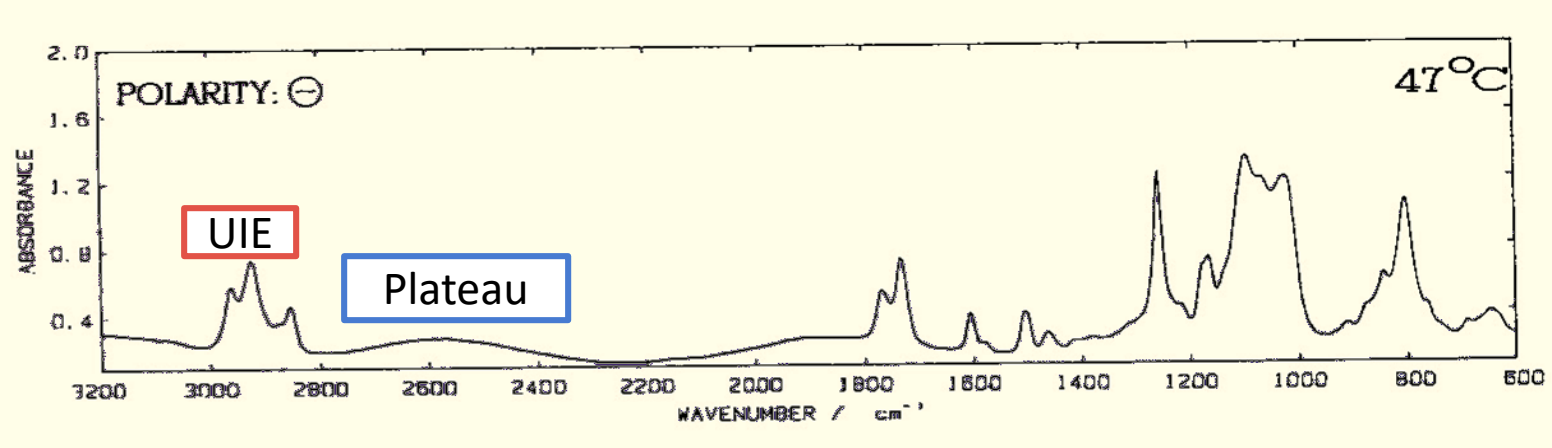
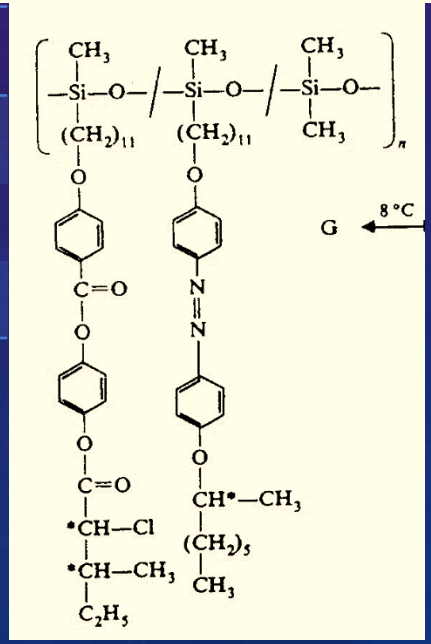
An Example of Broad IR Features

FT-IR Spectrum of a Liquid Crystal Polymer Known as FLCP



Molecule	FWHM (μm)
H_2**	0.003-0.004
FT-IR (PAH)	0.01
UIE	0.03



** Hsia and Tao (MUST)

Modern Polymer Spectroscopy
Edited by Giuseppe Zerbi

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UIE Carriers as Seen by Mathematics

$Properties = f(strcutue)$

structure space properties space

Spectral Similarity

$X = \{x_1, x_2, \ldots, x_i, \ldots, x_n\}$ target molecule intensity or wavelengths

$Y = \{y_1, y_2, \ldots, y_i, \ldots, y_n\}$ reference molecule intensity or wavelengths

$$r_p = \frac{\sum_i (x_i - \overline{x}).(y_i - \overline{y})}{\sqrt{\sum_i (x_i - \overline{x})^2 . \sum_i (y_i - \overline{y})^2}}$$ Pearson's product moment correlation coefficient.

r_p=1 prefect linear correlation or similarity.

For performing similarity we need

1- a pool of reference spectra with same wavelength resolution and normalized intensities with respect to the strongest peak.

2- the unknown spectra should be prepared to match The conditions of reference spectra.

UIE Carriers as Seen by Mathematics

Spectral Similarity

Theoretical database with more than 275,000 molecules up to the mass of 500 a.m.u
Calculated IR spectra at EDF2/6-31G* and ωB97X-D/6-31G*
EDF2 stands for Empirical density functionals

$$E^{EDF2} = a_1 E^{HF} + a_2 E^{LSDA} + a_3 E^{BLYP} + a_4 E^{B3LYP} + a_5 E^{EDF1}$$

a_i: is determined by least-square fit of HF, LSDA, BLYP, B3LYP and EDF1 harmonic frequencies to experimental data

$$E_{XC}^{EDF2} = b_1 E_X^{F30} + b_2 E_X^{D30} + b_3 E_X^{B88} + b_4 E_X^{EDF1} + b_5 E_C^{VWN} + b_6 E_C^{LYP} + b_7 E_C^{EDF1}$$

Overall RMS: $34\ cm^{-1}$,

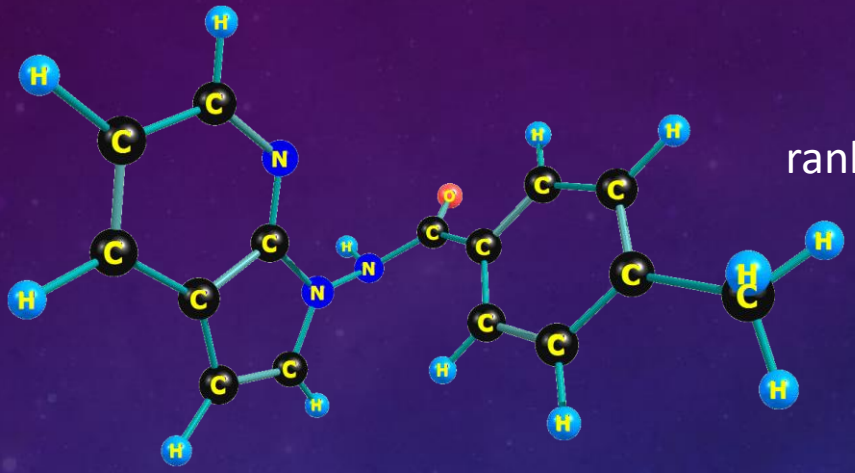
Target: Experimental IR gas phase (NIST)
Reference: EDF/6-31G* data base

Total: 35 tries (known Spectra)
Successful exact hit by Similarity: 13
Reliability : 37%

Lin, C. Y.; George, M. W.; Gill, P. M. W., *Australian Journal of Chemistry* 2004, *57* (4), 365-370.
Adamson, R. D.; Gill, P. M. W.; Pople, J. A., *Chemical Physics Letters* 1998, *284* (1–2), 6-11.

UIE Carriers as Seen by Mathematics

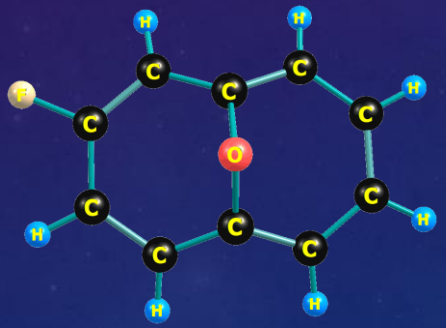
Spectral Similarity results for IRAS2128+5050



rank 1

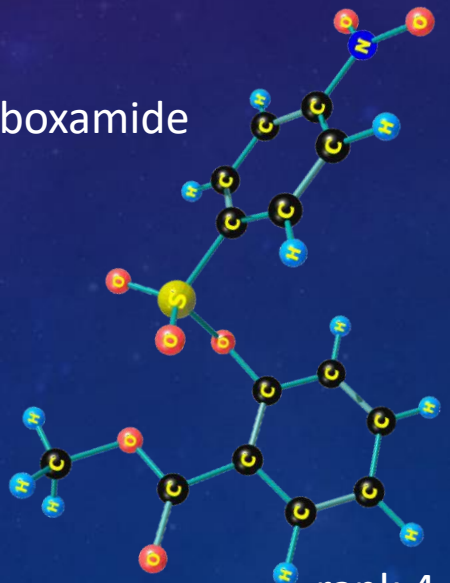
$C_{15}H_{13}N_3O$

4-mthyl-n-(1h-pyrrolo[2,3-b]pyridine-1-yl]benzenecarboxamide



rank 2

rank 3



rank 4

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Quantum Mechanics & Quantum Chemistry

Forces define the system and the Hamiltonian $\hat{H}$

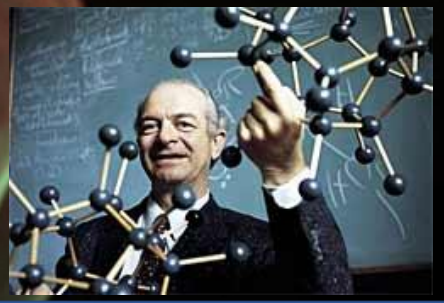
$i\hbar\,{}^{\partial\Psi}/_{\partial t} = \hat{H}\Psi$ | $\hat{H}\Psi = E\Psi$

Quantum mechanical observables

Hilbert space | Dirac's transformation theory

Eigenvalues and Expectation values

Equations of motion | ${}^{d\hat{F}}/_{dt} = \left({}^{i}/_{\hbar}\right)[\hat{H}, \hat{F}]$



Quantum Chemistry

BO approximation | One electron approximation | Many electrons approximations

Structure

Guzman and Bader, Coord.Chem.Review, 249:633-662 (2005)

Applications of Quantum Chemistry

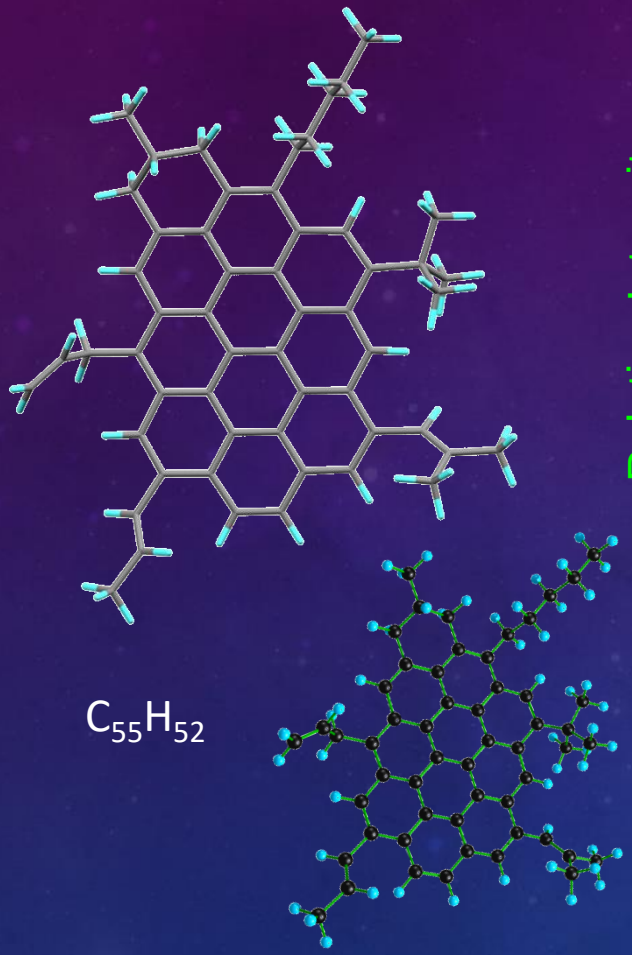
- Direct modeling of the UIE bands carriers.

- Understanding the vibrational origin of the UIE bands.

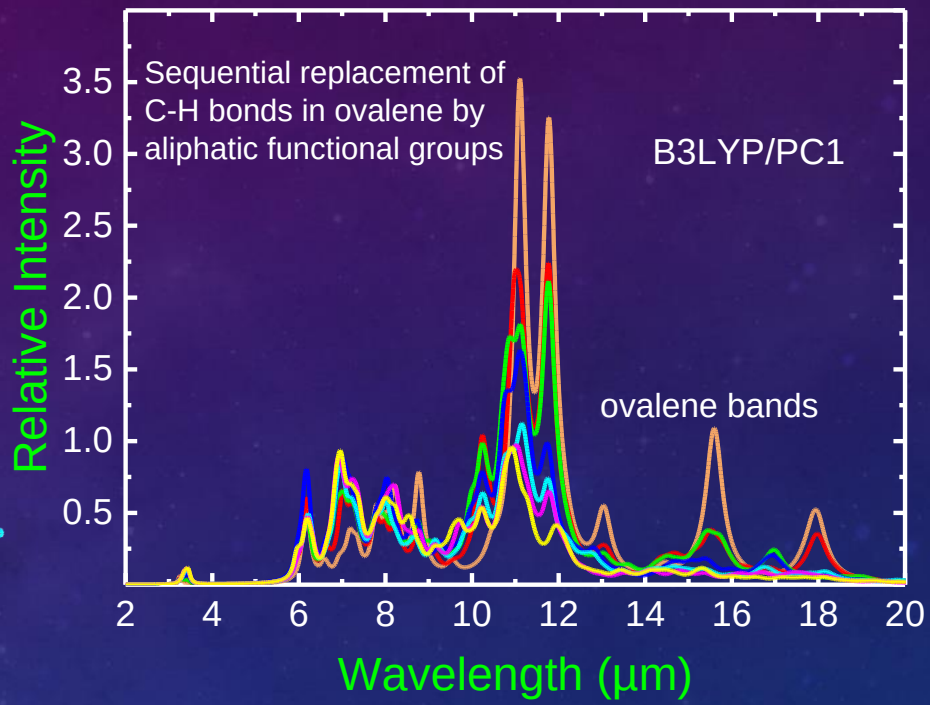
- Search for the new species

Direct Modeling of the UIE Bands

Adding Aliphatic Groups to the PAH Core



$C_{55}H_{52}$



1- How different IR features are formed by mixing aliphatic and aromatic functional groups.
2- Weather PAH bands are replaced or shifted.
3- Estimation of the accuracy of the calculations.
4- Developing simulation and vibrational analysis codes.
5- Quantitative interpretation of IR bands.

Sadjadi, Zhang and Kwok, ApJ, 801:34 (2015)

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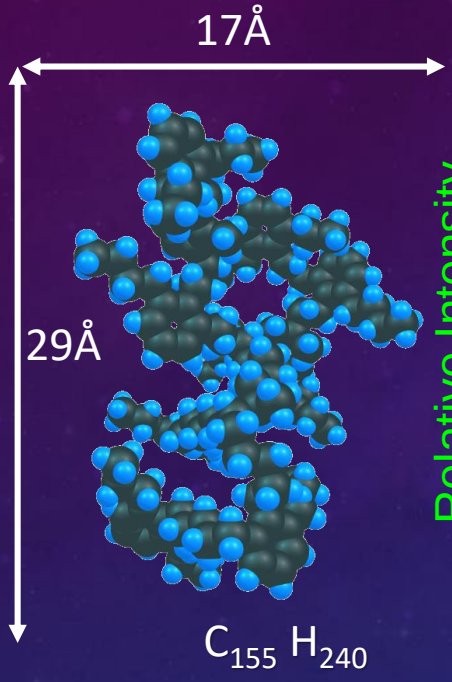
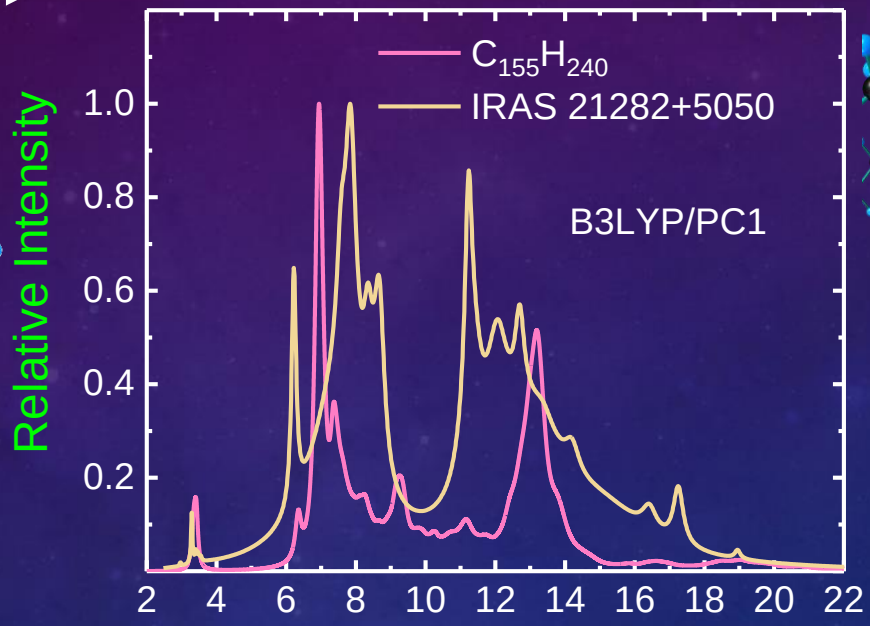
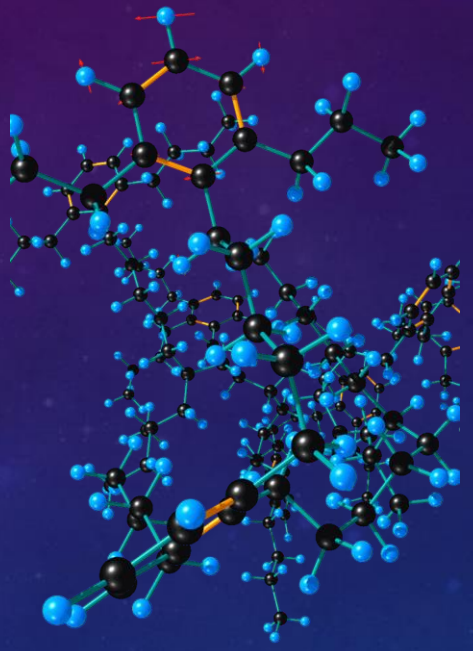
Direct Modeling of the UIE Bands

Mixed Aliphatic-Aromatic Organic Nanoparticles (MAONs)



Nano size hydrocarbon





6.35 μm

aromatic CC stretching mode coupled with C-H in-plane bending mode

We try to understand which fragments inside such a big molecule are responsible for the observed IR features. Then we can return back to the observations and track the existences of such fragments.

Sadjadi, Kwok and Zhang, Journal of Physics, Conference Series 728 (2016) 062003

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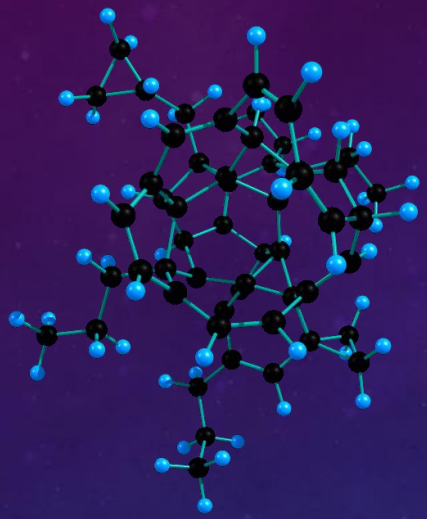
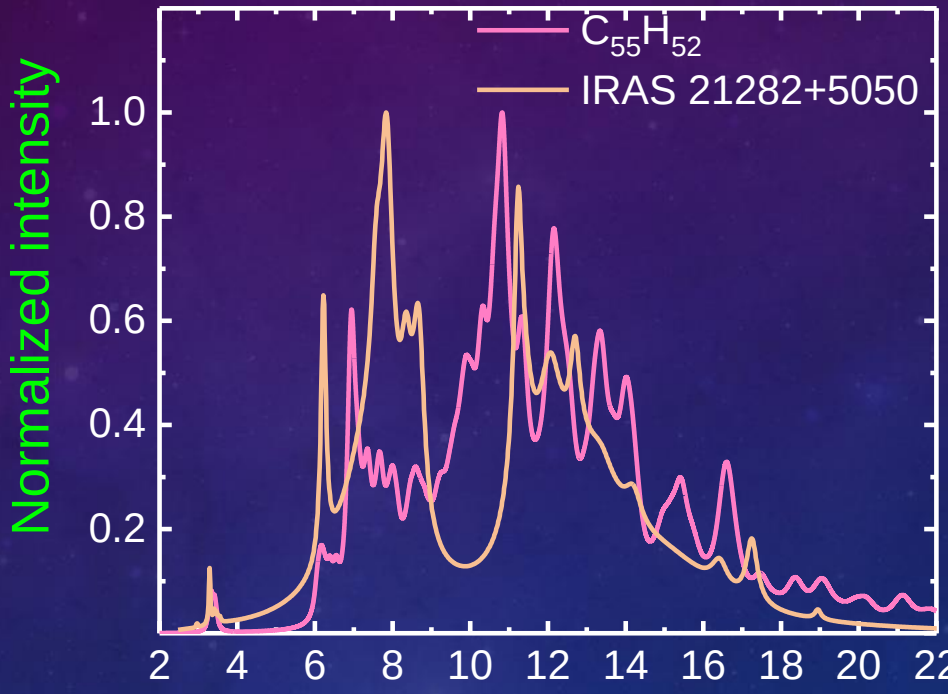
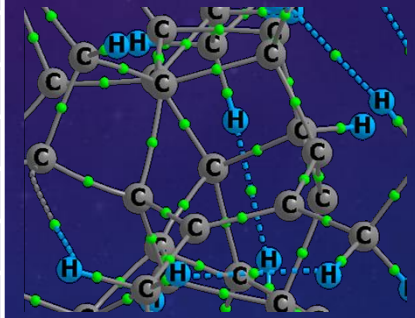
Direct Modeling of the UIE Bands

Amorphous Hydrocarbon



Classical Structure
C_{55} H_{52}





Part of
QTAIM Structure
C_{55} H_{52}

Amorphous hydrocarbon shows a very complex bonding pattern, this makes the interpretation of IR spectrum very difficult. Here the advanced bonding model via quantum theory of atoms in molecules (QTAIM) is applied to reveal the nature of bonds.

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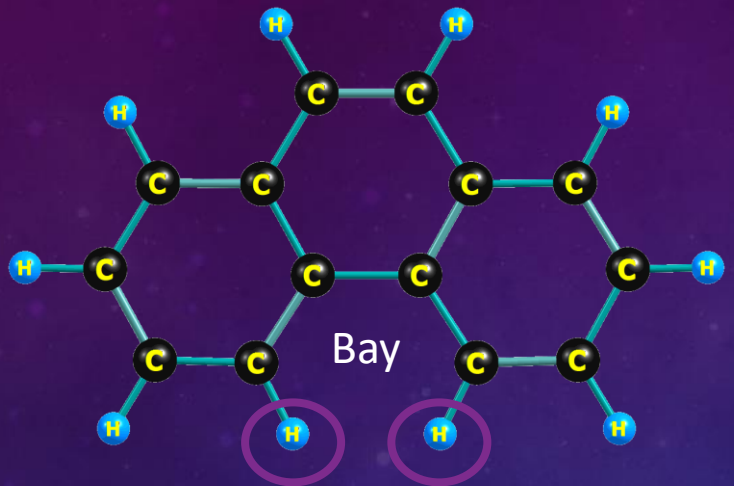
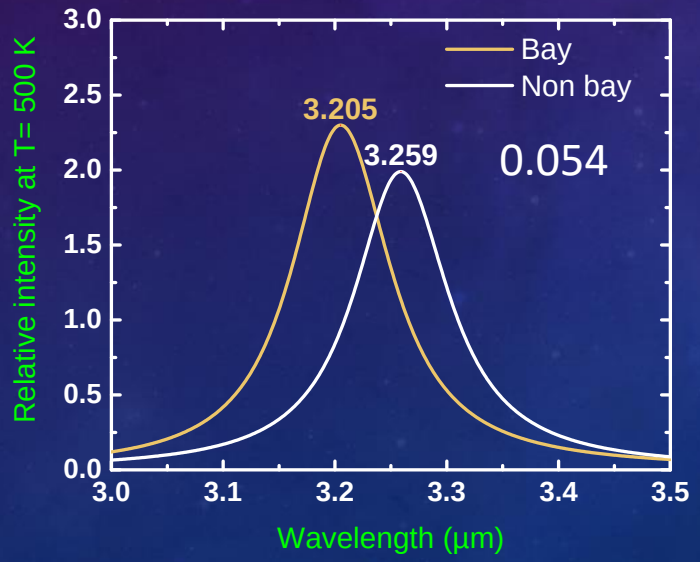
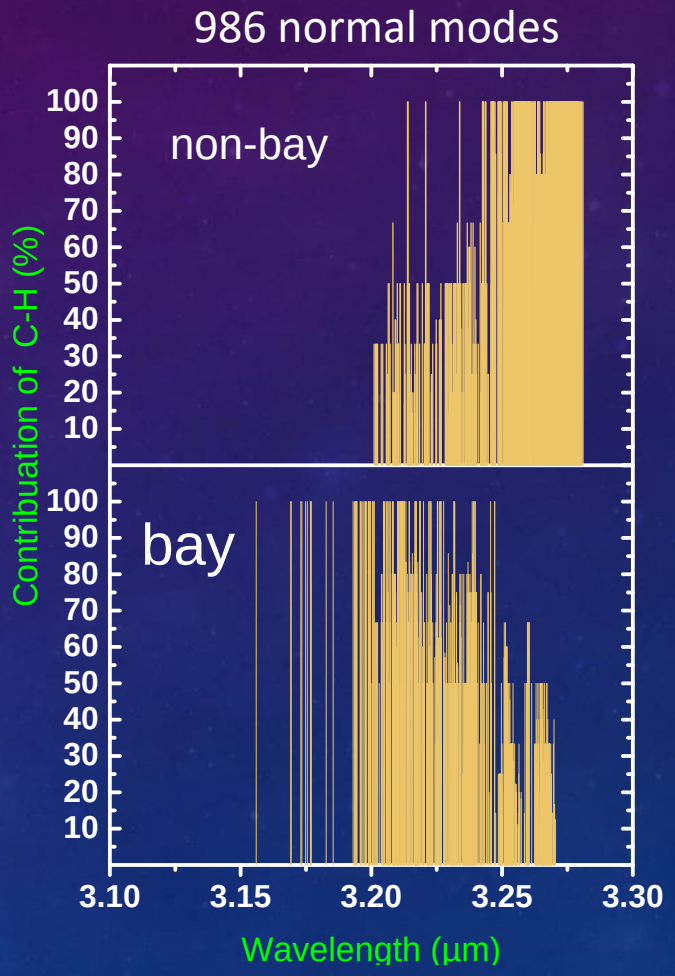
The Origin of the UIE Bands

3.28 and 3.3 μm components of 3 μm feature







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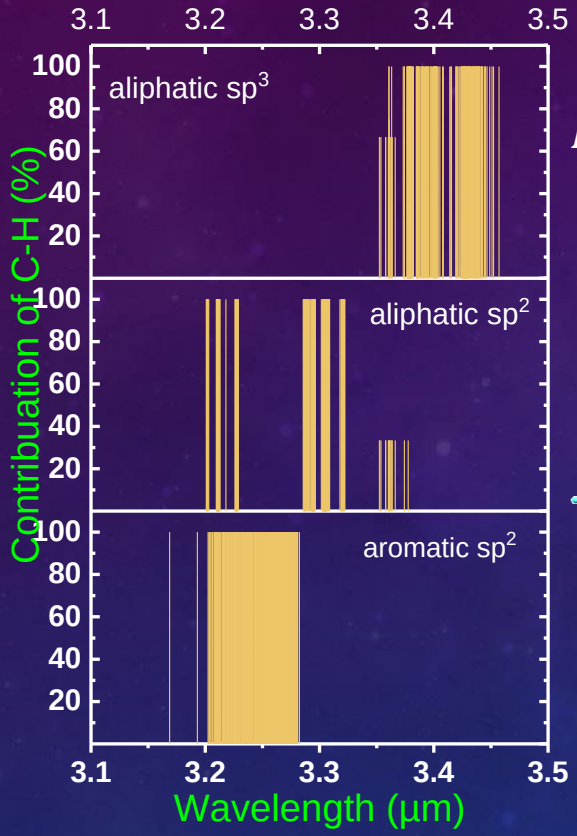
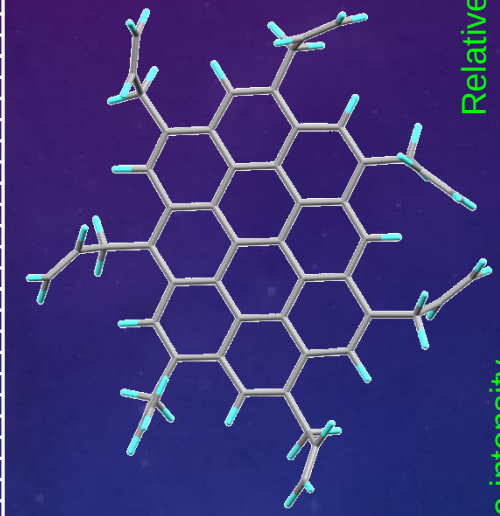
The Origin of the UIE Bands

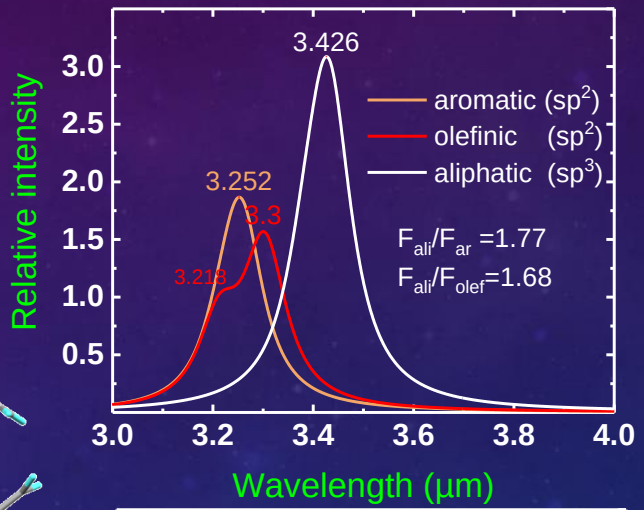
Vibrational analysis on 1248 modes within the range of 3.3-3.4 μm

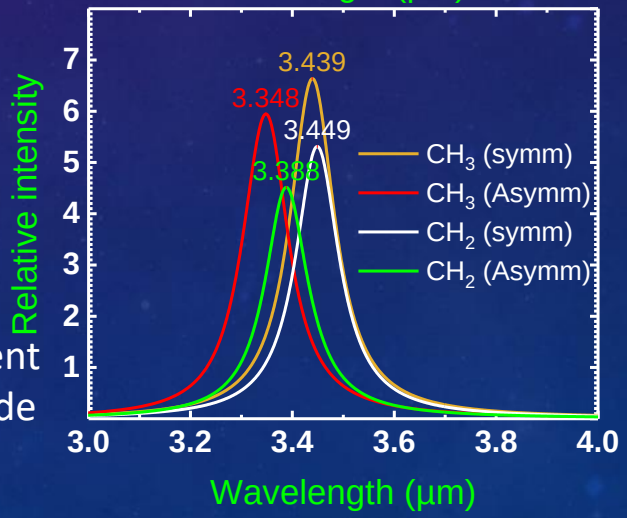


$$I_{k,i}^{CART} = \sum_{j}^{3N} \frac{D_{k,j} L_{j,i}}{\sqrt{m_k}}$$



$C_{53}H_{42}$





By analyzing the $I_{k,i}^{CART}$ matrix, the contribution of different fragments within a molecules in a particular normal mode vibrational motion. Is determined.

Sadjadi, Zhang and Kwok, ApJ, 845:123 (2017)

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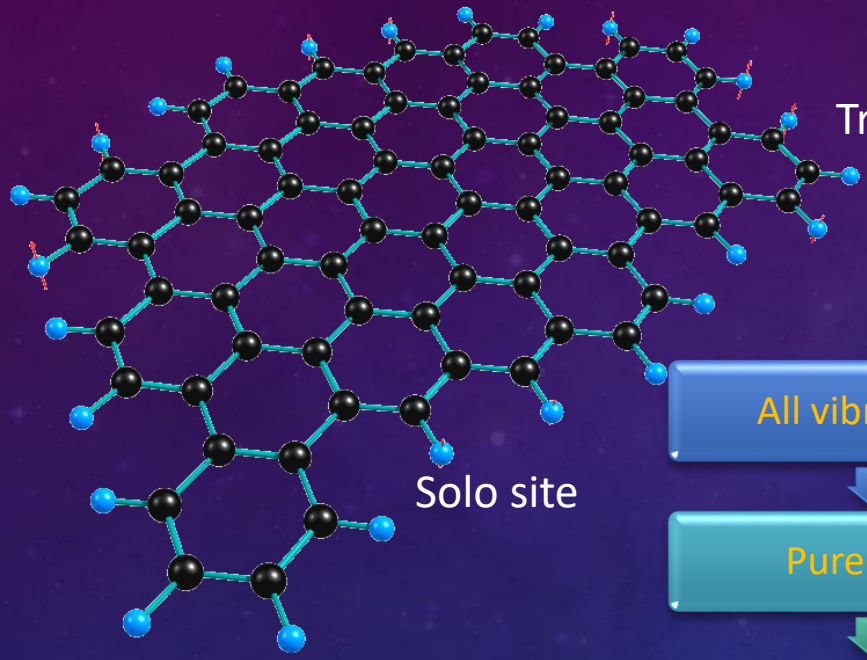
The Origin of the UIE Bands

Vibrational analysis within the range of 11-15 μm



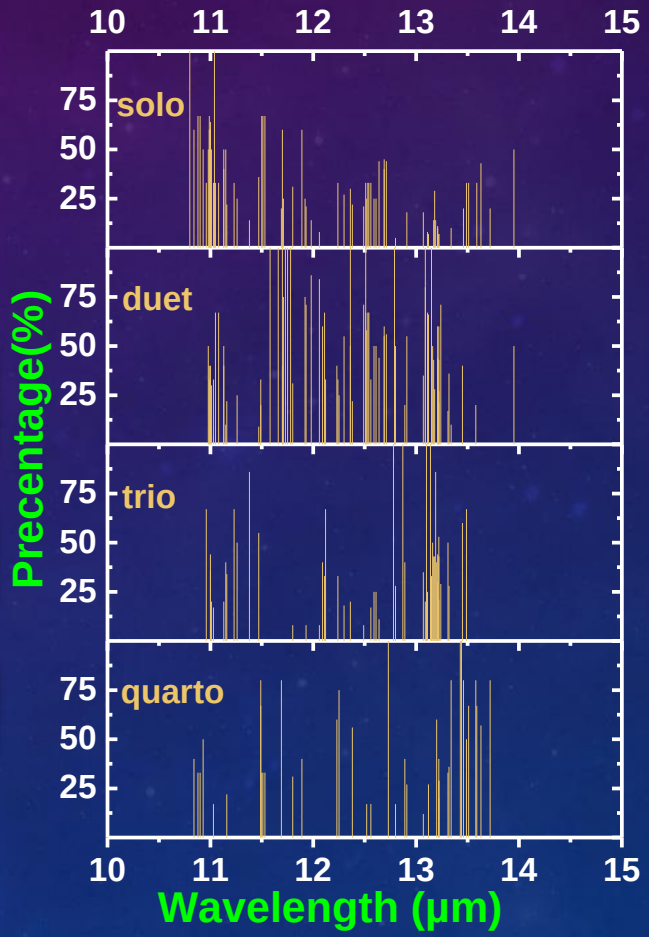
$C_{82}H_{26}$, 11.04 μm

B3LYP/PC1

All vibrations

Pure OOP

%solo, %duet, %trio, %quarto



The complex picture of OOP vibrations in a PAH molecule. Different aromatic C-H types participate in a specific normal mode vibrational motion

Sadjadi, Zhang and Kwok, ApJ, 807:95 (2015)

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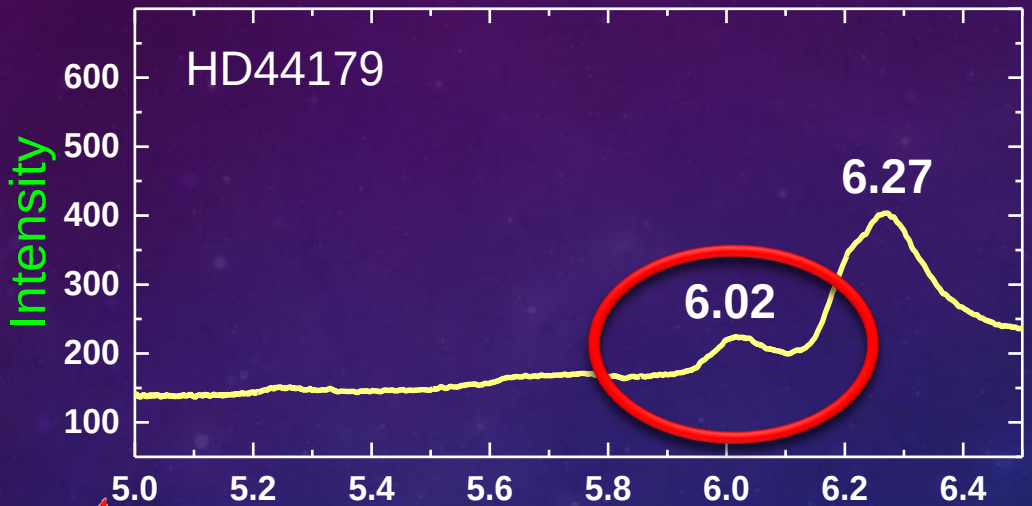
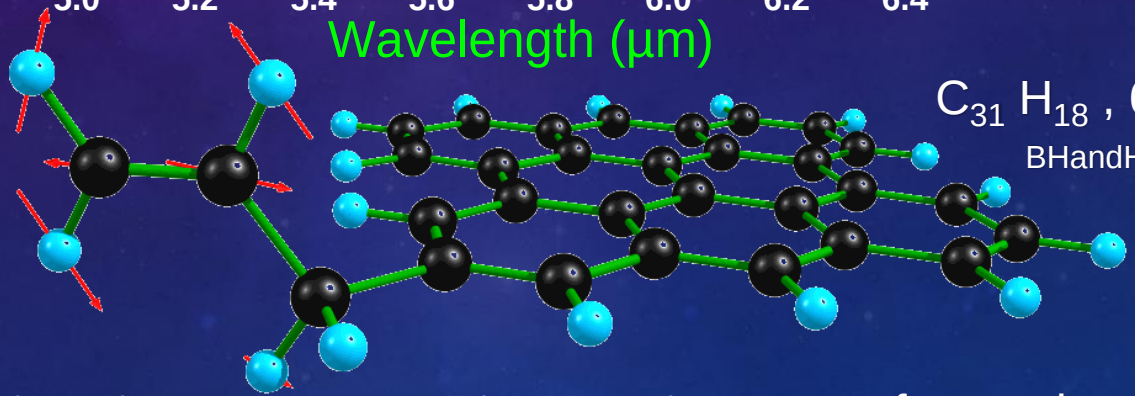
Search for New Species

Molecules with Olefinic Functional Group





$C_{31}H_{18}$, 6.00 μm

BHandHLYP/PC1

We provided an alternative new explanation that 6.0 μm feature is not due to CO but due to olefinic containing compounds (-C=C-)

Hsia, Sadjadi, Zhang and Kwok, ApJ,832:213 (2016)

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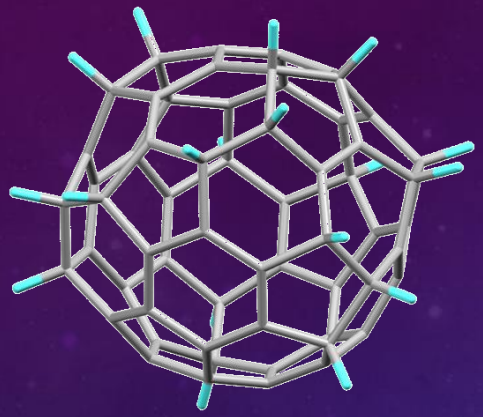
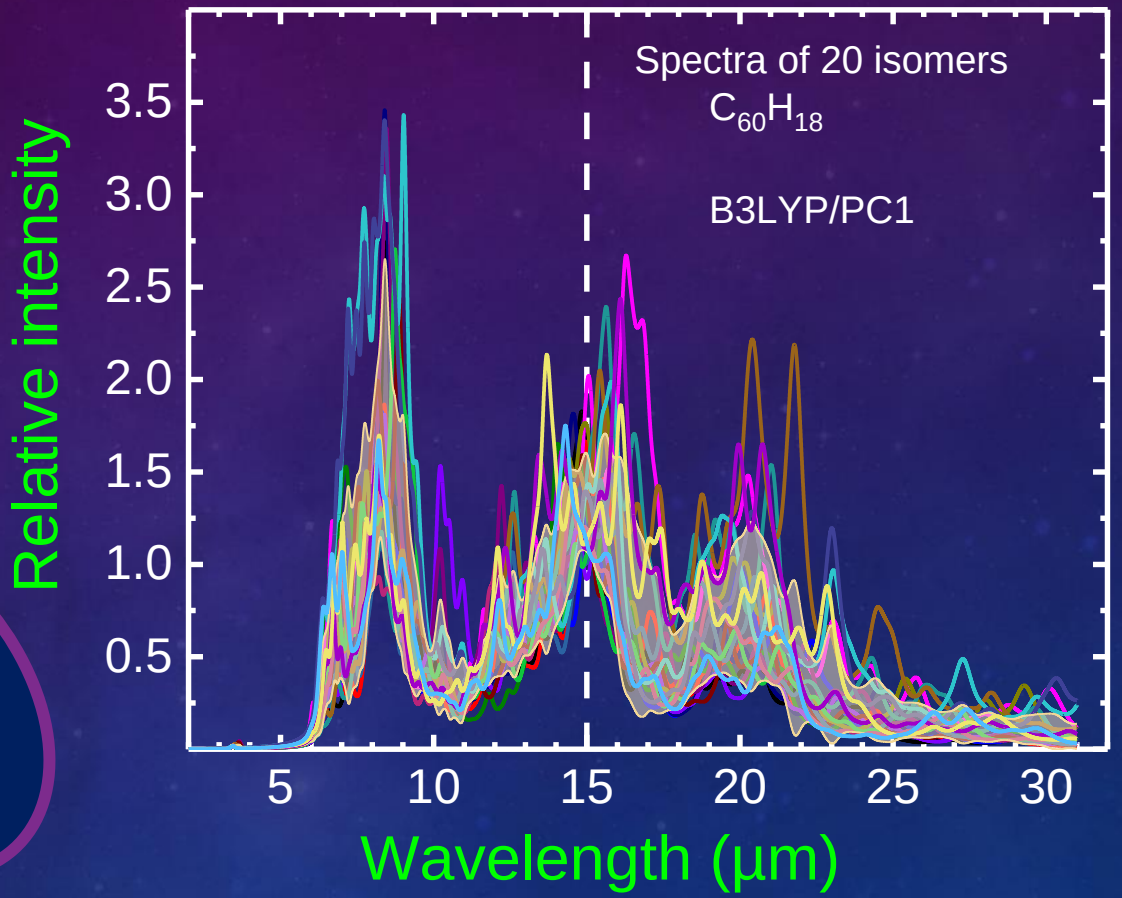
Search for New Species

Fulleranes



$C_{60}H_{18}$

Stable from
523 K to 98 K



$C_{60}H_{18}$ as one of the most kinetically and thermodynamically stable fulleranes shows unique IR feature at 15 μm. We use this feature to search for this species in space.

Zhang, Sadjadi, Hsia and Kwok, ApJ,845:76 (2017)

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Our List of Questions for Subaru

- What elements are these UIE carries made of?
- How many atoms they have?
- What are their molecular structures?
- What electric charges they carry (+, ++, …)?
- What are their electronic states (Singlet, Doublet,…)?
- At what temperature and pressure are they formed?
- How do they form?
- Are they entirely formed by the gas phase reactions or condensed phase reactions?
- Where do they form?. At the center of the stars or other places?
- How can we get the confirmation/rejection of our understandings of these complex phenomena obtained in the mid-infrared region, in another region of spectra like optical or near infrared regions?

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Acknowledgements

Professor Quentin Parker and LSR Members

Dr. Hsia, Dr. Zhang, Prof. Kwok and Abdi

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