The Spectroscopic Role of Molecular Carbon & other Chemical Species as Indicators of Stellar Processes

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OAKLAND UNIVERSITY

Outline

Molecules in the Cosmos

- Carbon Chemistry Nomenclature

  hybrid orbital, valence electron configuration

  -ane=sp3; -ene= sp2; -yne= sp

- Small carbon molecules:

  carbenes (free radicals) HC, H2C:, :C=C: or .C=C.

  polyynes (chains) -C=C-C=C-

- PAH (C + H)
- Fullerenes (only C)
- Meteorites
- Carbon in the Cosmos

Partial List of Molecules (over 130) found in the ISM.

Formula	Name	Structure or Notes	Reference
C2	Dicarbide	Free radical	Kipper 2007
C3		Free radical	Kipper 2007
C2H2	Ethyne	HC≡CH	Kipper 2007
CO	Carbon Monoxide	Isotopologues: 12CO, 13CO, C18O	Polychroni2012 Buckle2012 Kipper 2007
CN	Cyanide radical	Extremely reactive	Kipper 2007
HCN	Hydrogen Cyanide		Kipper 2007
DCN	Deuterium Cyanide		Chaisson2014
C2N2	Cyanogen	N≡C-C≡N	
C2H3N	Methyl Cyanide	H3C-CN	Buckle2012
NH3	Ammonia		Chaisson2014
H2O	Water		Chaisson2014
SO2	Sulphur Dioxide		Chaisson2014
SO	Oxy Sulphur	Sulfur Monoxide	Buckle2012
H2S	Hydrogen Sulfide		Chaisson2014
CH4O	Methanol	13C isotope H3C-OH	Buckle2012
C2H6O	Ethanol	H3C-CH2-OH	Chaisson2014
CH5N	Methyl Amine	H3C-NH2	Chaisson2014
H2CO	Formaldehyde		Chaisson2014
[HCO]+	Formyl cation		
H2CO2	Formic Acid		Chaisson2014
C2H6O	Dimethyl ether	H3C-O-CH3	
CH3OCHO	Formic Acid Methyl Ester		Buckle2012
C2H4O	Acetaldehyde	CH3CHO	Buckle2012

Some molecules that have been identified in various Astrophysical environments are highly reactive, free radical species, generated under plasma conditions.

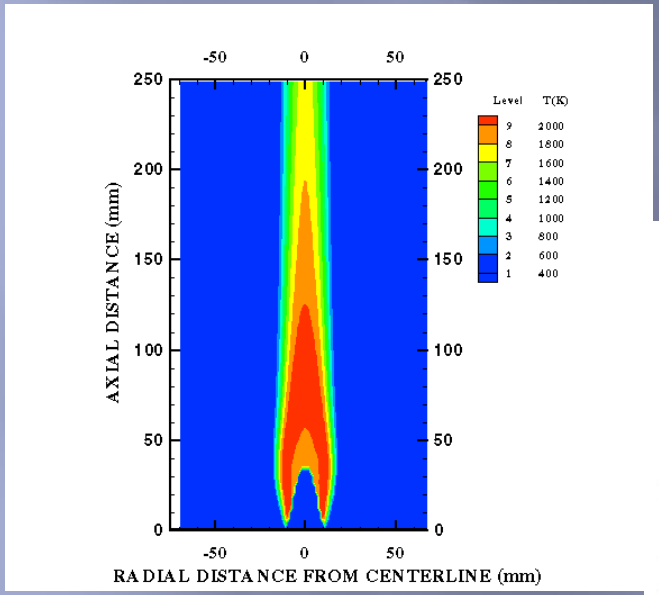
Over 130 molecules have been observed. This is a partial list.

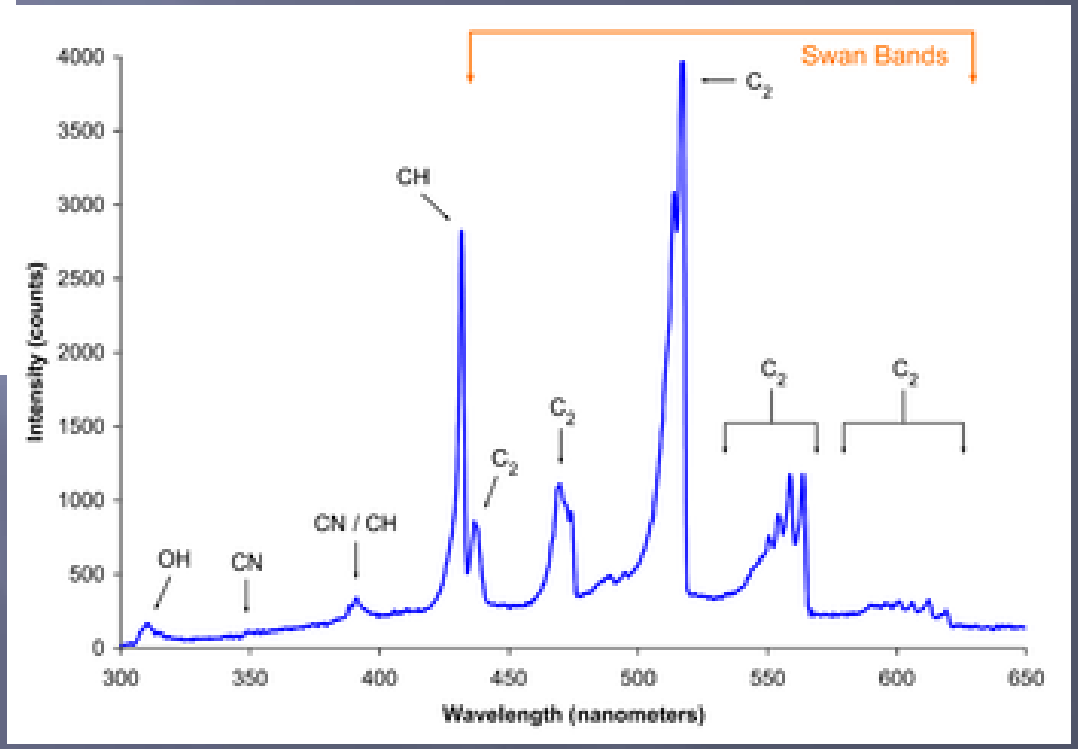
The Simplest Multi-carbon Molecule

- Abundances of C_2 give information about the chemistry of interstellar clouds, especially the formation of long-chain, carbon molecules.
- These long chain carbon molecules may be connected with carriers of the diffuse interstellar bands (DIB).
- DIB: 5780.4, 5796.9, 6283.9, 6613.9, 4437, 2175 (broad plateau) Angstrom
- C_2 lines can be used to determine physical conditions in interstellar clouds.

Kazmierczak, ArXiv: 1009.5188v1 [Astro-ph] 27 Sept 2010

Example of C2 Swan Bands generated from a blue flame





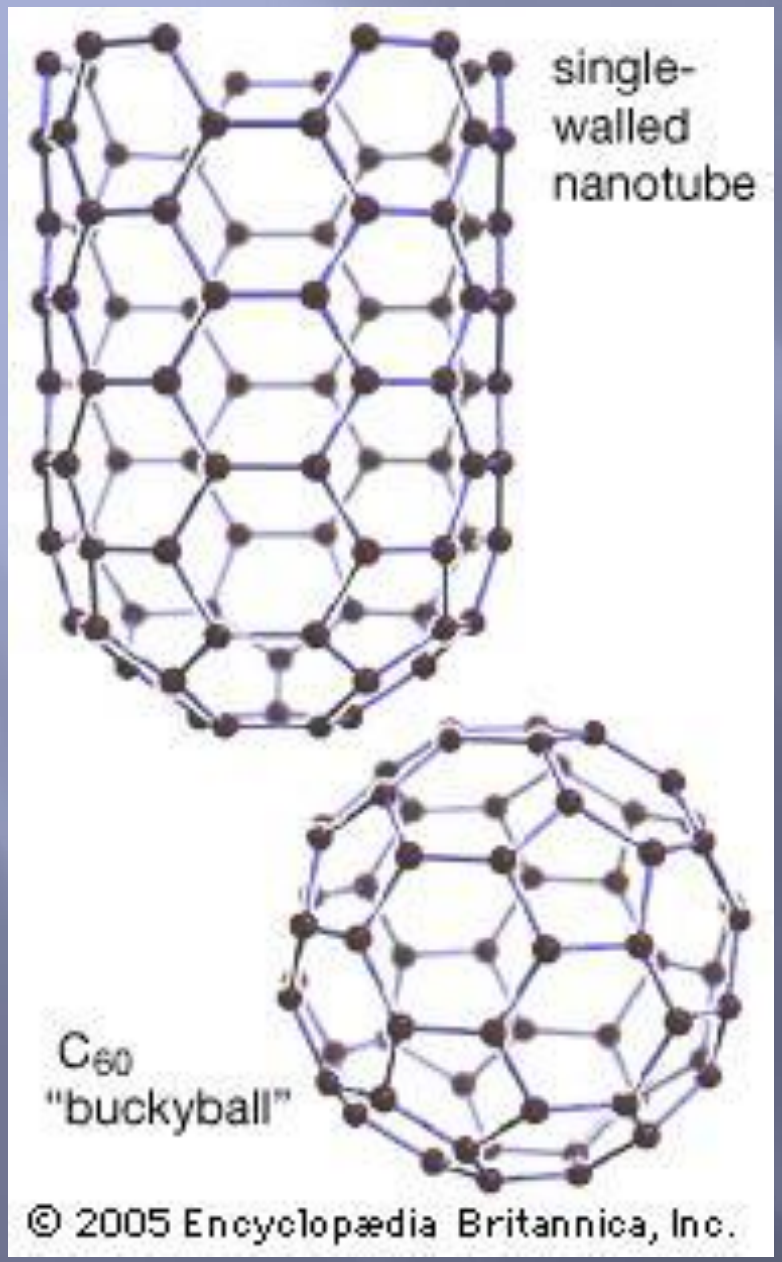
C2 (Swan) bands are generated in plasmas, in carbon arcs, in flames, and in many processes in the cosmos.

P. Su, et al, J. Chem Theo. Comput. 2011, 7, 121-130.
E.D. Jemmis, et al, Chem Comm 2006, (2164-2166).

In C2, the bond length is close to that of a triple bond, making the molecule a highly reactive diradical. There is also some evidence suggesting that C2 has an unusual quadrupole bond.

S. Shalik, et al, Nat. Chem 2012, 4, 195-200.

Carbon as Fullerene



In 1985 Kroto and Smalley developed a mass spectrometric technique for studying refractory clusters generated in a plasma by focusing a pulsed laser on graphite.

Their goal was to simulate conditions in the atmospheres of Red Giant Stars under which carbon will undergo nucleation.

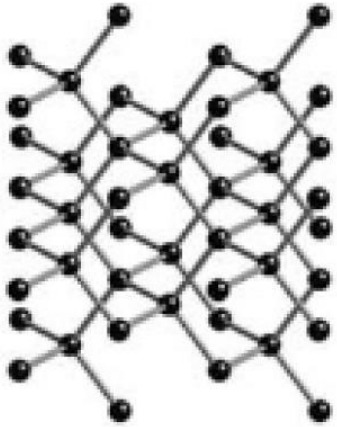
The clusters that formed, cyanopolyynes, HC_7N and HC_9N had been detected in space.

Polyynes have the formula, H_2C_x and consist of chains of carbon atoms with alternating single and triple bonds. H–C≡C-C≡C-H

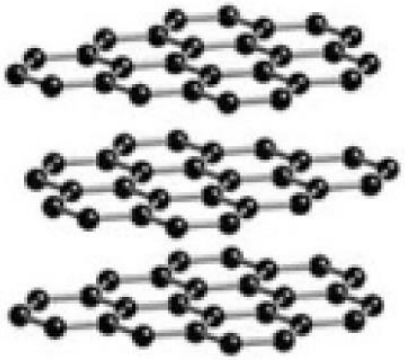
Kroto, Smalley, and Curl received the Nobel Prize for the discovery of the Fullerenes that resulted from this study.

- Kroto et al, ApJ, 1978, 219, L133.
- Avery, et al, ApJ, 1976, 205, L173.
- Kroto et al, Nature, 1985, 318,162.
- Hirsch, Fullerenes Chemistry and Reactions, 2005, Wiley- VCH.

Allotropes (polymorphs) of Carbon

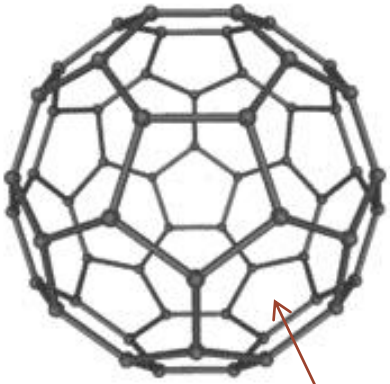


Diamond
sp3 - Tetrahedral



Graphite
sp2 - Planar

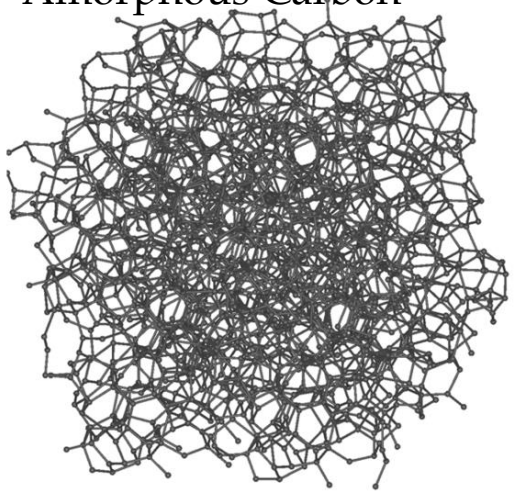
Images: Australian Academy of Science, Nov. 1999, 22 Mar. 2007.



Carbon-60 Cage Molecule
Buckminster Fullerene
Truncated Icasohedron Structure
20 Hexagons 12 Pentagons

Wikipedia - Buckyball

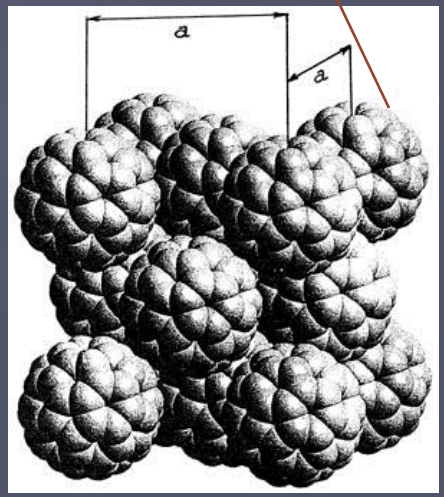
Amorphous Carbon



Commons.wikimedia.org/w/index.php?title=File.Amorphous_Carbon.png

-C60 Fullerene forms a FCC cubic molecular crystal called Fullerite .

-The amorphous form of carbon exhibits overlapping sp, sp2, and sp3 electron configurations. Ex., coal, bitumen, coke.



Fullerite FCC Crystal

Molecular Carbon in Grains

Pre-solar Grains are inorganic compounds formed from condensation nuclei in the gas cloud containing elements created in stellar processes. Carbon plays a major role.

Carbides, especially SiC, nitrides, silicates, nano diamonds and graphite are major constituents of the grains [Hynes09].

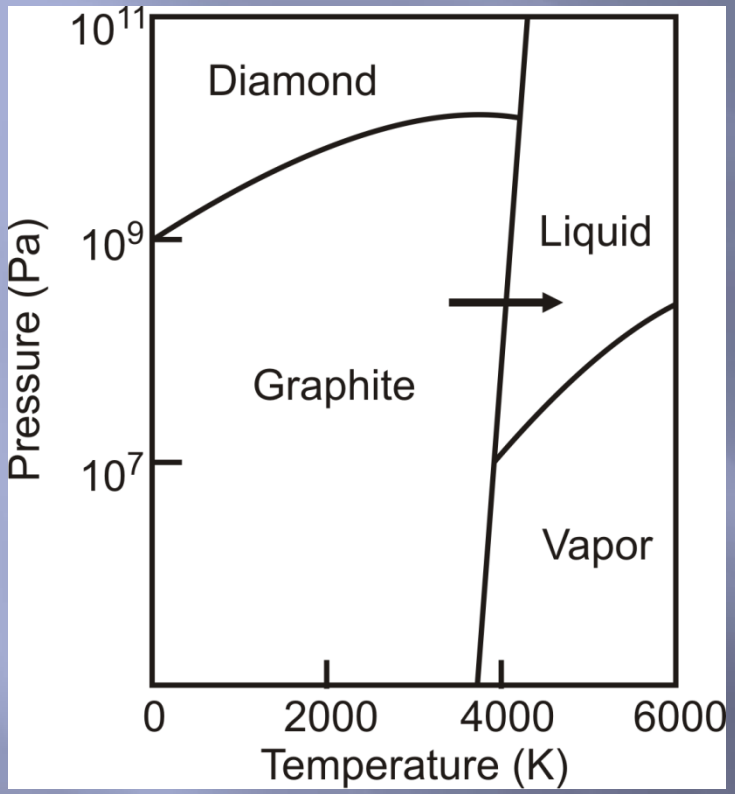
Core-mantle grains are made of crystalline material coated with dirty water ice. This coating is a protective molecular layer most likely derived from high molecular weight, organic refractory material [Mayo Greenberg96] such as PAH or Fullerenes.

Some cosmic Grains sequestered much of the carbon in the universe, perhaps 20% [Boersma]. These grains appear to be coated with (PAH) Poly Aromatic Hydrocarbons [Krishnaswamy10].

Grains can be aggregates of amorphous carbon or they can exist in crystalline form

Very bright PAH emission comes from nebula where protostars and exoplanets are forming . Researchers have found that PAH coated grains are responsible for the molecular peaks in UV spectra and are the primary cause of interstellar extinction which attenuates or obliterates the spectroscopic signal due to absorption and scattering processes. [Hudgins 2005].

Grains: Refractory Material



Grains are made of Refractory materials with:

- High thermal stability
- High melting or sublimation points
- Strong atomic bonding (3D networks)
- High degree of hardness (Mohr Index)
- High thermal shock resistance
- Plasma resistance (used in tokamaks)

Electric Refractory Materials, Yukinobu Kumashiro, editor

Table 3.2. Density of Some Refractory Materials

HANDBOOK OF CARBON, GRAPHITE, DIAMOND AND FULLERENES
Properties, Processing and Applications – H.O. Pierson

	g/cm3	Temperature (K)
Graphite	2.26	4000 S (1atm); 4200 M (100Atm)
Molybdenum	10.22	
Rhenium	21.04	
Tantalum	16.6	
Tungsten	19.3	
Titanium diboride	4.50	
Hafnium carbide	12.20	4220 M
Tantalum carbide	13.9	4270 M
Boron nitride	2.25	
Aluminum oxide	3.97	
Zirconium oxide	5.89	

Carbon is considered to be the most refractory of all the elements. However, Hafnium Carbide (M=4220K), Tantalum Carbide (M=4270K) & TaHfC are the most refractory of all materials.

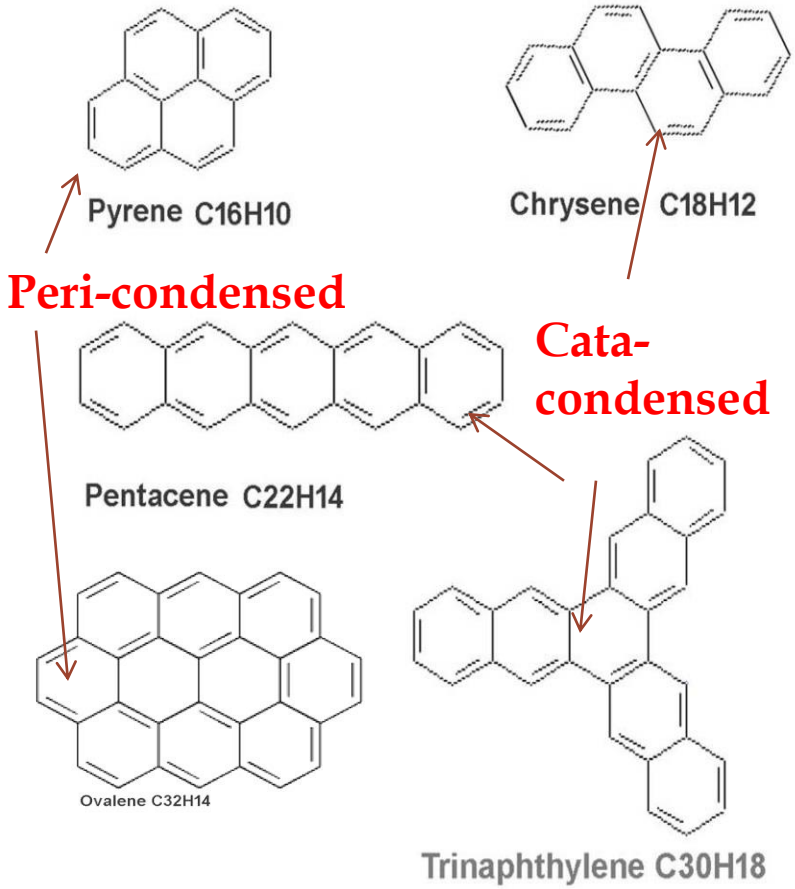
Handbook of Industrial Refractories Technology – S. Caniglia et al., 1992 Technology & Engineering

Carbon as Poly Aromatic Hydrocarbons – PAH

PAH is observed in dust clouds and it is believed to be the major cause of stellar extinction and the carrier of the UIR band. However…

- The contribution of individual PAH cannot be resolved from the spectral lines.
- Since PAH molecules exhibit similar characteristics, they will absorb and emit photons in the same general region of the spectrum.
- Either lab generated spectra or spectra obtained from ab initio calculations (DFT) are added together and then subtracted from the data.
- Extensive databases are necessary.

Poly Aromatic Hydrocarbons –PAH IR Emission Features



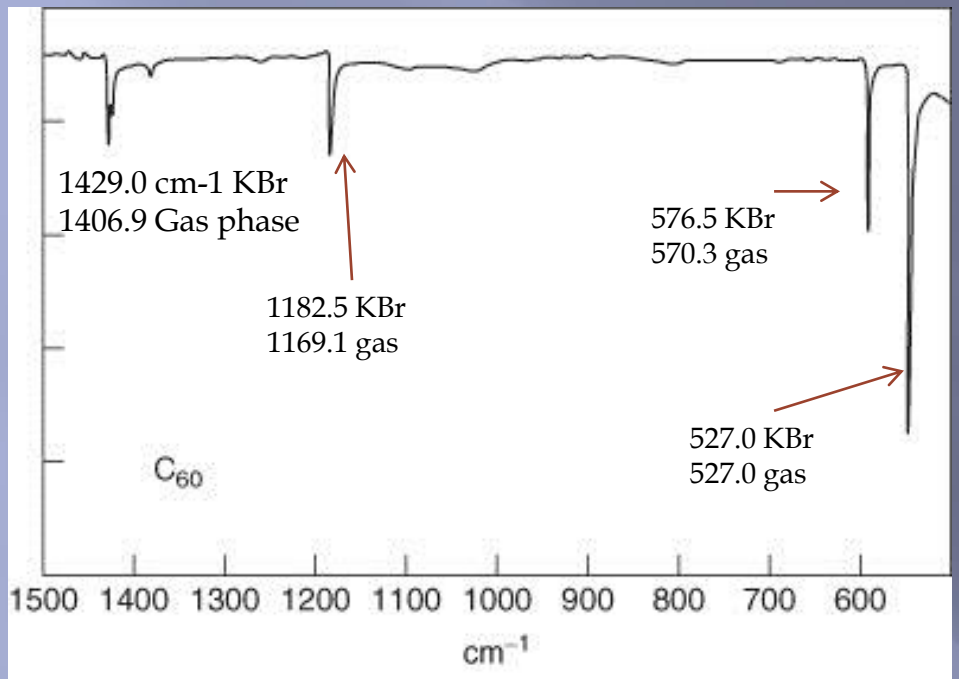
The peri and cata condensed PAH classes have similar abundance ratios for certain features.

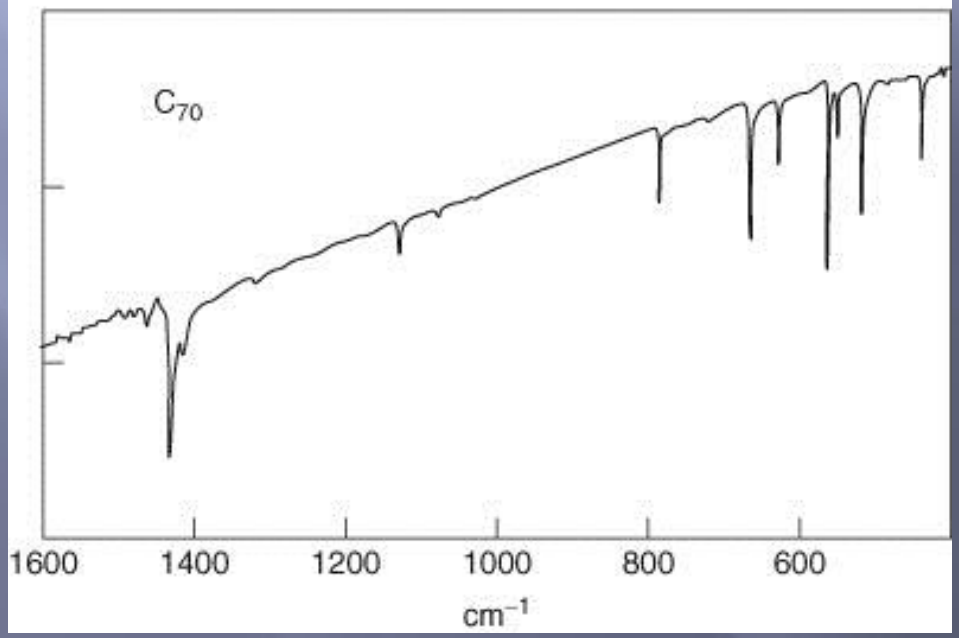
- Vibrational Modes

μ m	cm-1	
3.3	3030	C-H stretch
6.2	1613	C-C stretch
7.7	1299	C-C stretch + C-H in-plane bend
8.6	1163	C-H in-plane bend
11.2	893	Collective features + C-H out-of-plane bend

Also there are Far IR features beyond 20 μm that may be more specific to large, individual PAH.

Review Articles: Tielens 2005, 2008; Joblin, Tielens 2011; Peeters 2011, 2014; Yamamoto & Satoshi ISBN 978-4-431-54171-4 (2017); Rastogi 1996.





IR LAB spectrum for Fullerene C60

Out of the 174 vibrational modes for C60, 42 are non-degenerate and 4 are active in IR.

Lab IR spectra acquired on KBr plates. IR Spectrum from solid is dependant on temperature and pressure. Note the difference in wavenumber between solid (KBr) and gas phase Lab spectra.

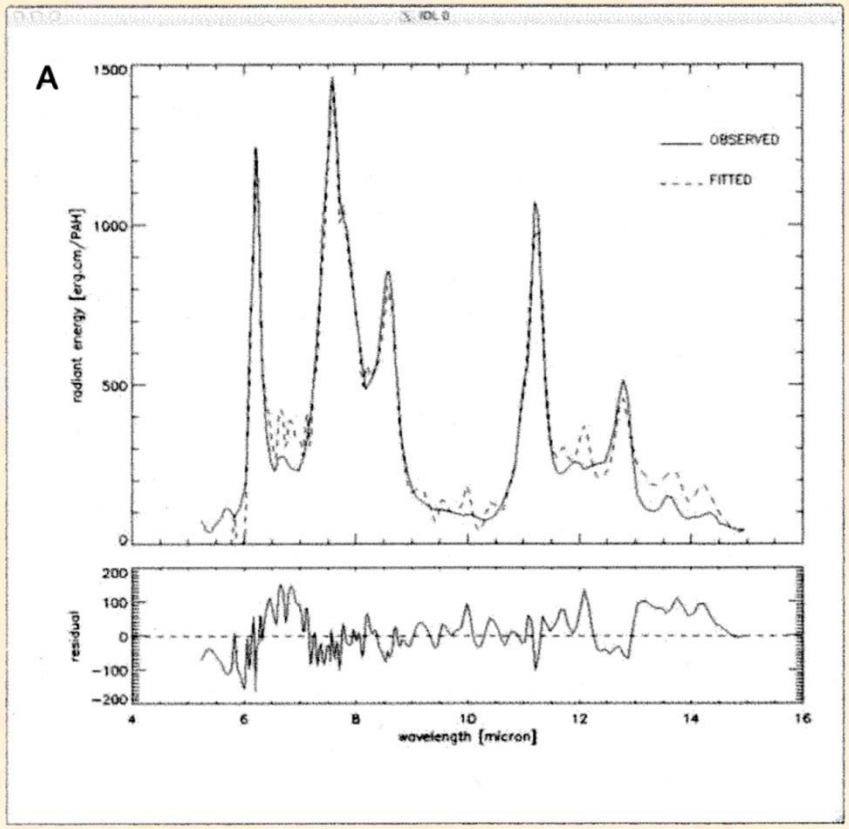
IR LAB Spectrum for Fullerene C70

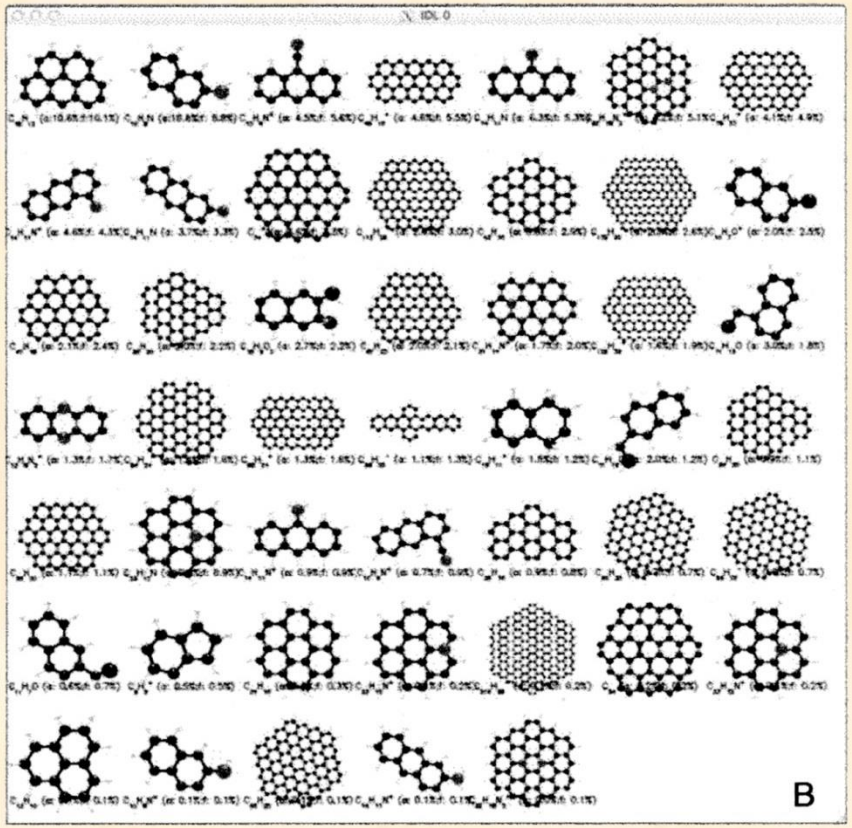
About 11 vibrational modes are active in IR for C70.

J.P. Hare, et al, J. Chem Soc Chem Commun, 1991, 0, 412-413.

S.J. Cyvin et al, Chem Phys Lett, 1988, 143, 377.

UIR Bands in the reflection nebula NGC 7023





A) Spectral fit of the UIR region in the reflection nebula NGC7023 using B) PAH from the NASA Ames PAH IR Spectroscopic Database. from [Boersma14]

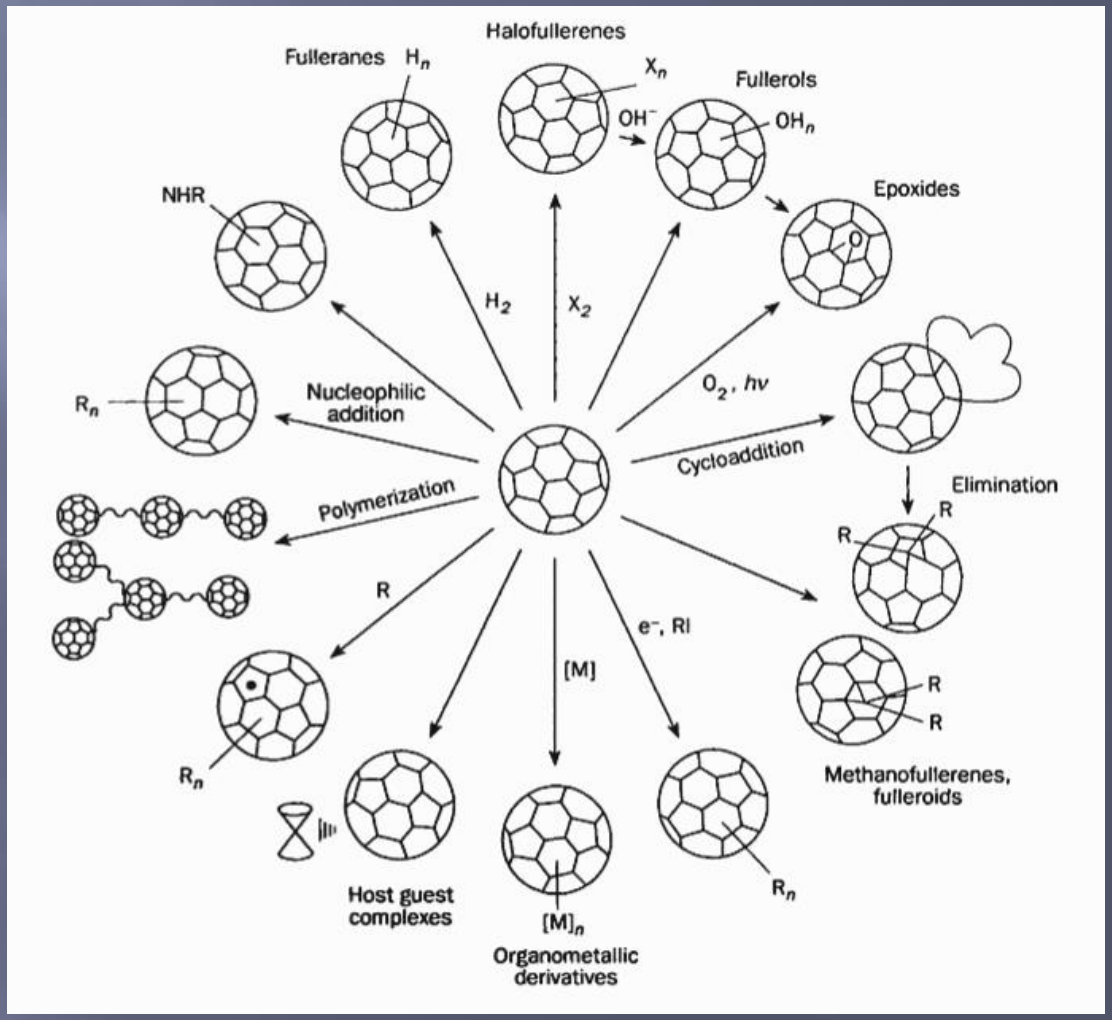
The residuals plot beneath the fitted and observed graphical overlay is an indication of the 'goodness of fit'. In order to achieve an even greater match, more PAH and Fullerene molecules should be added to the template.

Fullerene Reactions

Possible reactions C_{60} and C_{70} (to a lesser extent) may undergo

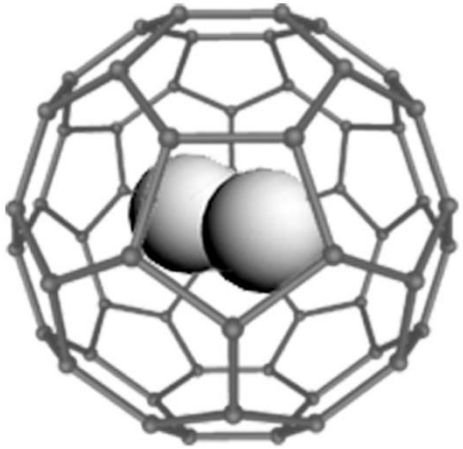
- Additions
- Polymerization
- Substitutions
- Host/Guest molecules
- Nested molecules

The Fullerenes act as a substrate to align reactions of adduct molecules that attach to the surface.



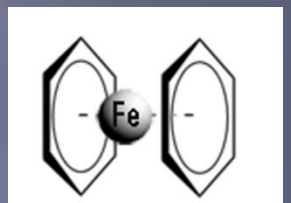
Taylor, Roger, and David R. Walton. "The Chemistry of Fullerenes." Nature 363 (1993): 685-693. 23 Mar. 2007

As a class, the fullerenes can form metal inclusion complexes, referred to as encapsulated or endohedral metal fullerenes [Akasaka96] and their identification in the cosmos, especially in star-obscuring molecular clouds, may become important for spectroscopic observations of heavy isotopes.

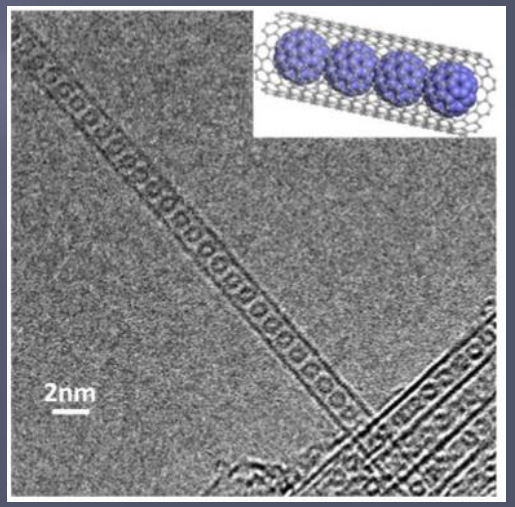


M@Carbon-60
Endohedral Fullerene
M= atom, ion, or molecule

Inclusion complexes include nested Fullerenes such as concentric spheres known as Carbon onions and nanotubes filled with C60 Fullerene, known as Nano peapods.



Ferrocene
Sandwich



Nano peapods

Other Types of Fullerenes that may Influence the UIR Band Identification

-Dendritic C60 (at right) contain aliphatic and aromatic groups and hetero-atoms. This should be accounted for in the comparison template.

-Polymeric C60 (ex. compressed nano-peapods) or host compounds like clathrates.

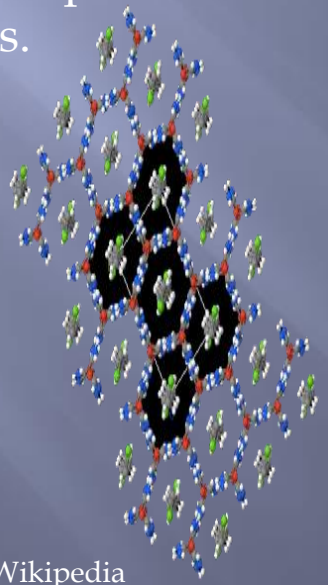
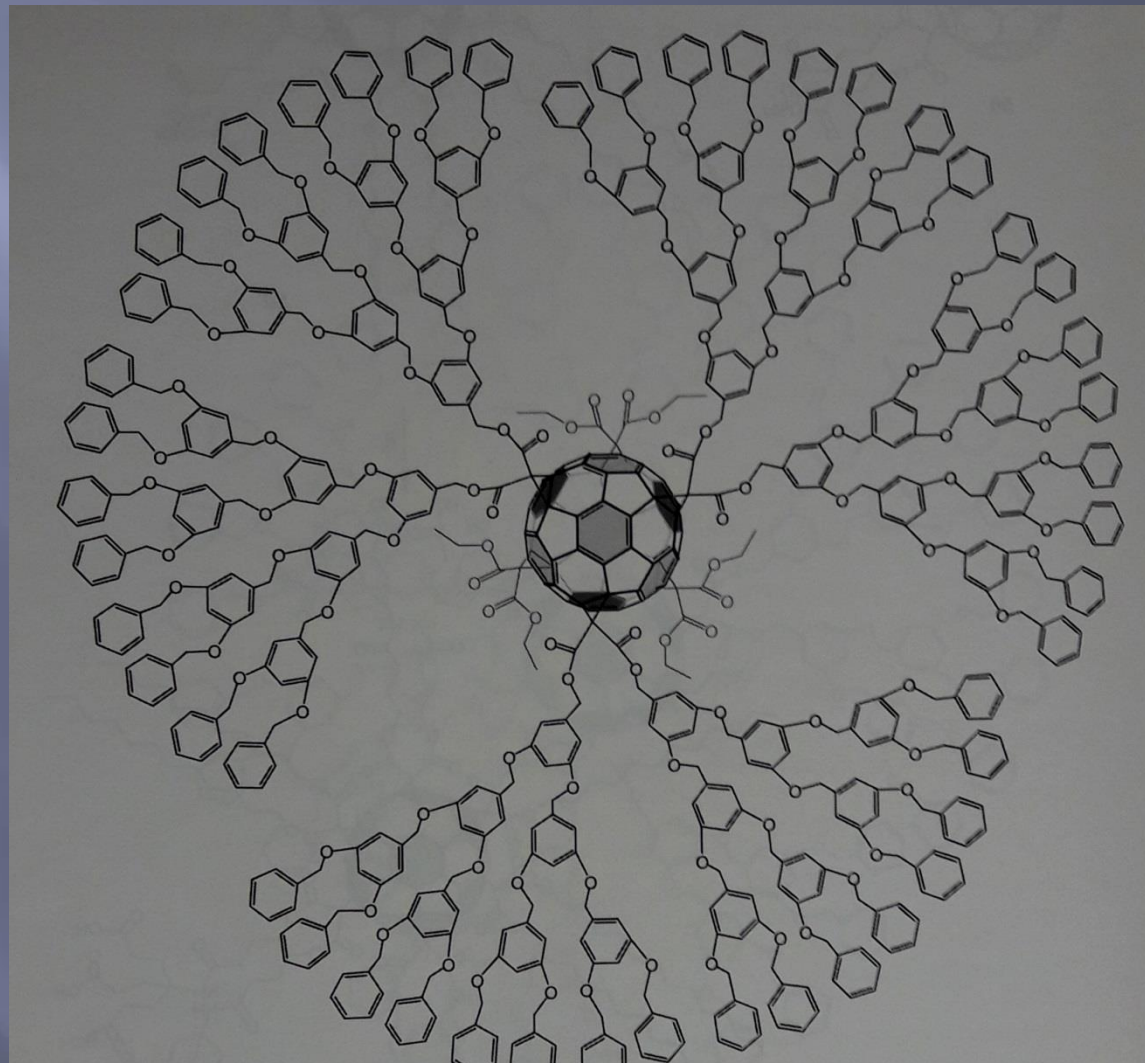


Image: Wikipedia



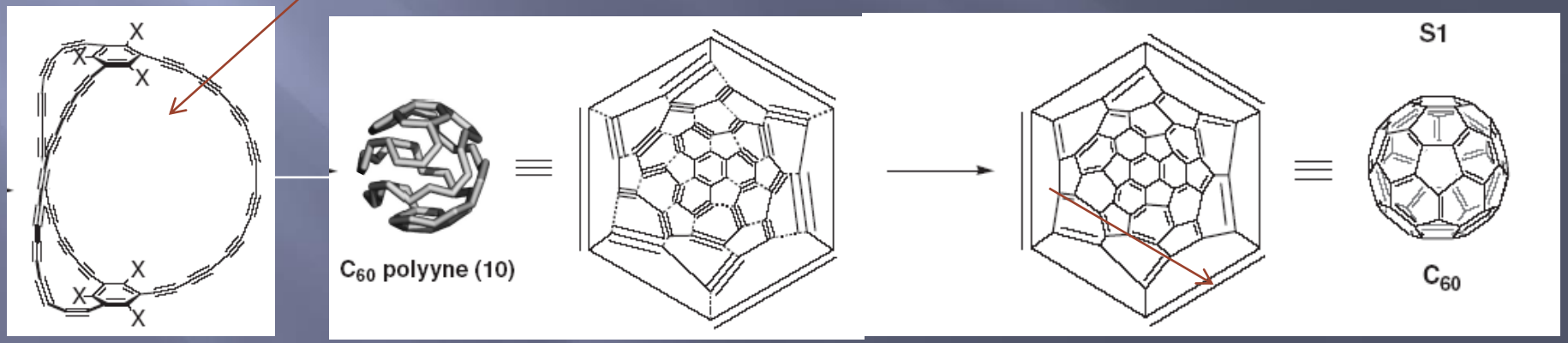
Hirsch and Brettreich Fullerenes, Wiley-VCH 2004.

Proposed Mechanism: C60 Formation

Dynamic self-assembly mechanism of fullerene :

- is irreversible under non equilibrium conditions of hot carbon and vapor.
- Is a consequence of the chemistry of polyyne chains, stabilization from pi-conjugation, and the dynamics of giant fullerene cages.
- Polyyne chains lead to exothermic, curved, pi-stabilized, sp2 networks.

- Cyclization: Polyyne chain folds onto itself. Compression causes new carbon bonds to form. (Dotted lines) Zipper mechanism.

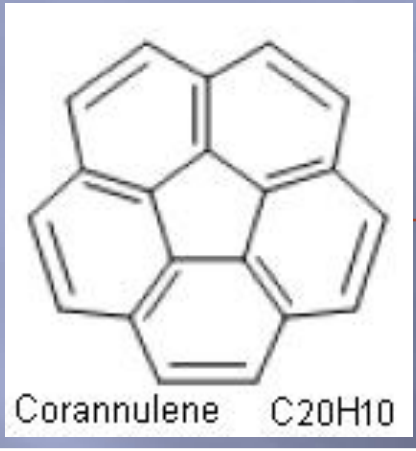


Umeda, Rui, et al, *Chemistry Letters* 34 (2005). J-Stage. University of Rochester. 22 Mar. 2007.

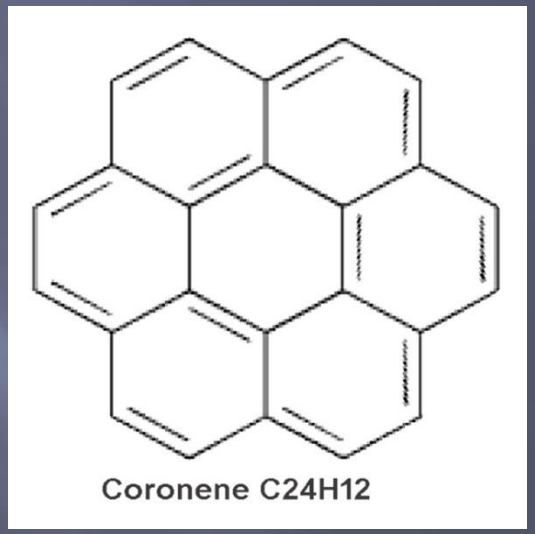
Proposed Mechanism: C60 Formation

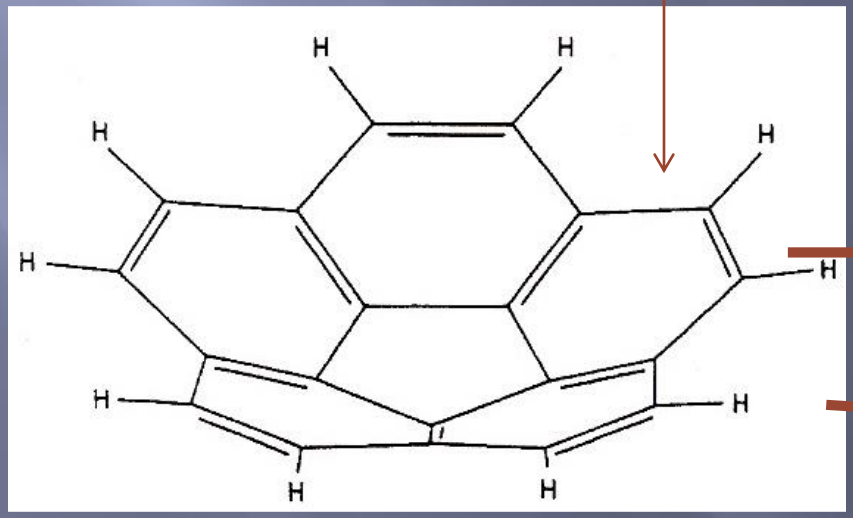
The trigonal planar (flat) structure of Coronene can turn into a curved, bowl shape with the substitution of a pentagon which adds steric strain to the molecule.

Corannulene -nonplanar assembly of C
1 central pentagon + 5 hexagonal rings



Coronene – planar assembly of C
1 central hexagon + 6 hexagonal rings



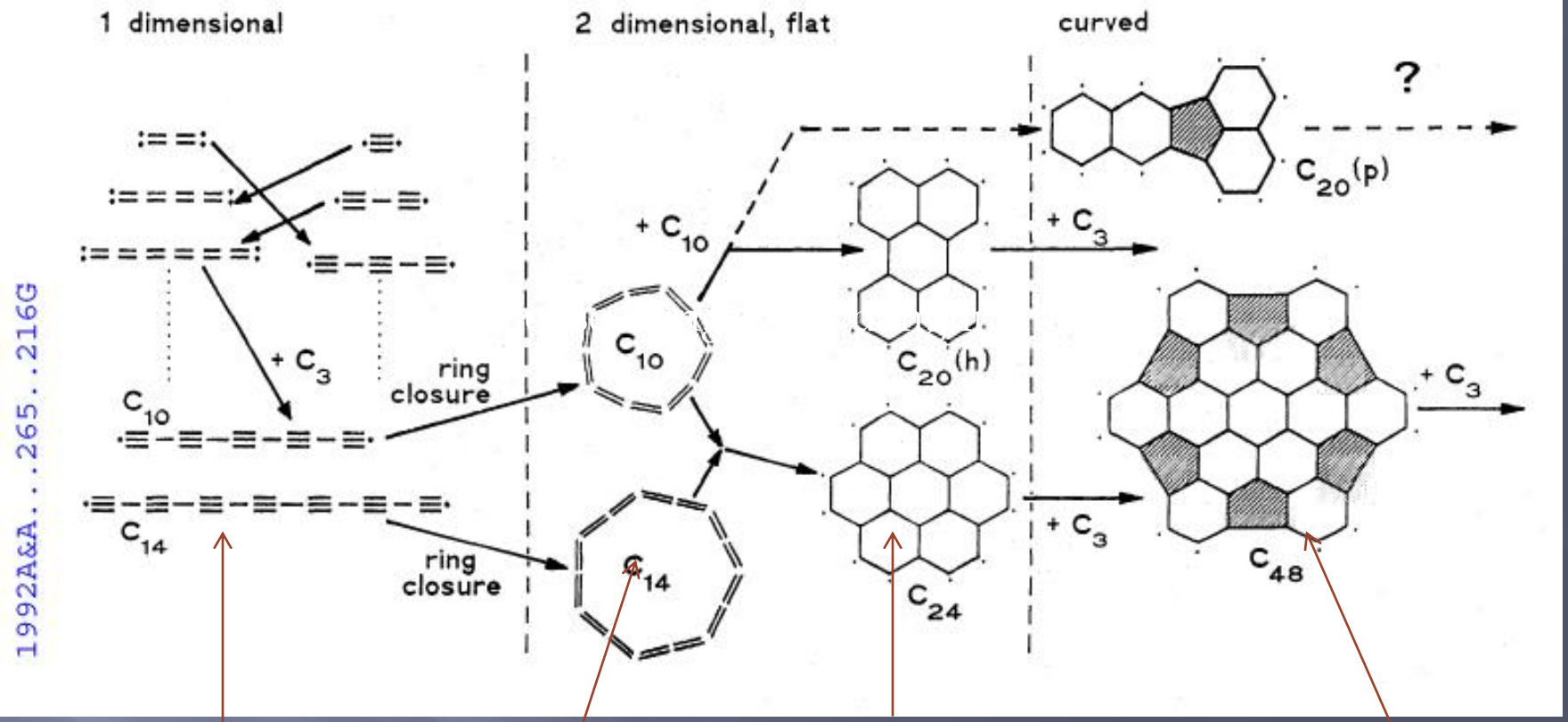


This can assemble into:
- **C60 Buckyball**
  Or
- **Fullerene Nanotube**

Haymet, A. D. J. JACS, 108 (1986): 319-321.

Proposed Mechanism: C60

This shows the effect of the self-assembly mechanism in conjunction with the rounding of the molecule due to the position of the pentagonal structures.



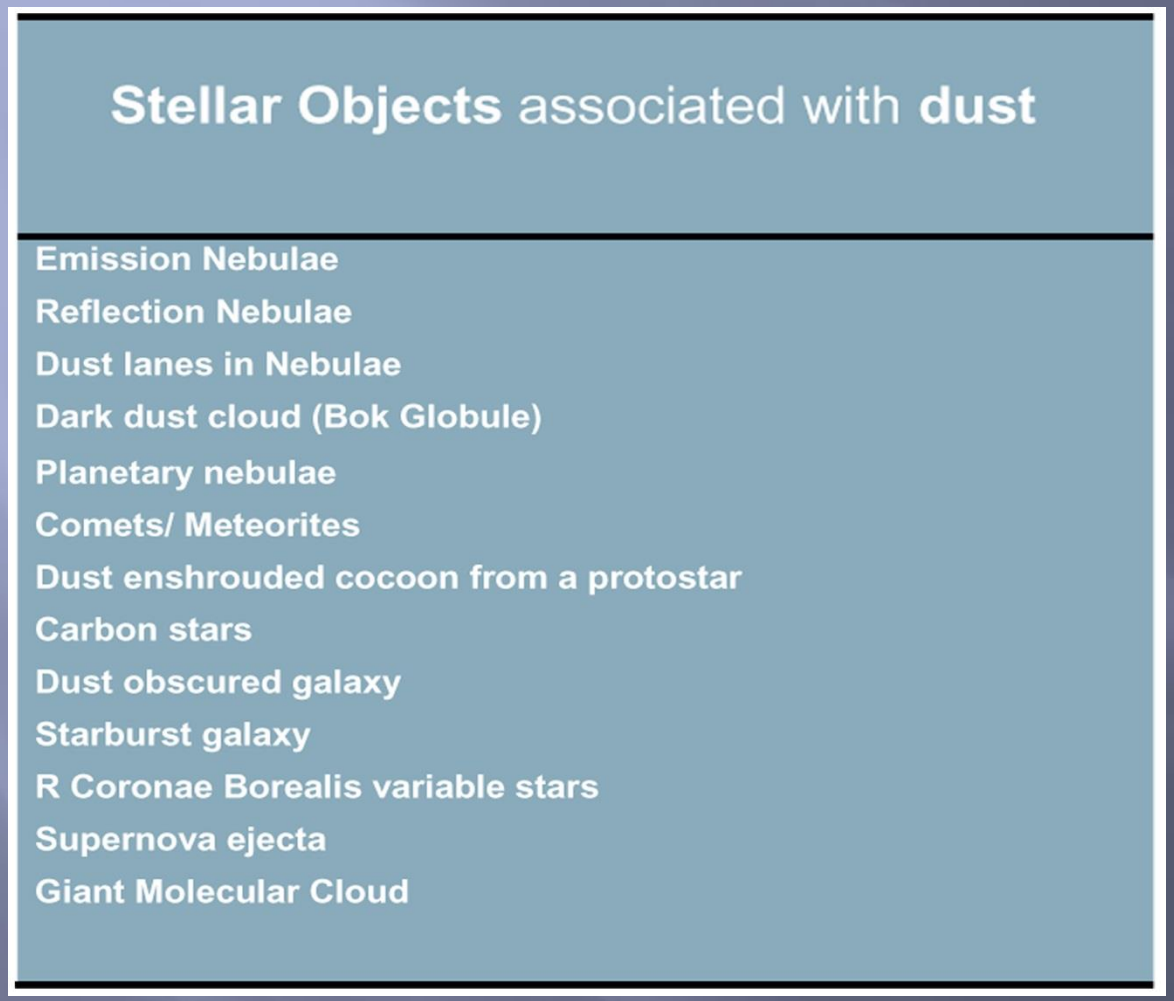
condensed rings with dangling bonds

Polyyne chains

Polyyne rings

C3 addition

Proposed Mechanism: C60 Formation



Dust is composed of gases and ices and the grains upon which they condensed.

Many refractory grains are composed of nano-diamonds.

The following study showed that nano-diamonds can be reversibly transformed into nested Fullerenes (aka carbon onions) under irradiation with UV light.

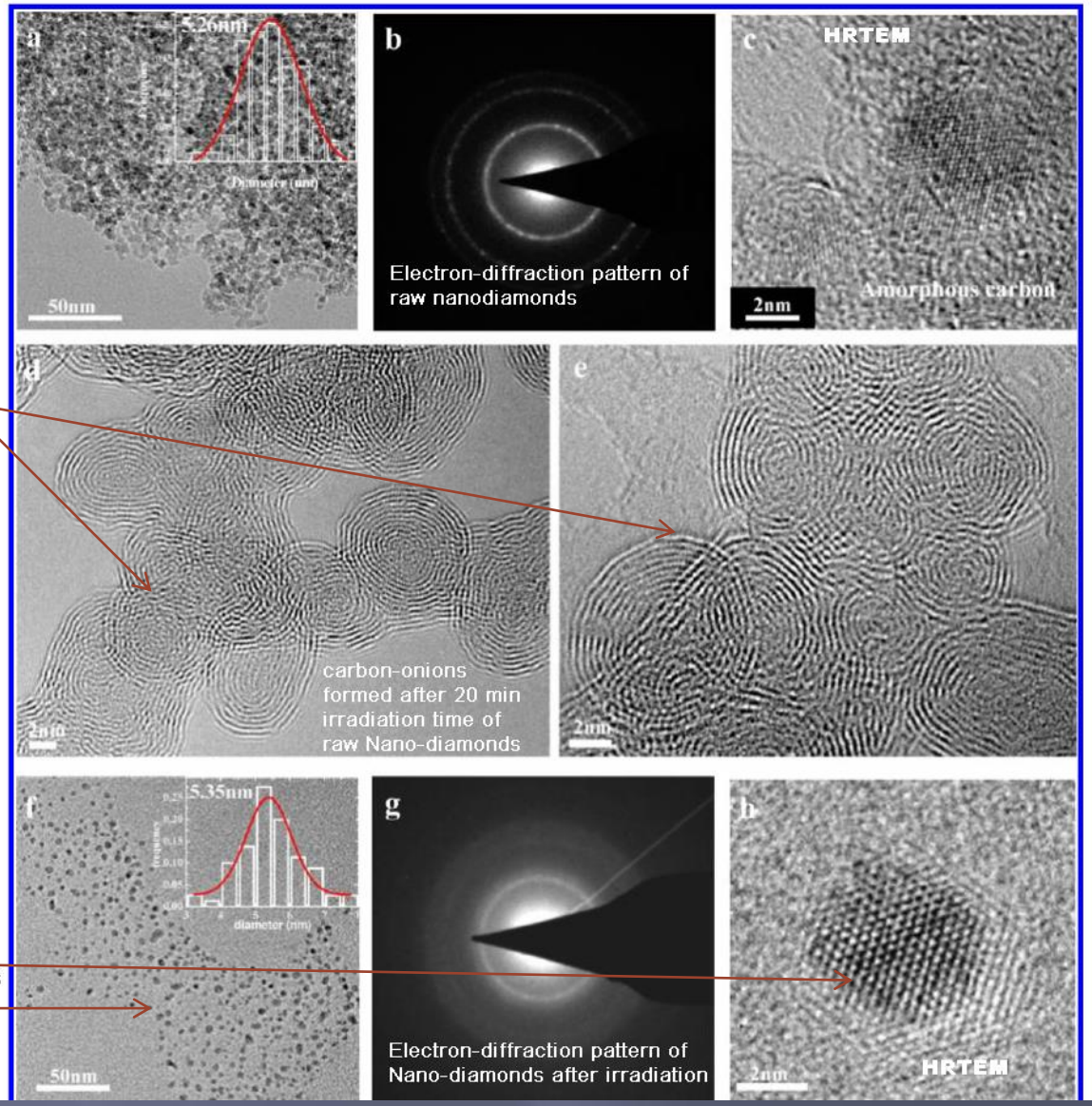
This may have interesting implications for reactions with molecular carbon.

Proposed Mechanism: C60 Formation

Reversible Nanodiamond–Carbon Onion Phase Transformations

Nano Letters dx.doi.org/10.1021/nl5014234 | Nano Lett. 2014, 14, 6455−6461 Letter

Nd:YAG laser device wavelength of 532 nm, pulse width of 10 ns, laser pulse power of 150 mJ



Carbon onions

Nano-diamonds regenerated after 40 min irradiadion

The phase transformation between Nanodiamond and Carbon Onions is reversible under UV irradiation.

J. Xiao, et al, 2014 Nanoletters

Fullerenes in the Cosmos

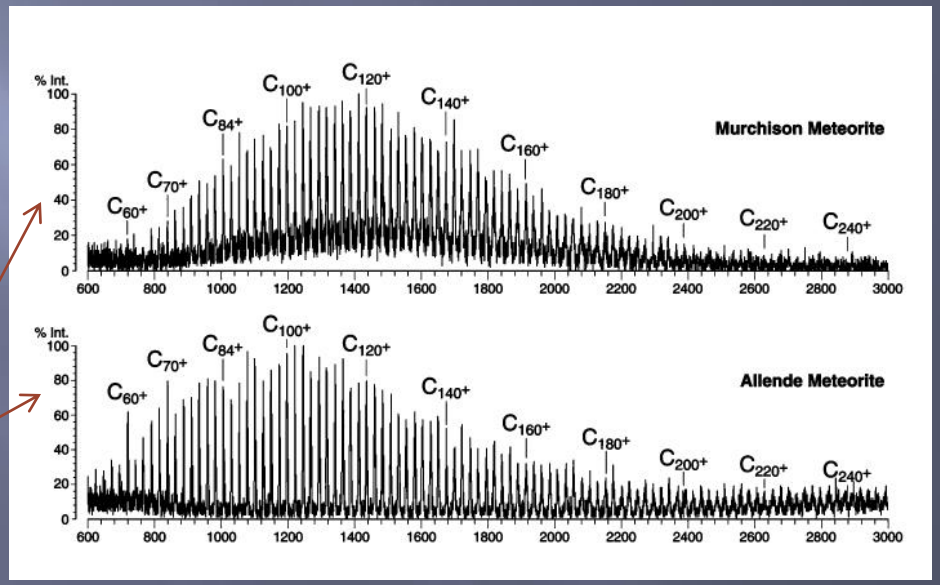
- 1st gaseous C60 detected in 2010 in the small Magellanic Cloud using Spitzer Space Telescope.

- 1st solid C60 identified by J. Cami et al 2012 in the Planetary Nebula Tc1.

Fullerenes in the Cosmos

Carbonaceous Chondrite Meteorites contain fullerenes

- Allende
- Murchison
- Tagish Lake

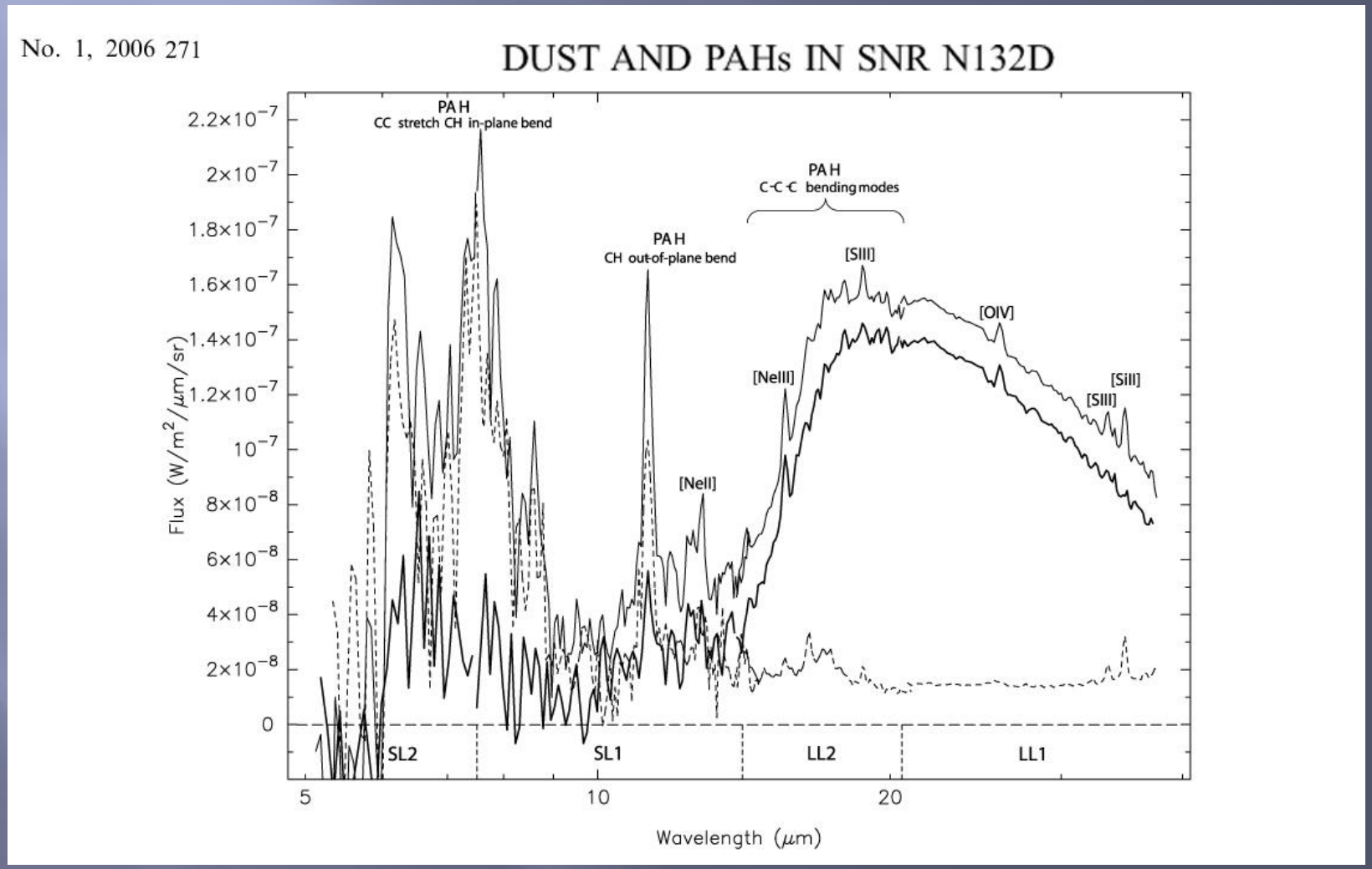


Mass spectral profile of fullerenes found in the meteorites.

Carbonaceous Chondrite Meteorites also contain endohedral fullerenes – trapped Nobel gases with non-terrestrial isotopic composition.

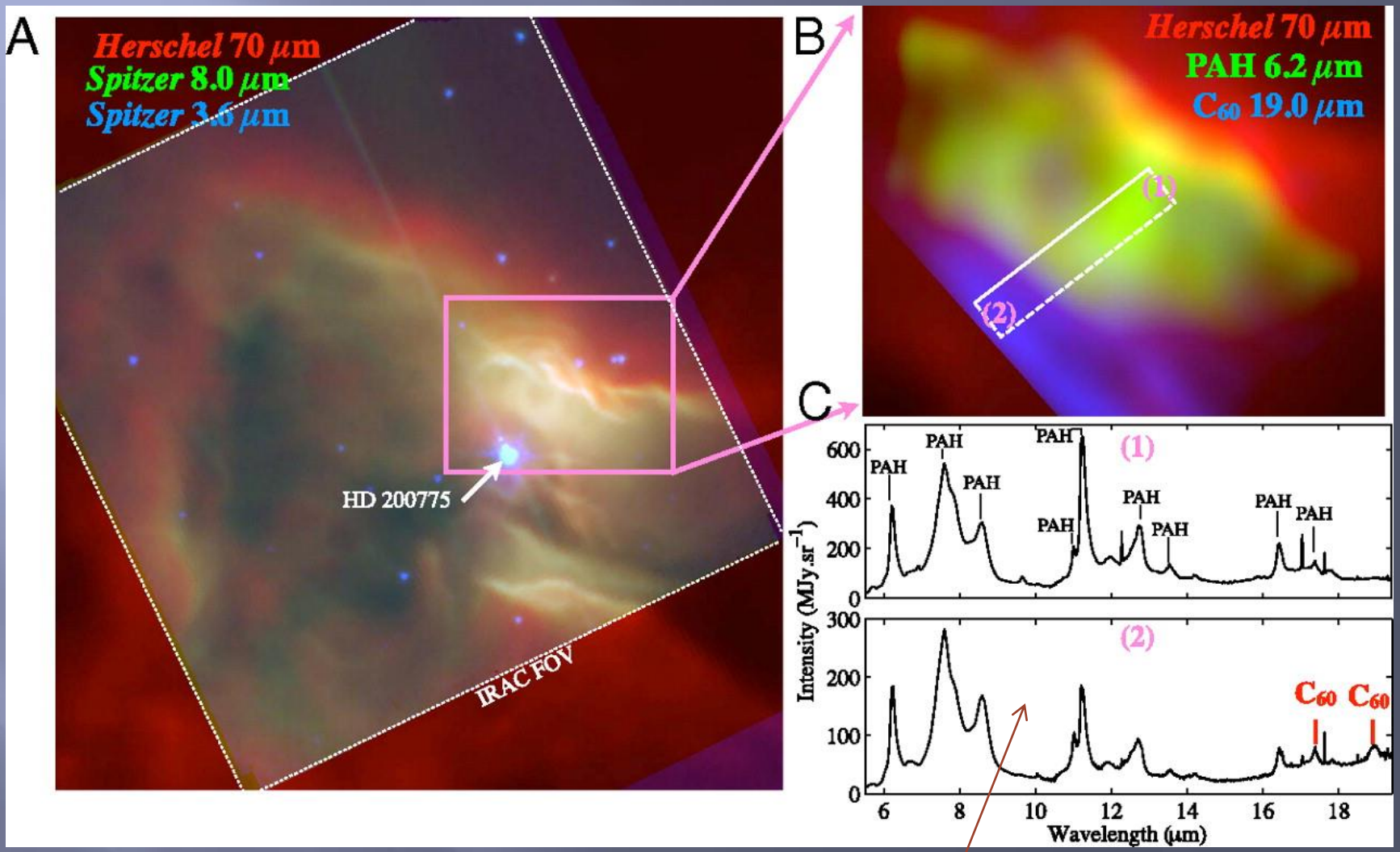
Shanos, G. T., Meteorite, Aug. 2010.

Oxygen-rich Large Magellanic Cloud (LMC) supernova remnant N132D (SNR 052569.6) using all instruments on board the Spitzer Space Telescope, IRS, IRAC, and MIPS (Infrared Spectrograph, Infrared Array Camera, and Multiband Imaging Photometer for Spitzer)



The Astrophysical Journal, 653:267Y279, 2006 December 10

Overview of the NGC 7023 nebula.



UIR Band

Olivier Berné, and A. G. G. M. Tielens PNAS 2012;109:401-406

In Summary

Tracking molecular carbon through the cosmos involves the careful assembly of a large database of potential PAH and Fullerene molecules that reflect the atmosphere within the region of interest (i.e., reducing, oxygenated, HI, HII, presence of UV emitters, etc.) The following may be useful:

Data bases of interest:

- WUSL (Washington University in St. Louis) Presolar Grain database [Hynes and Gynard, 209,LPSC XL, Abstract # 1198]
- NASA Ames PAH Spectroscopic database [www.astrochem.org/pahdb/
- NIST web for Ionization Potentials, spectra, etc.
- DFT- B3LYP/4-31G spectra from Theory