Jan Cami

The Role of Cosmic Fullerenes

Key Points

Fullerene family is present in space

In evolved stars, ISM, YSOs.
IR: Mostly neutral C_{60}, some C_{70}, but also fullerene derivatives.
C_{60}^{+} DIBs have been confirmed!

Formation: PAHs → C_{60} in Reflection Nebulae

Planetary Nebulae may require other route.
Possibly closed network growth in SNe.

Something happens to the fullerenes

Fullerene signature disappears in PNe → evolution into.. ?

Outline

Introduction

Astronomical detections of the IR vibrational modes of C_{60} (and C_{70})

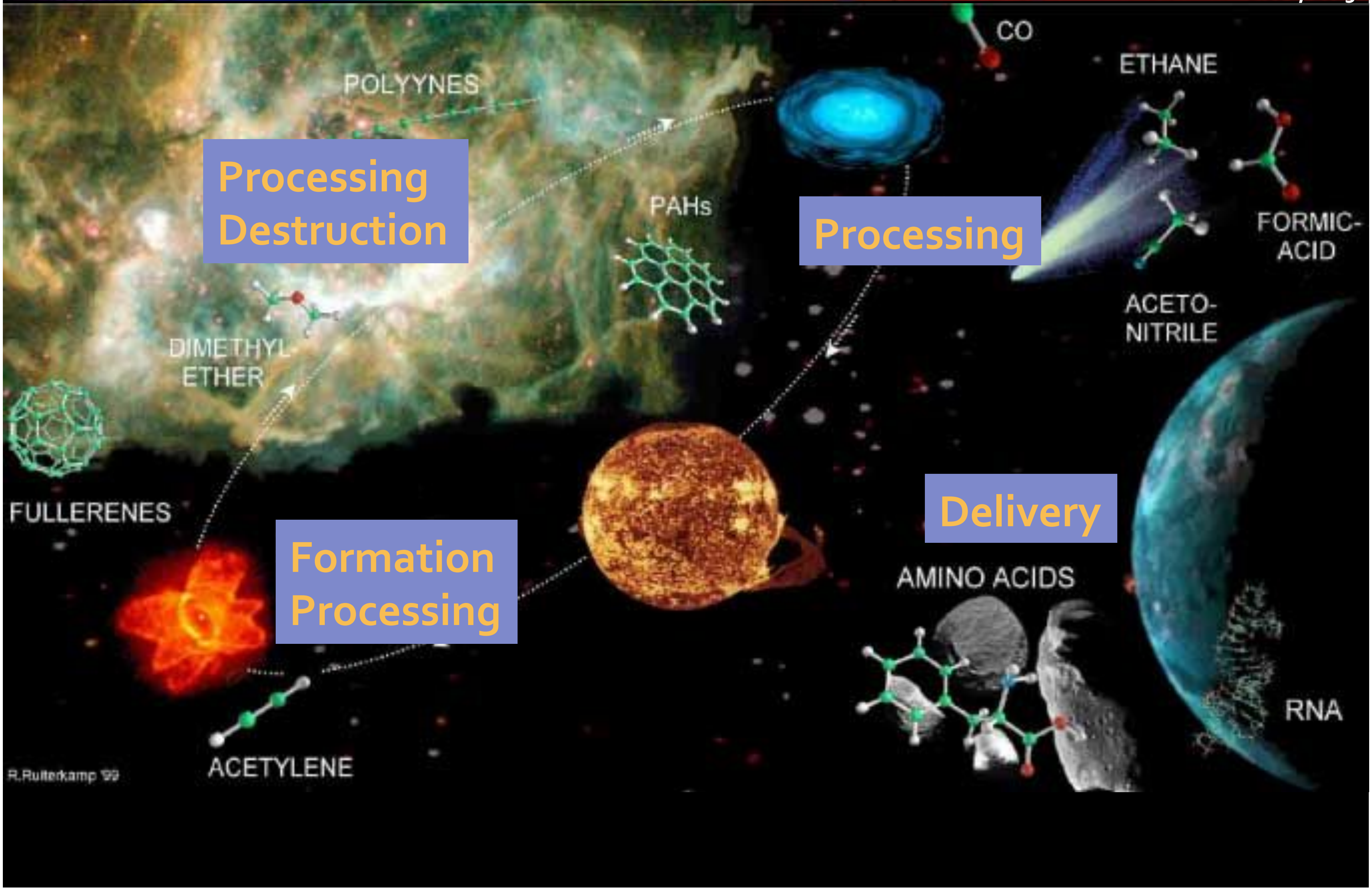
Formation of Interstellar Fullerenes

Peering at Problematic Planetary Nebulae

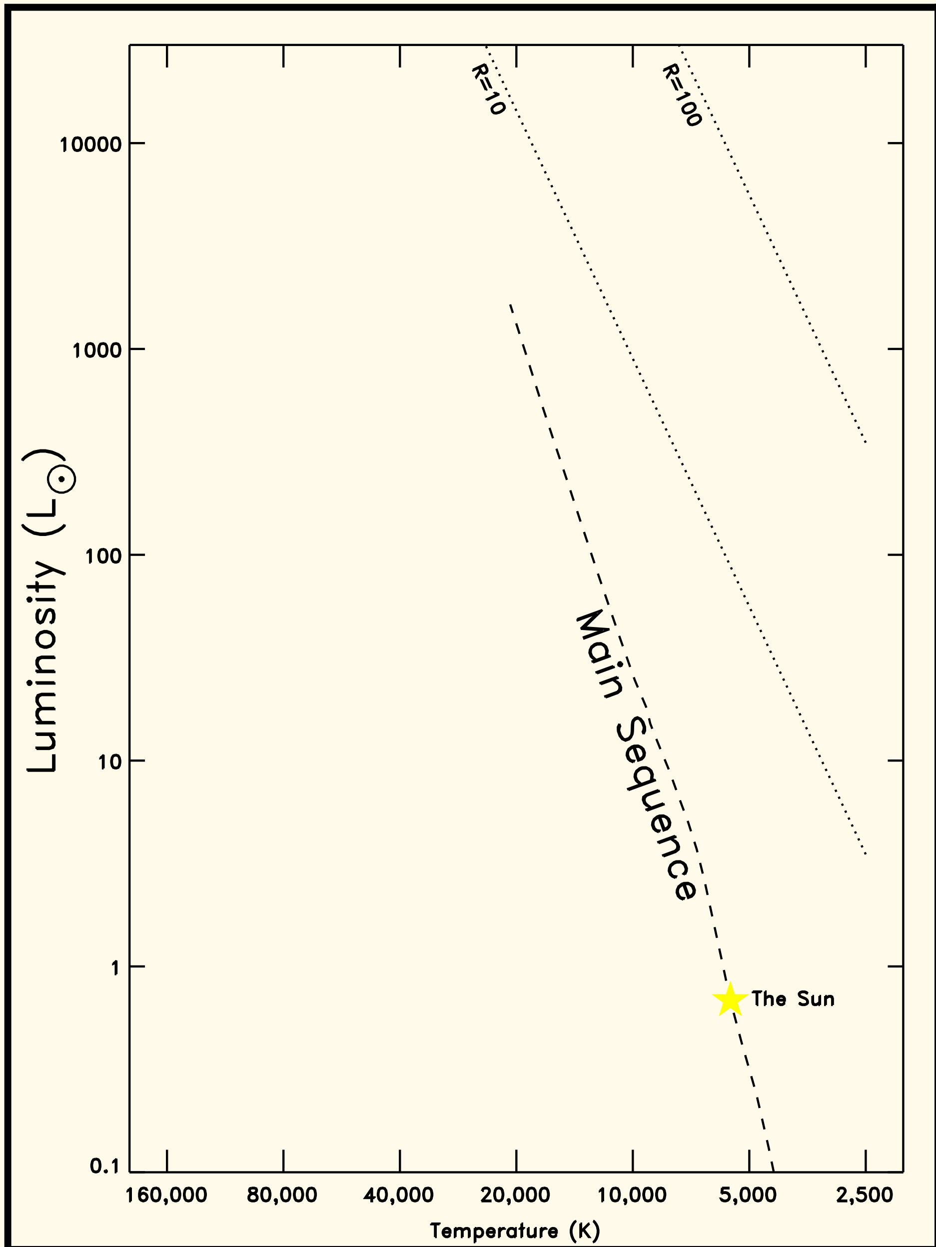
Evidence for fullerene derivatives

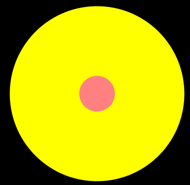
Wrap-up and outlook

Carbon (re)cycling in space



Main Sequence



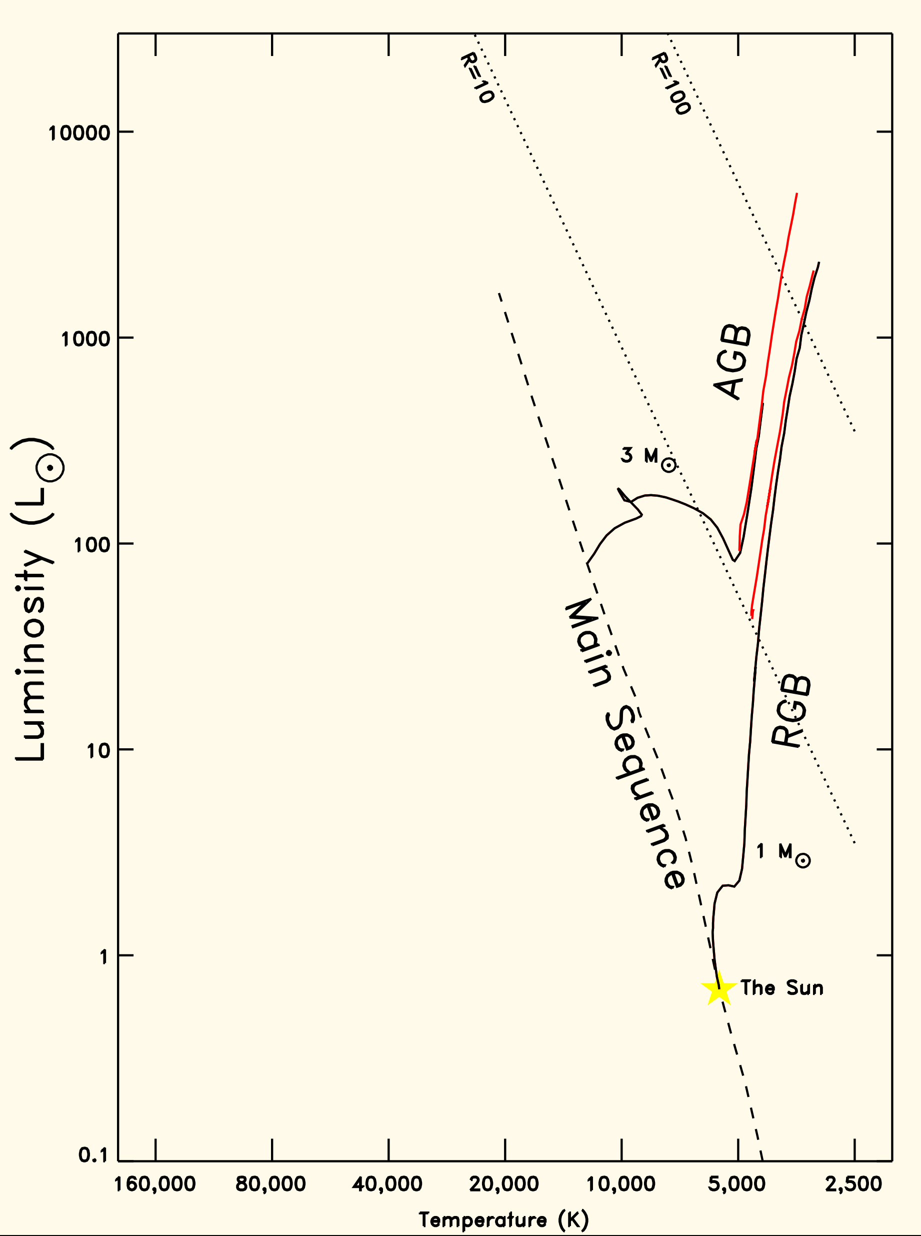


Core H burning

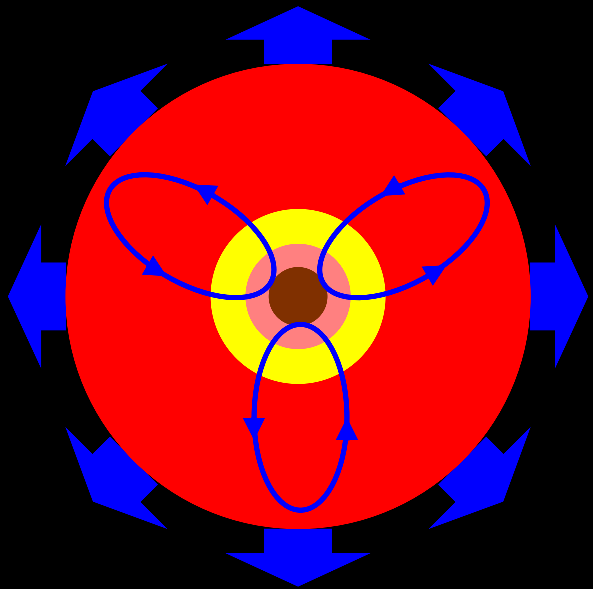
H –> He

Hydrogen Mantle

t ~ 10 billion yr



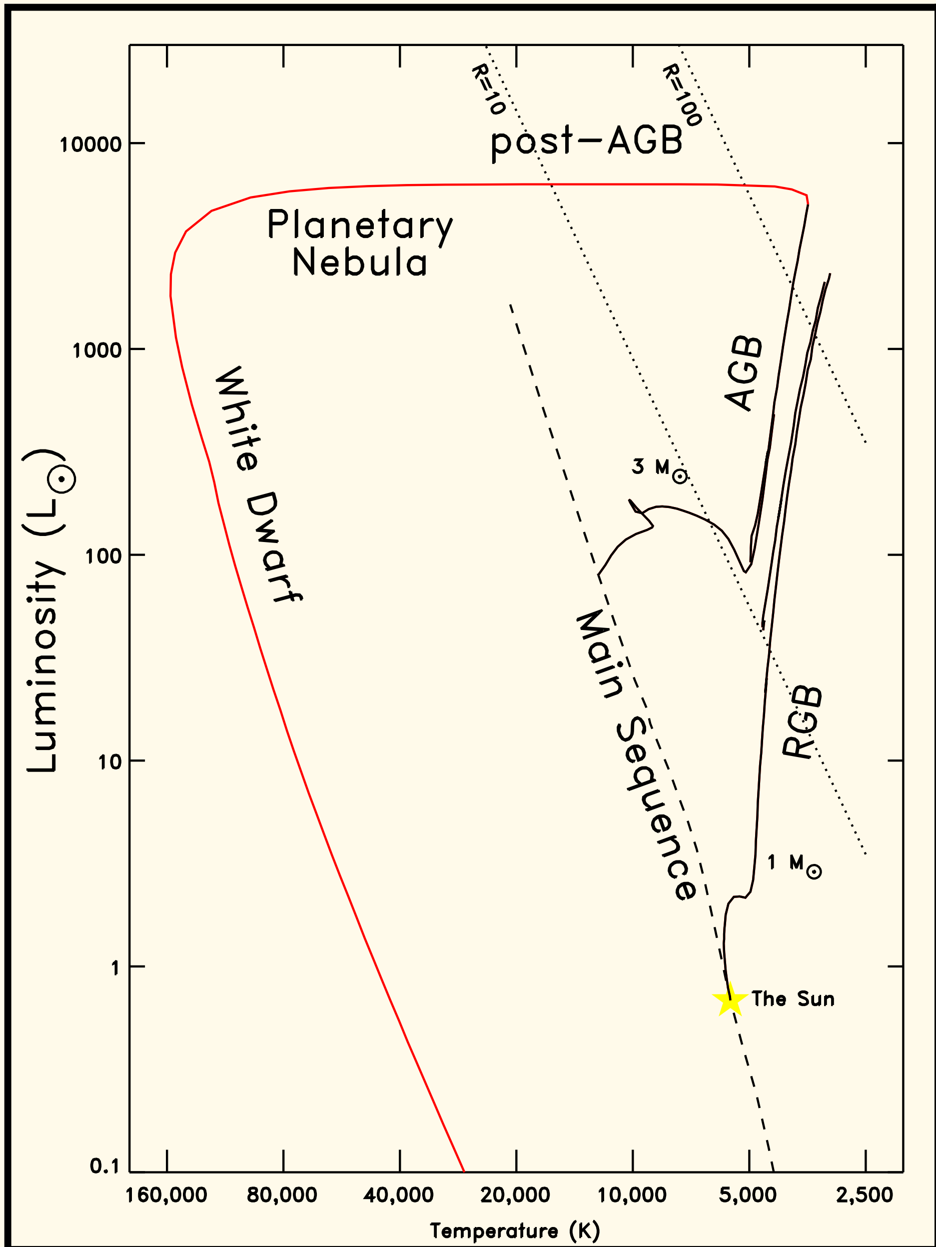
Asymptotic Giant Branch

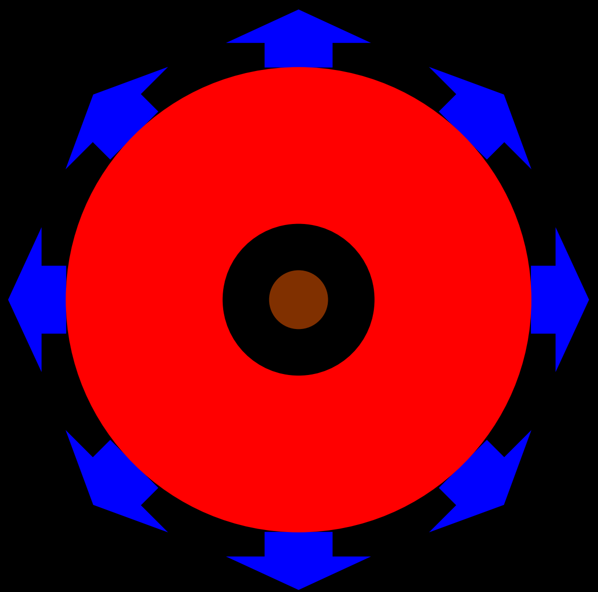


Degenerate CO core
He shell burning
H shell burning
Thermal Pulses / Dredge–up
Expanding envelope
Severe mass loss

t ~ 10 million yr

post–AGB – Planetary Nebula



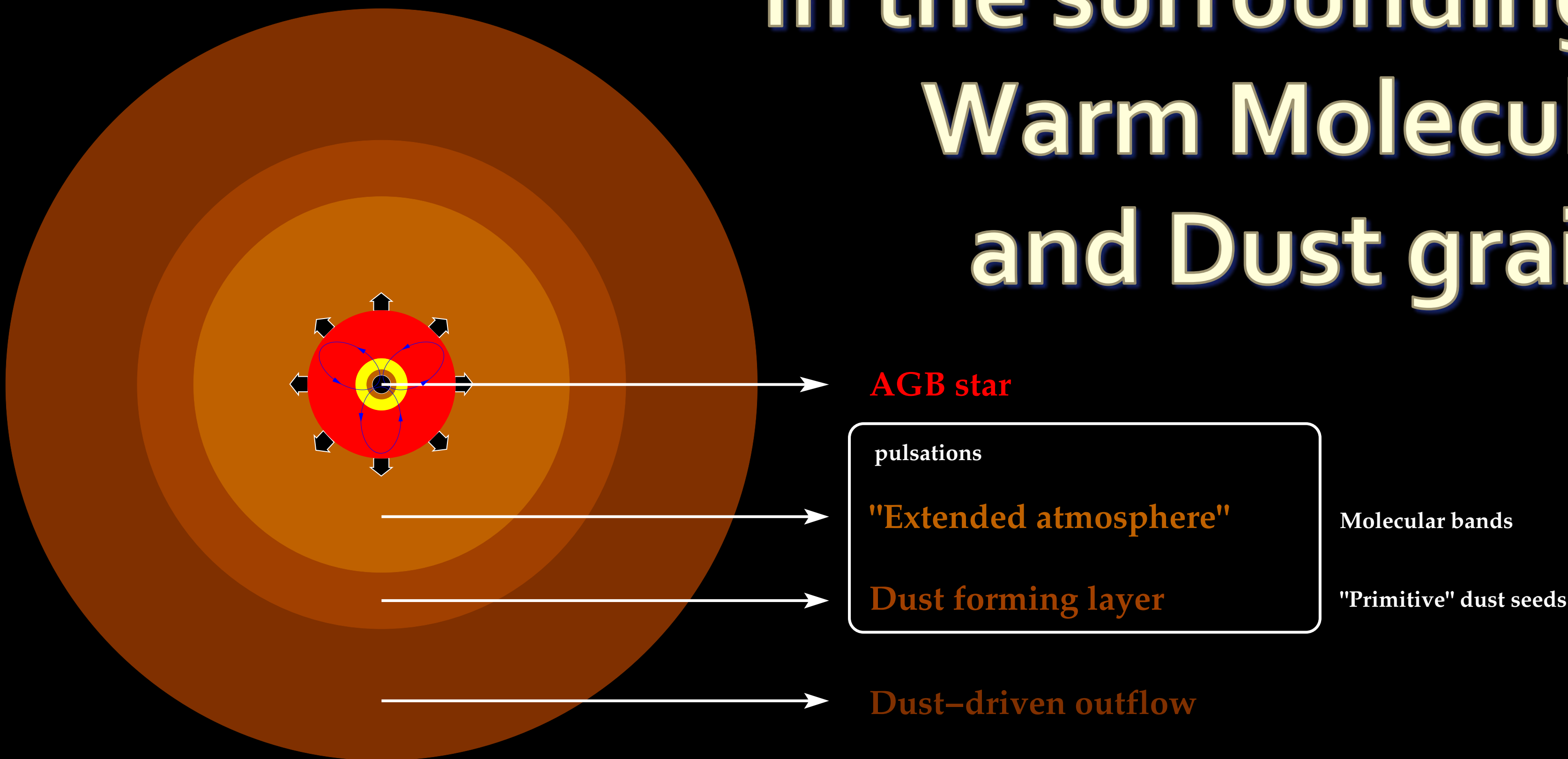


Degenerate CO core
= White Dwarf

Expanding envelope
might become PN

t ~ 10,000 yr

In the surroundings: Warm Molecules and Dust grains



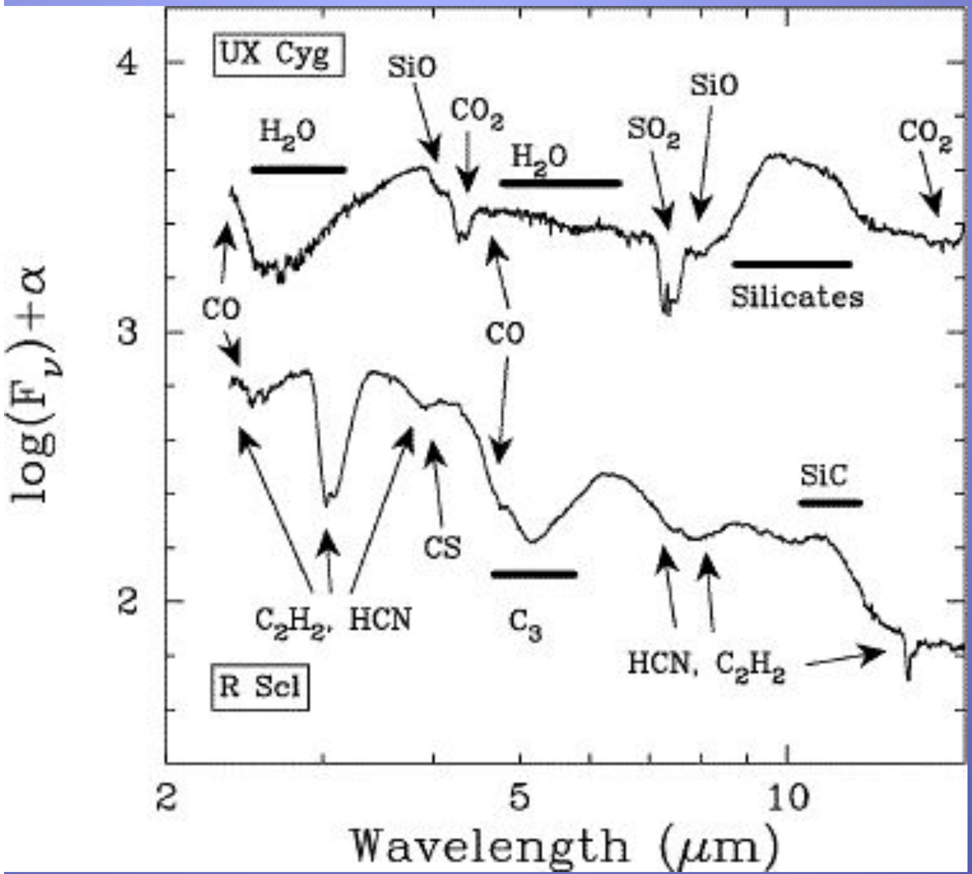
Molecular bands in photosphere and extended atmosphere

Structure of extended atmosphere

Connection with pulsations

Identification of possible "primitive" dust species

Sand or soot ?



- All stars O-rich initially
- Fusion + dredge-up
- C abundance ↑
- If [C/O] > 1 → Carbon star
- Also CS abundance C-rich
- Totally different chemistry in circumstellar matter

Yamamura et al. (1999)

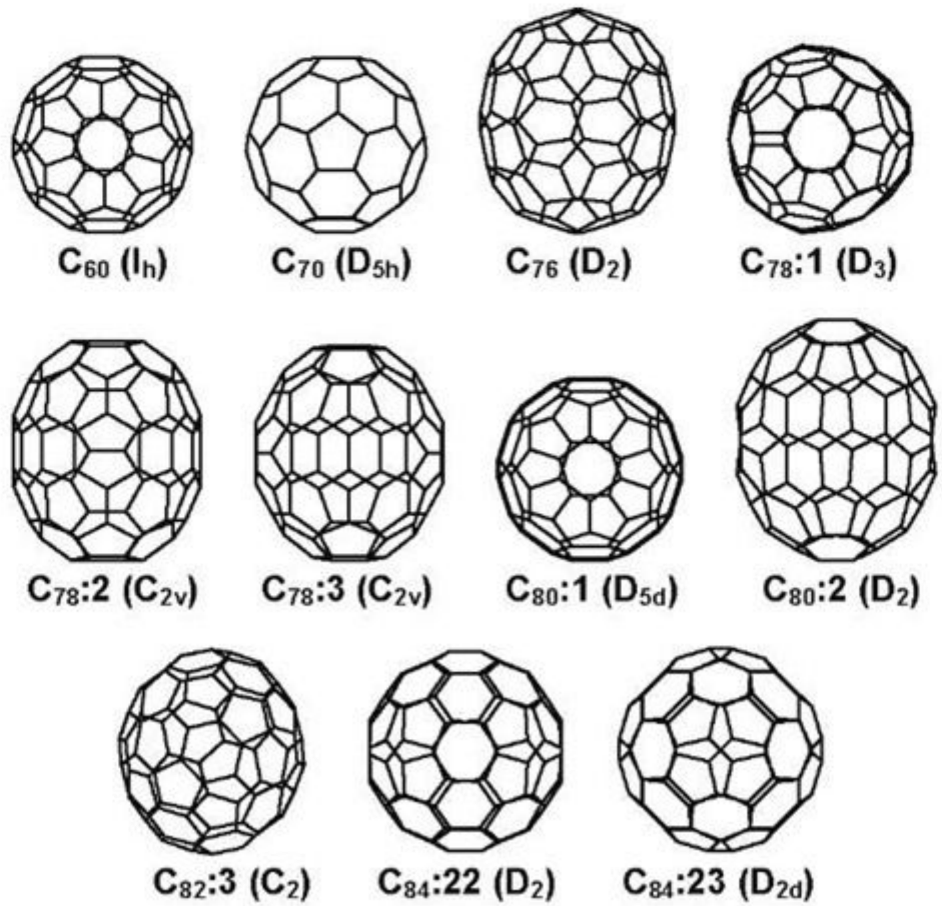
Top 3 reasons to study these in the IR:

1. AGB stars are cool (~3,000 K); their surroundings even cooler → peak of energy distribution in IR.

2. Molecules have ro-vibrational bands in the IR.

3. Dust grains have characteristic vibrational modes in the IR.

Meet the Fullerenes

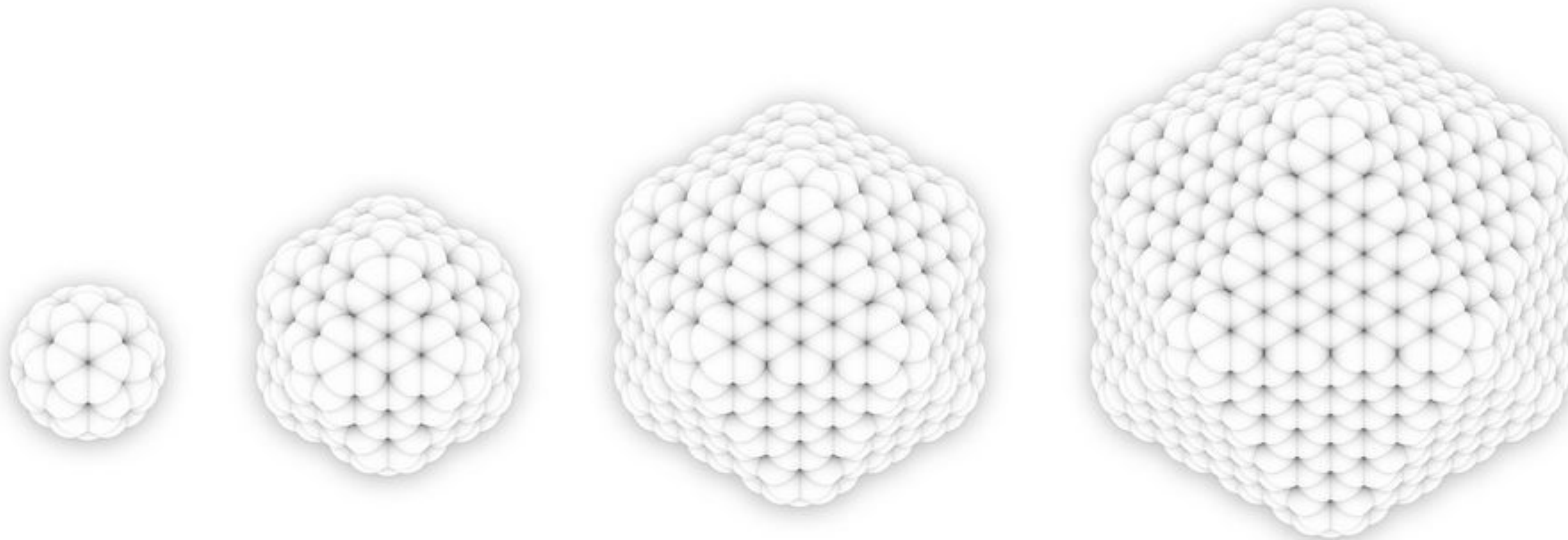


Fullerenes:

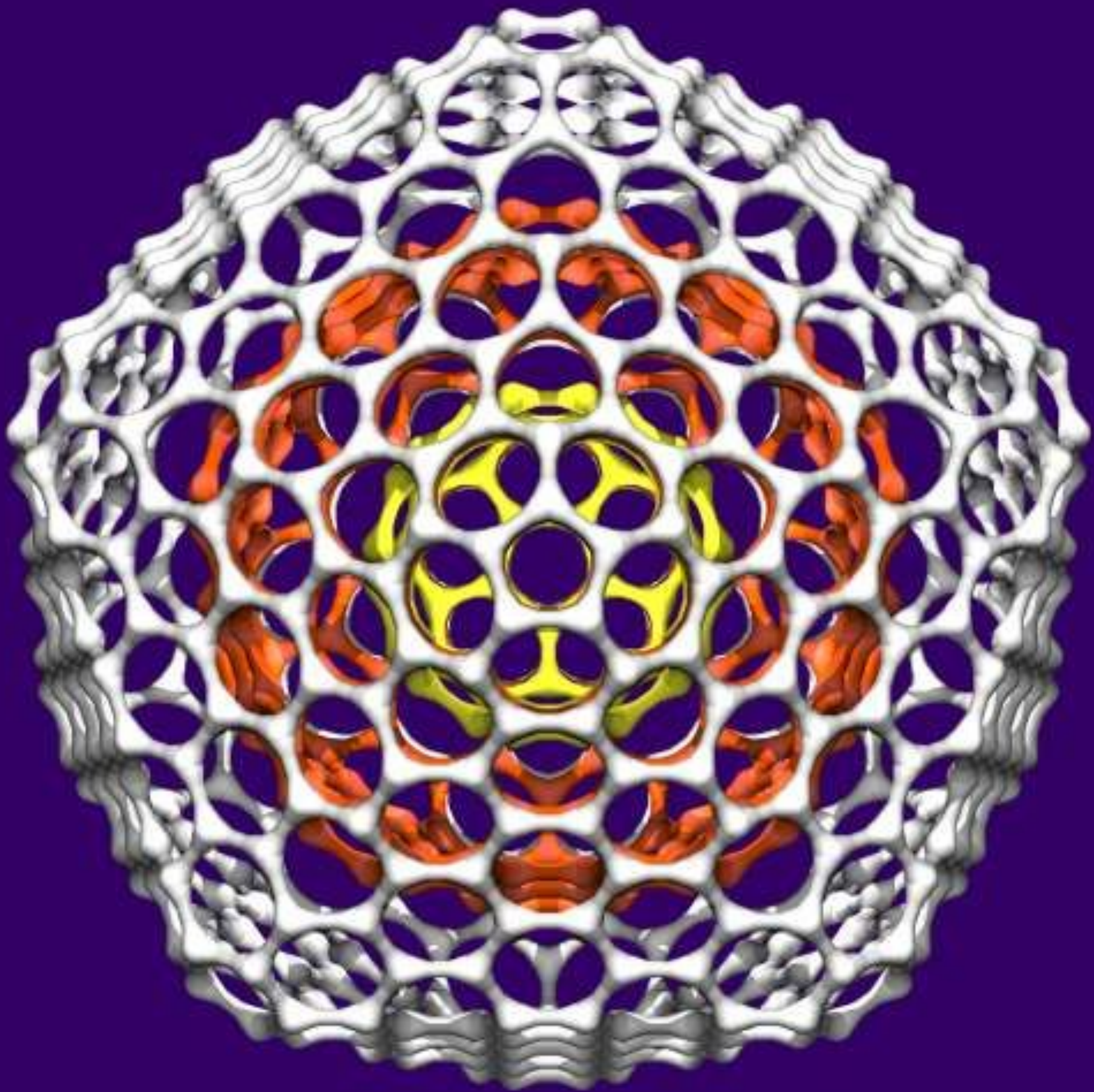
large cage-like molecules made of carbon.

Meet the Fullerenes

A Fullerene Family



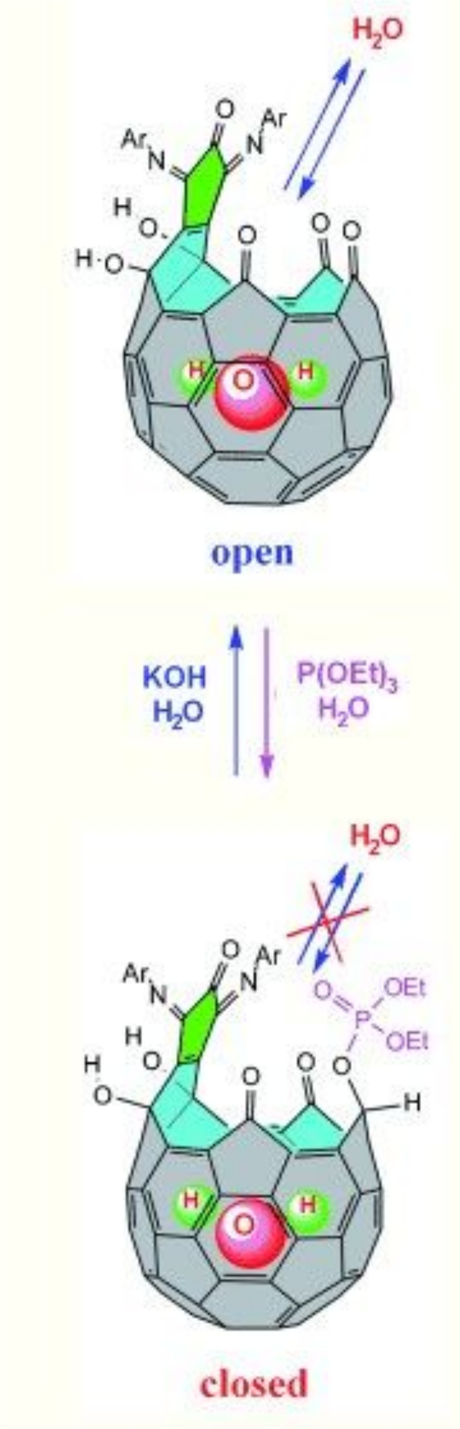
C_{60} C_{240} C_{540} C_{960}



"BuckyOnion"

"Bucky Bottle"

Dec 2, 2015



Angewandte Chemie International Edition

GDCh

Communication

Switchable Open-Cage Fullerene for Water Encapsulation†

Qianyan Zhang[1], Dr. Tobias Pankewitz[2], Shuming Liu[1], Prof. Dr. Wim Klopper[2,3,*], Prof. Dr. Liangbing Gan[1,4,*]

Article first published online: 16 NOV 2010

DOI: 10.1002/anie.201004879

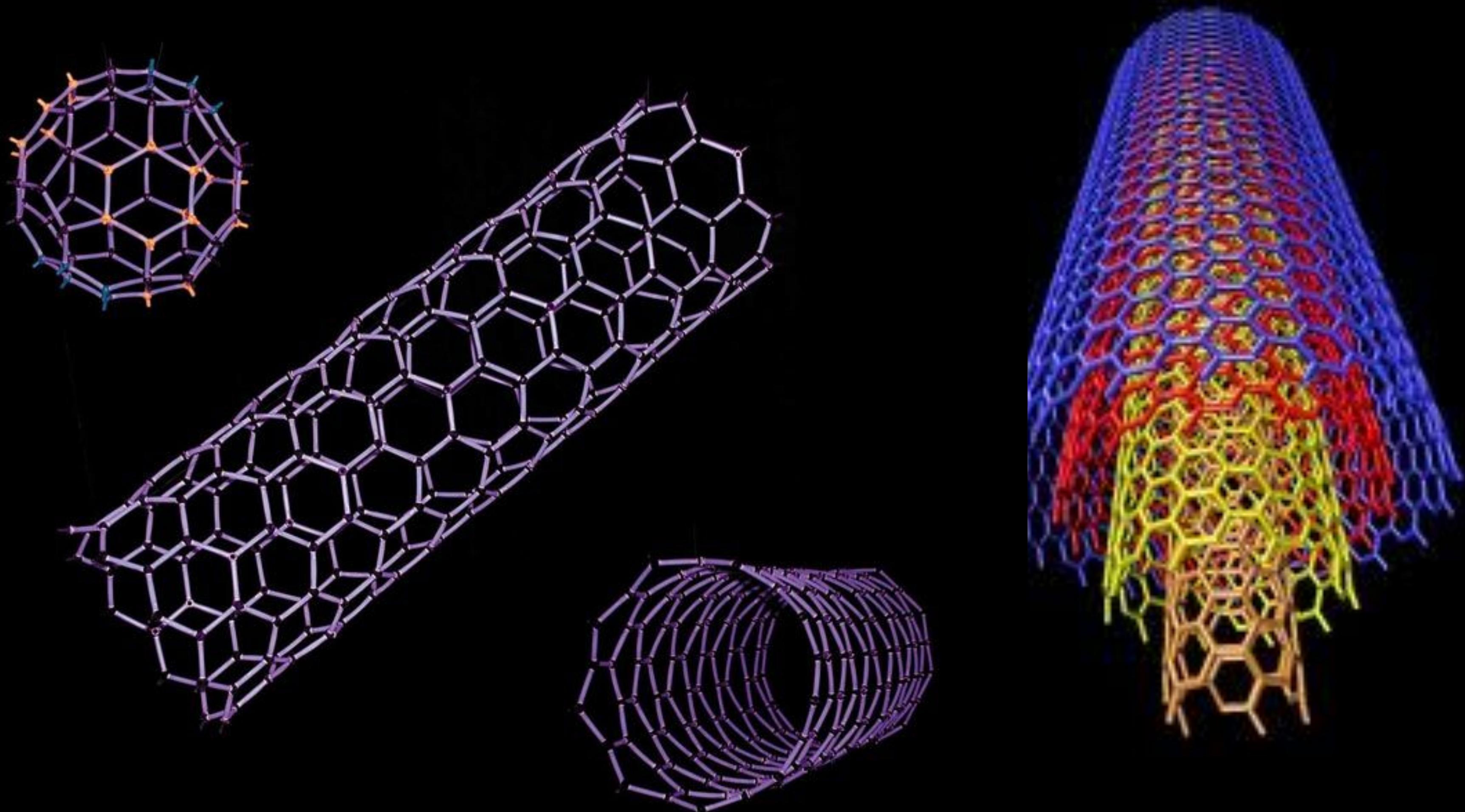
Issue

Angewandte Chemie International Edition

Volume 49, Issue 51, pages 9935–9938, December 17, 2010

Single water molecule trapped in stoppered molecular cage.

Carbon nanotubes



"They are stronger than steel and as flexible as plastic, conduct energy better than almost any material ever discovered and can be made from unexotic raw materials such as methane gas." (CNET)

Buckminster Fuller ("Bucky")

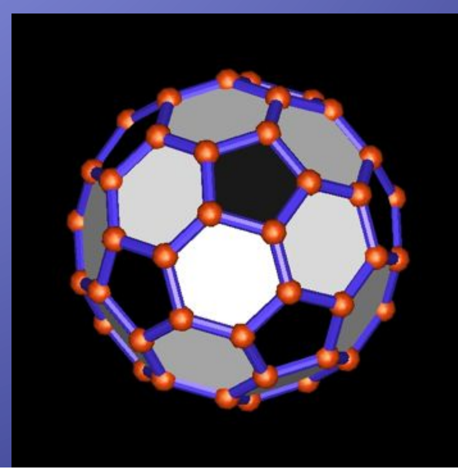
1895-1983

- Architect
- Engineer
- Author
- Designer
- Inventor
- Futurist

"Selfishness is unnecessary and hence-forth unrationalizable…. War is obsolete."

Geodesic Domes

Full geodesic domes from hexagons and pentagons – the pentagons cause the "rounding" of the dome.



NATURE
NATURE VOL. 318 14 NOVEMBER 1985

The discovery of C_{60} and C_{70}

Kroto et al. 1985

Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C_{60} molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.

"C_{60}:Buckminsterfullerene"

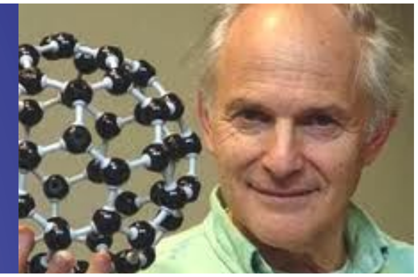
We are disturbed at the number of letters and syllables in the rather fanciful but highly appropriate name we have chosen in the title to refer to this C_{60} species. For such a unique and centrally important molecular structure, a more concise name would be useful. A number of alternatives come to mind (for example, ballene, spherene, soccerene, carbosoccer), but we prefer to let this issue of nomenclature be settled by consensus.

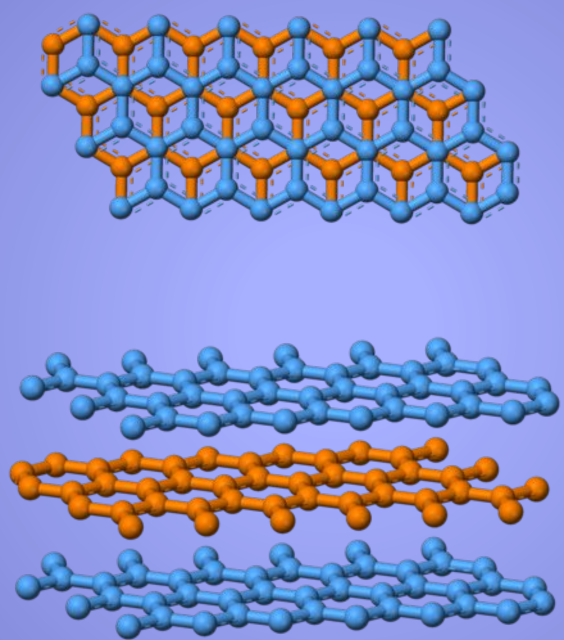
Why do we care?

- Fullerenes are ***messengers***: they are the ***only*** identified large aromatics in space, they tell us what happens to their large extended family.
- They tell us ***we don't understand*** some of the physics and interstellar chemistry that's happening in space, ***give us clues***, and show what the role is of super-stable carbonaceous species in space.
- They could play ***a role in some unexplained spectral phenomena*** (DIBs, ERE, BL, extinction).

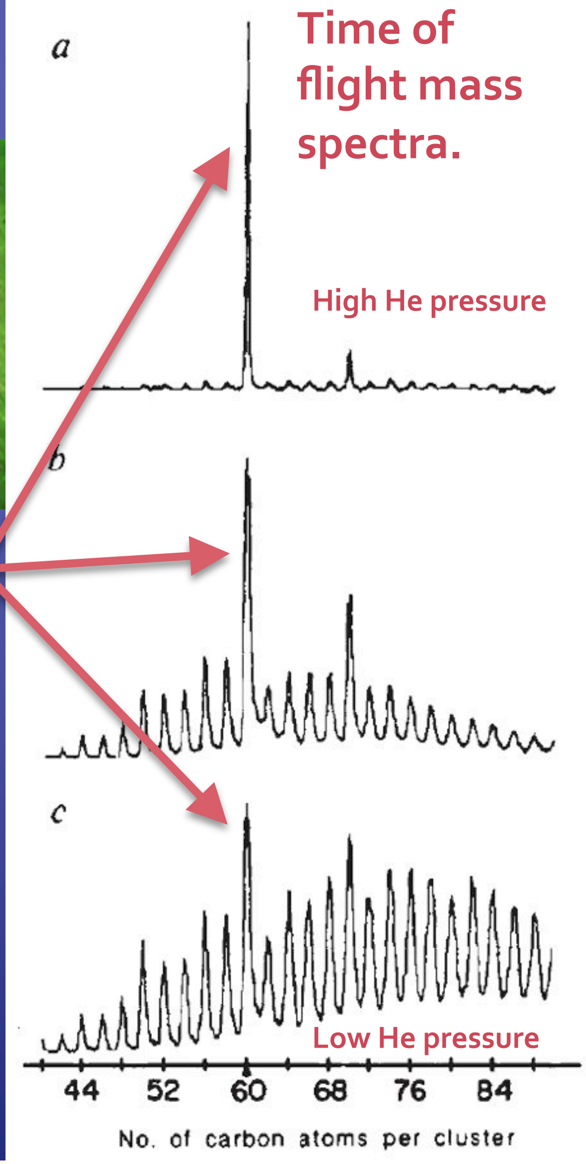
The discovery of C_{60} and C_{70}

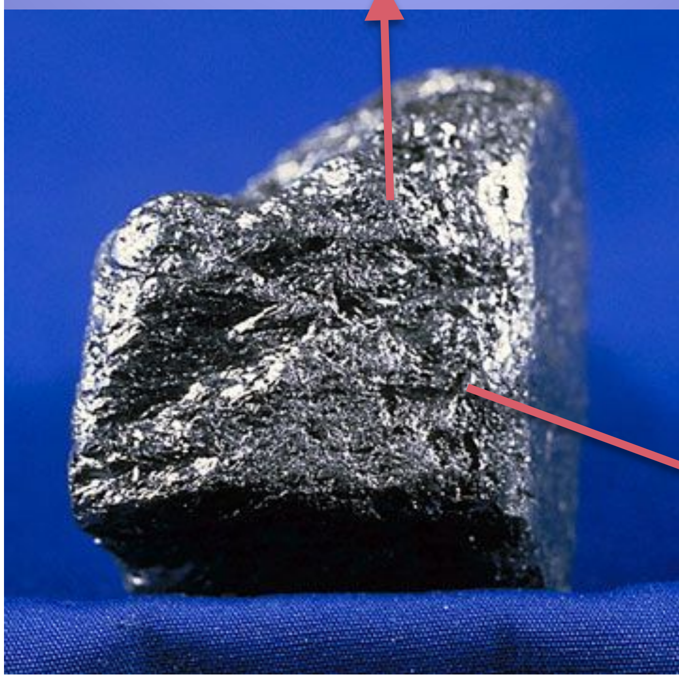
Kroto et al. 1985





Time of flight mass spectra.

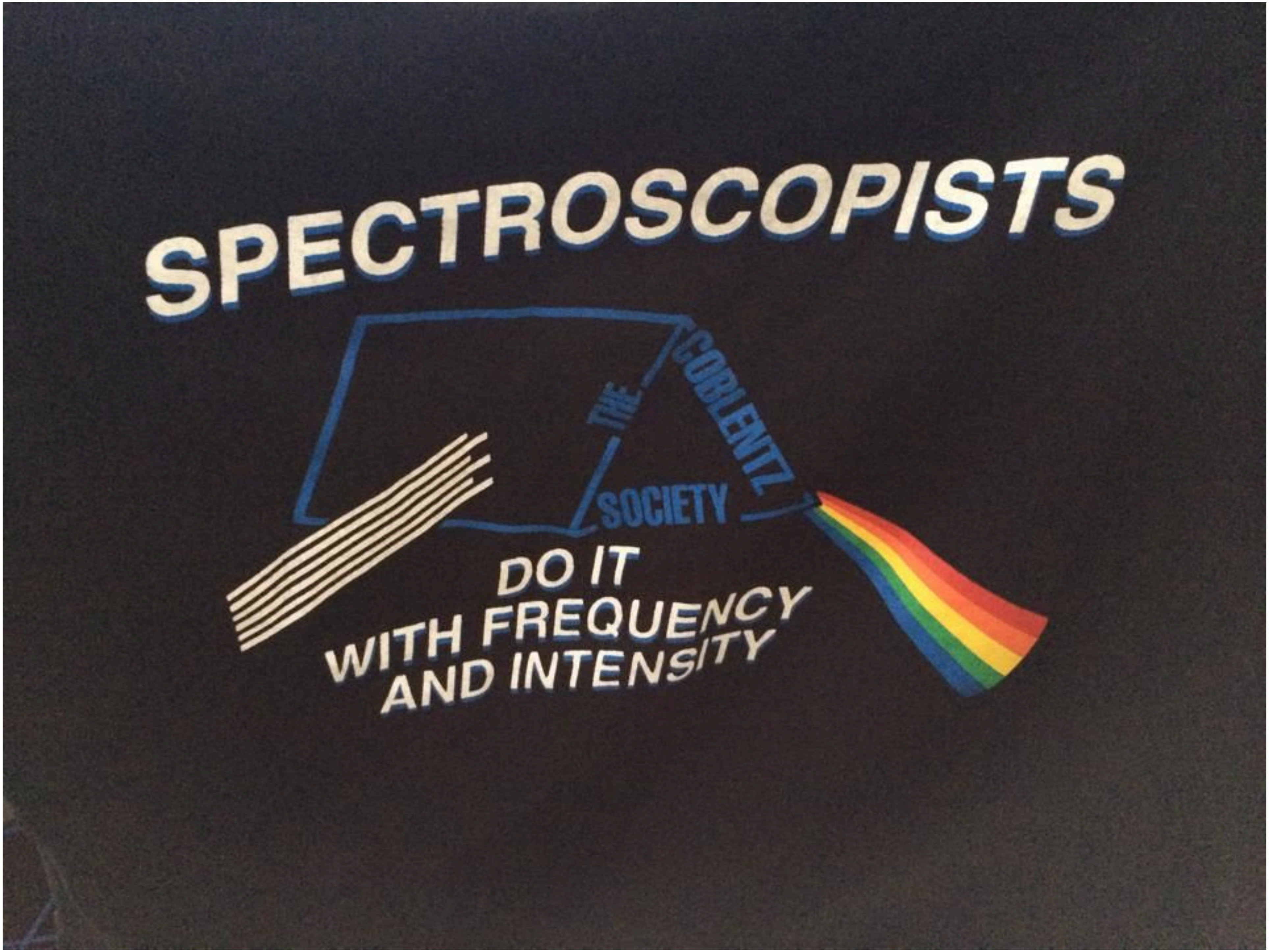




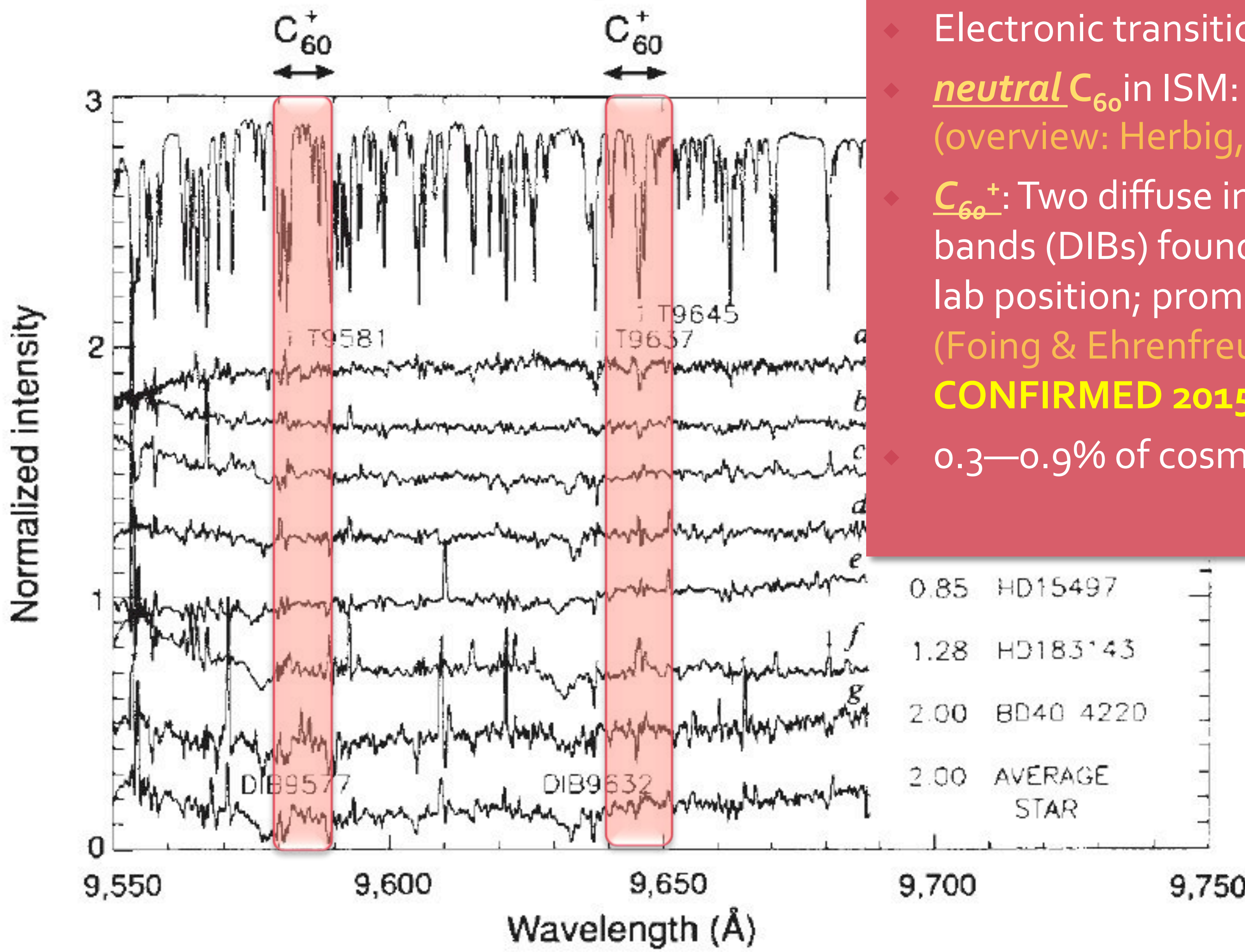
Survival of the fittest: discovery of C_{60} and C_{70}.

Widespread and abundant in space?

Graphite vaporization.


SPECTROSCOPISTS
THE COBLENTZ SOCIETY
DO IT
WITH FREQUENCY
AND INTENSITY

Early Searches



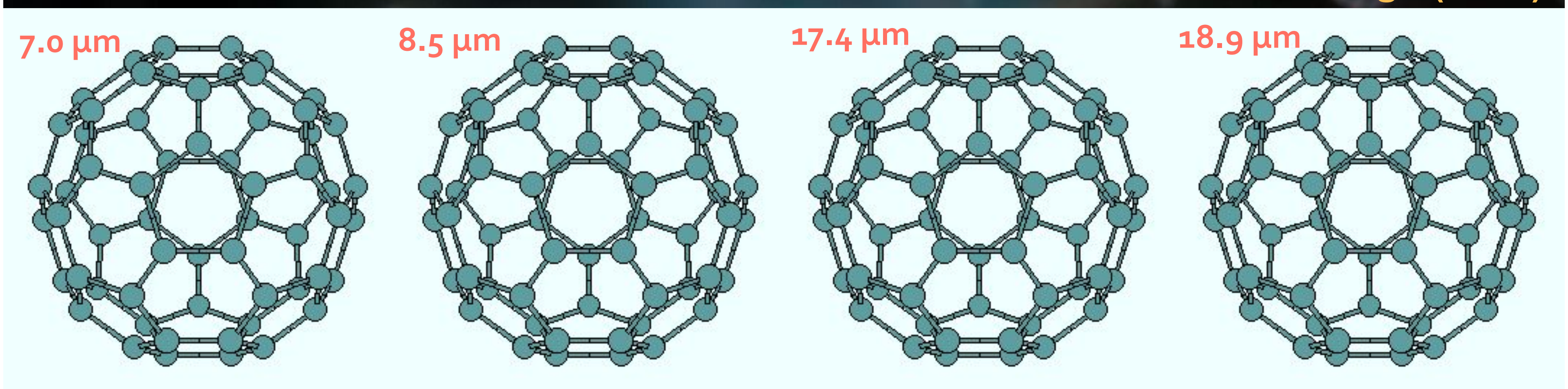
- Electronic transitions.
- ***neutral*** C_{60} in ISM: not found (overview: Herbig, 2000).
- C_{60}^{+}: Two diffuse interstellar bands (DIBs) found close to lab position; promising case, (Foing & Ehrenfreund, 1994). **CONFIRMED 2015!**
- 0.3—0.9% of cosmic C in C_{60}^{+}.

C_{60} & C_{70} vibrational modes

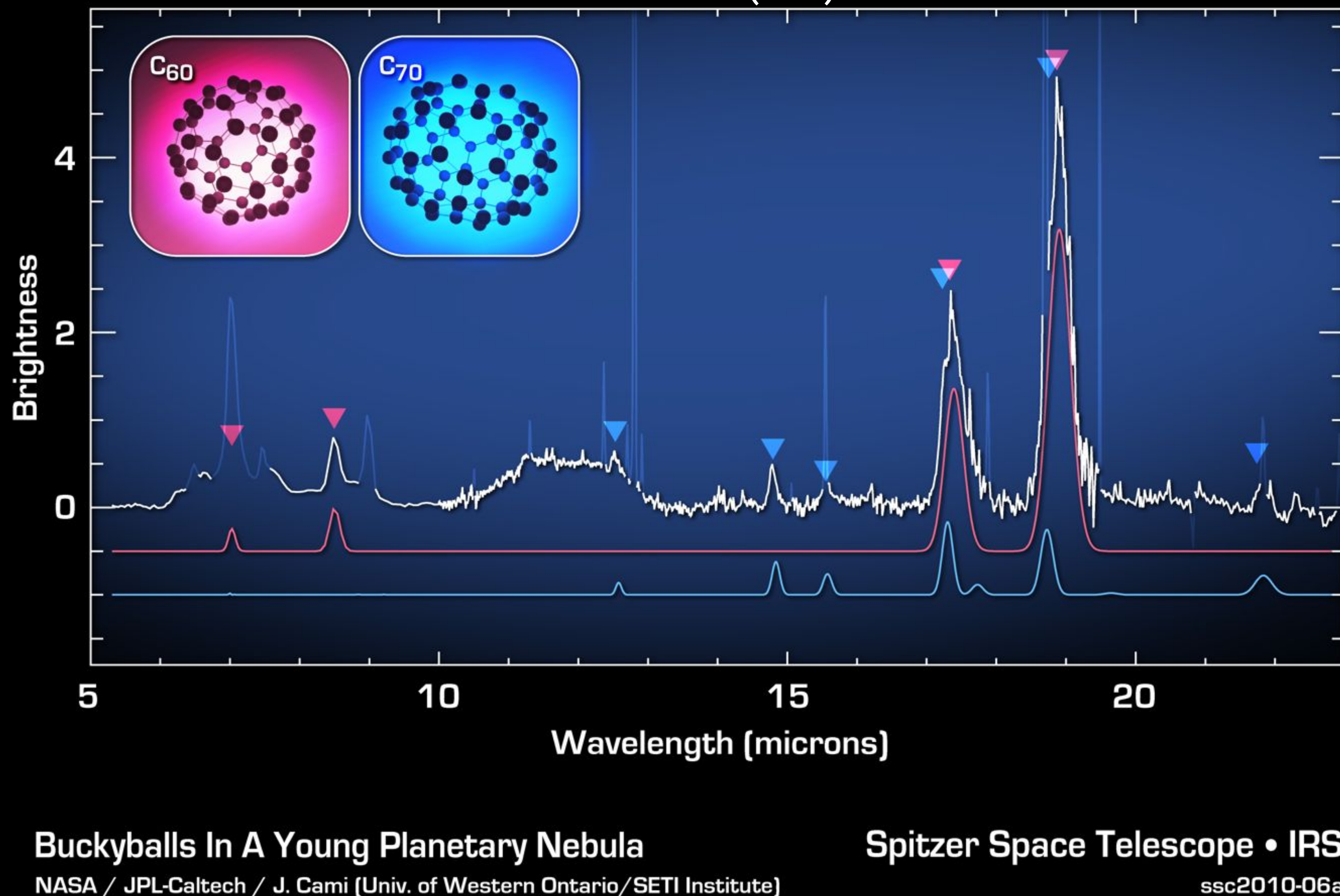
- Neutral C_{60}: 4 IR active modes: 7.0, 8.5, 17.4, 18.9 µm.
- Dedicated searches (ISO/SWS: Clayton et al., 1995; Moutou et al., 1999) & tentative detection (Spitzer: Sellgren et al., 2007).
- Note: cation spectra different (see e.g. Berné et al., 2013)

- Neutral C_{70}: 32 IR active modes.

Menéndez & Page (2000)



Wavelengths, widths & relative strengths
match measured (lab) values.



Cami et al. (2010)

More C_{60} Detections

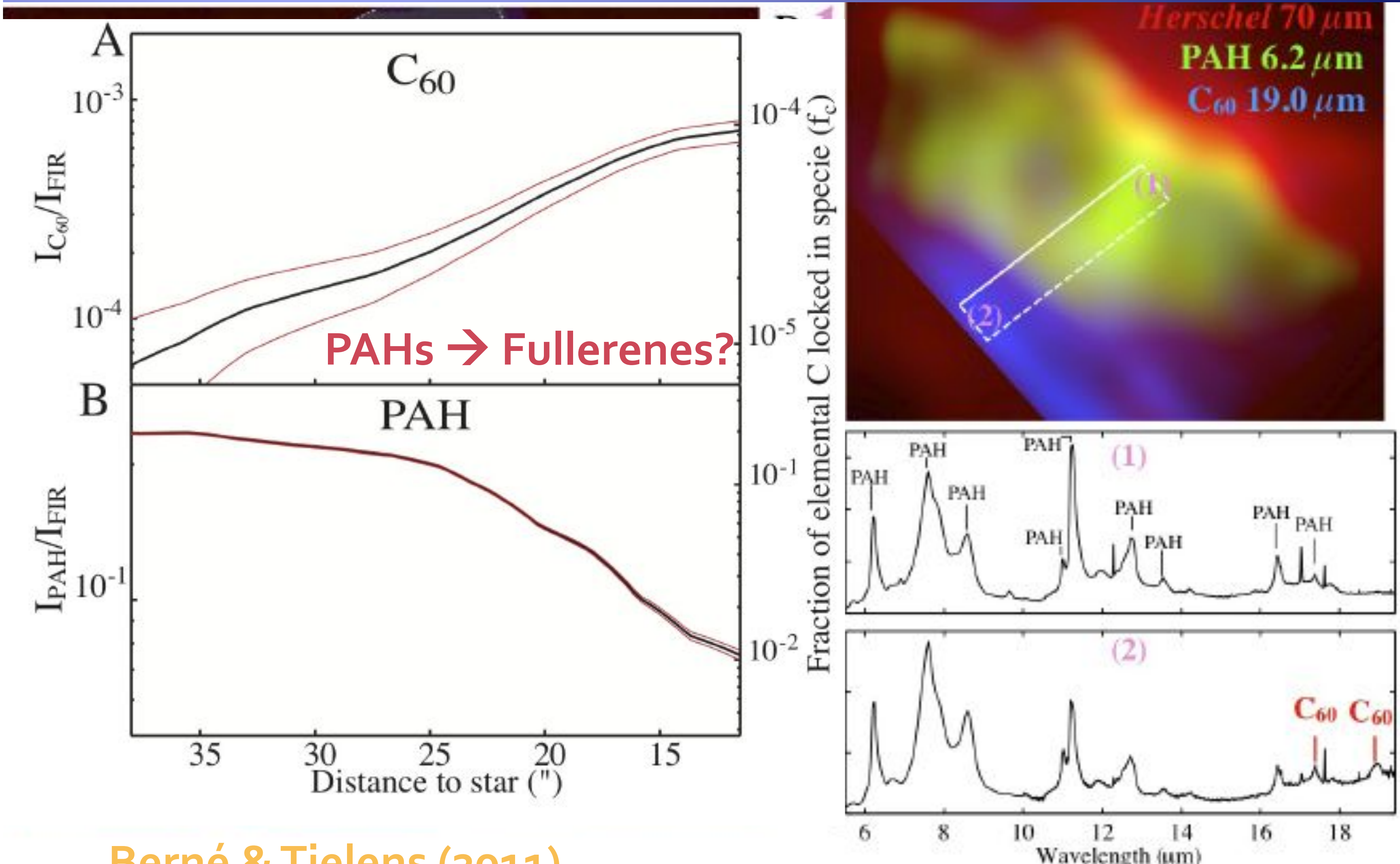
- Evolved stars:
  - PN: García-Hernández et al. (2010, 2011); Bernard-Salas et al. 2012, Otsuka et al. 2013.
  - Proto-PN: Zhang & Kwok 2011.
  - R Cor Bor: García-Hernández et al. 2011, Clayton et al. 2011.
  - Post-AGB (O-rich?): Gielen et al. 2011.
- ISM:
  - Reflection Nebulae: Sellgren et al. 2010, Peeters et al. 2012
  - Orion Nebula: Rubin et al. 2011, Boersma et al. 2012.
- YSO: Roberts, Smith & Sarre, 2012.

Incomplete list!

Key Questions

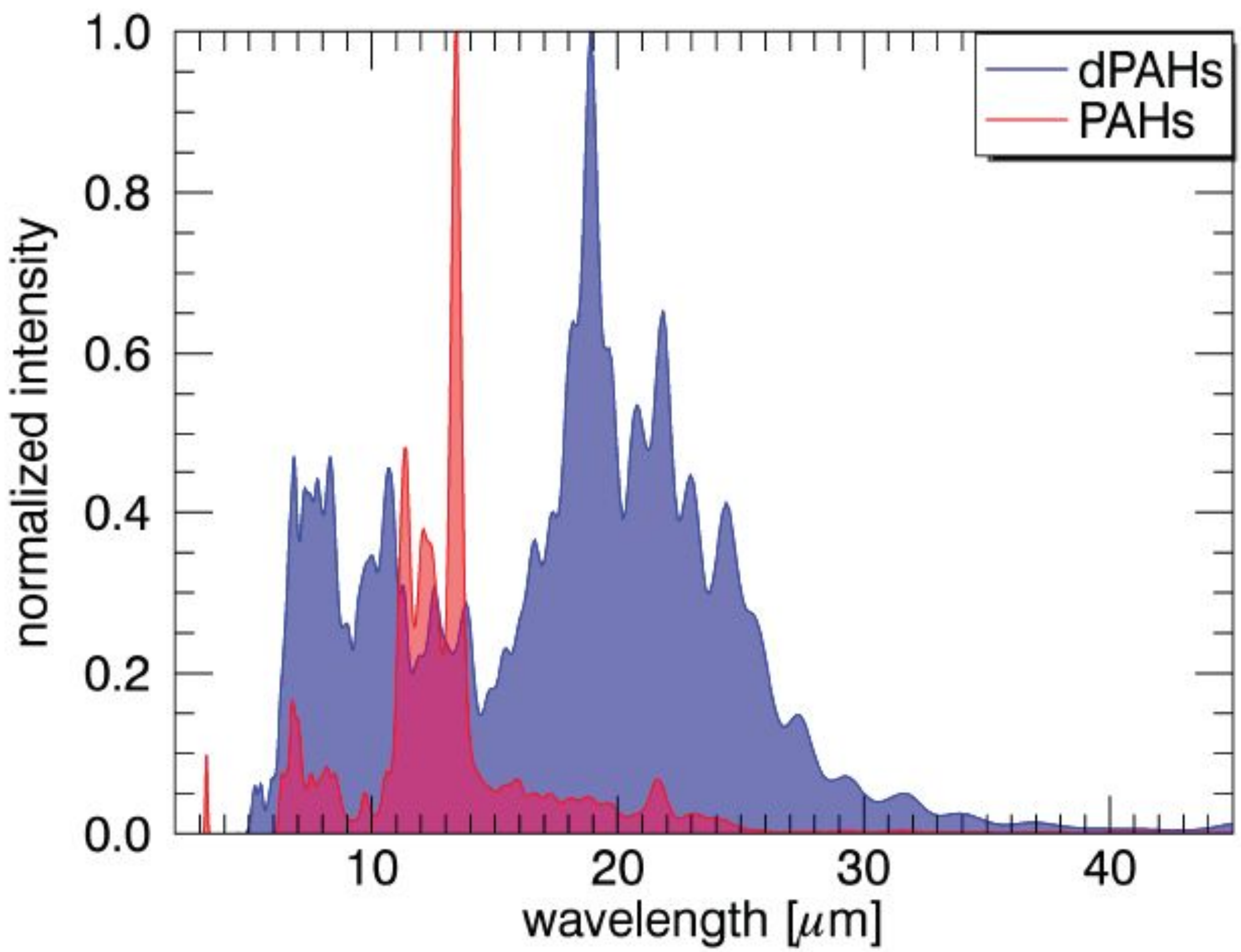
- How do you form fullerenes in space?
- What other fullerenes exist in space?
- What is their relation to other dust components?
- How much C_{60} is there?
- What happens after formation?

PAHs & C_{60} in NGC 7023



Berné & Tielens (2011)

Dehydrogenated PAHs

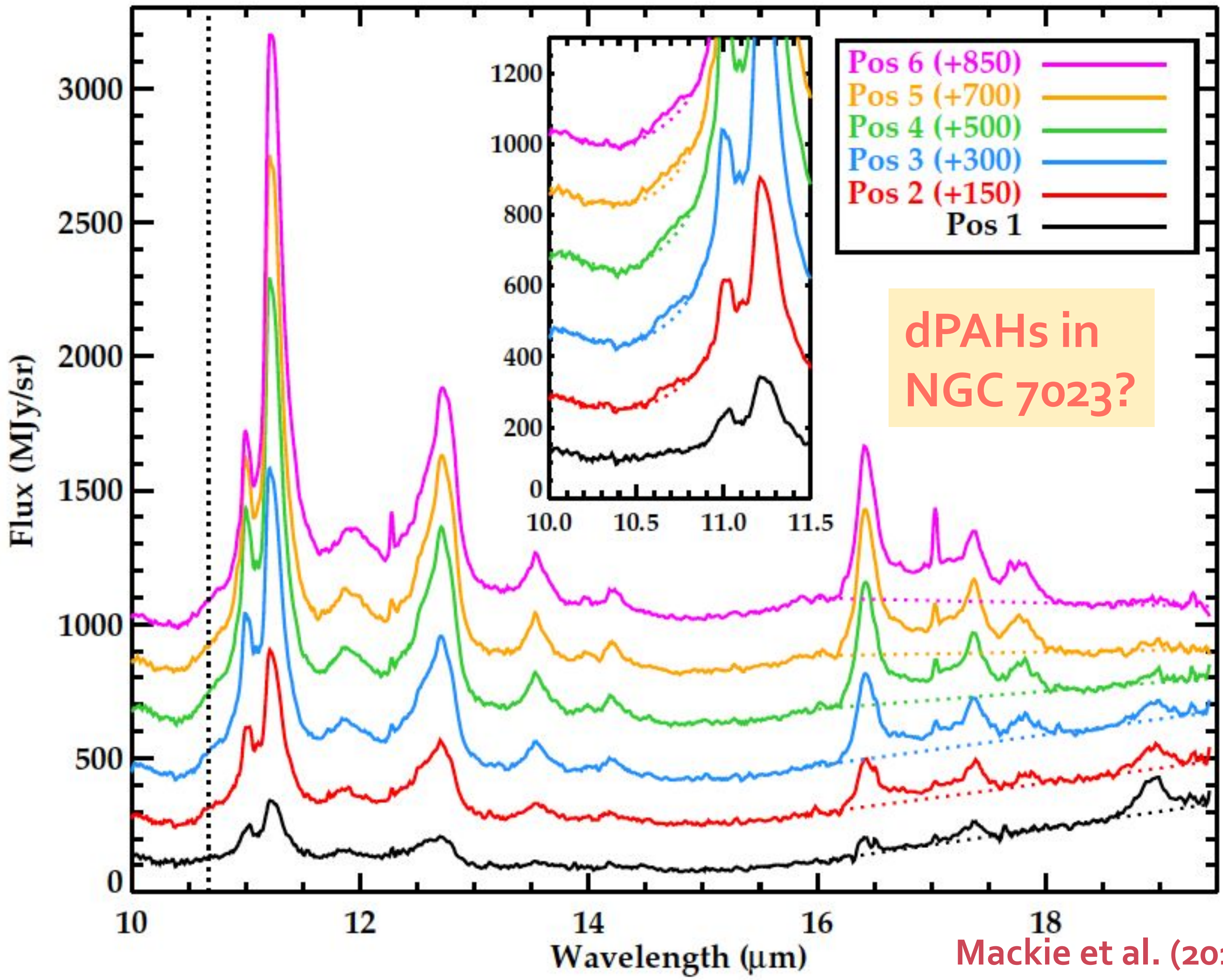


For (small) dPAHs: Expect specific features around 5.5, 10.6 and 19µm.

Consistent with larger PAHs.

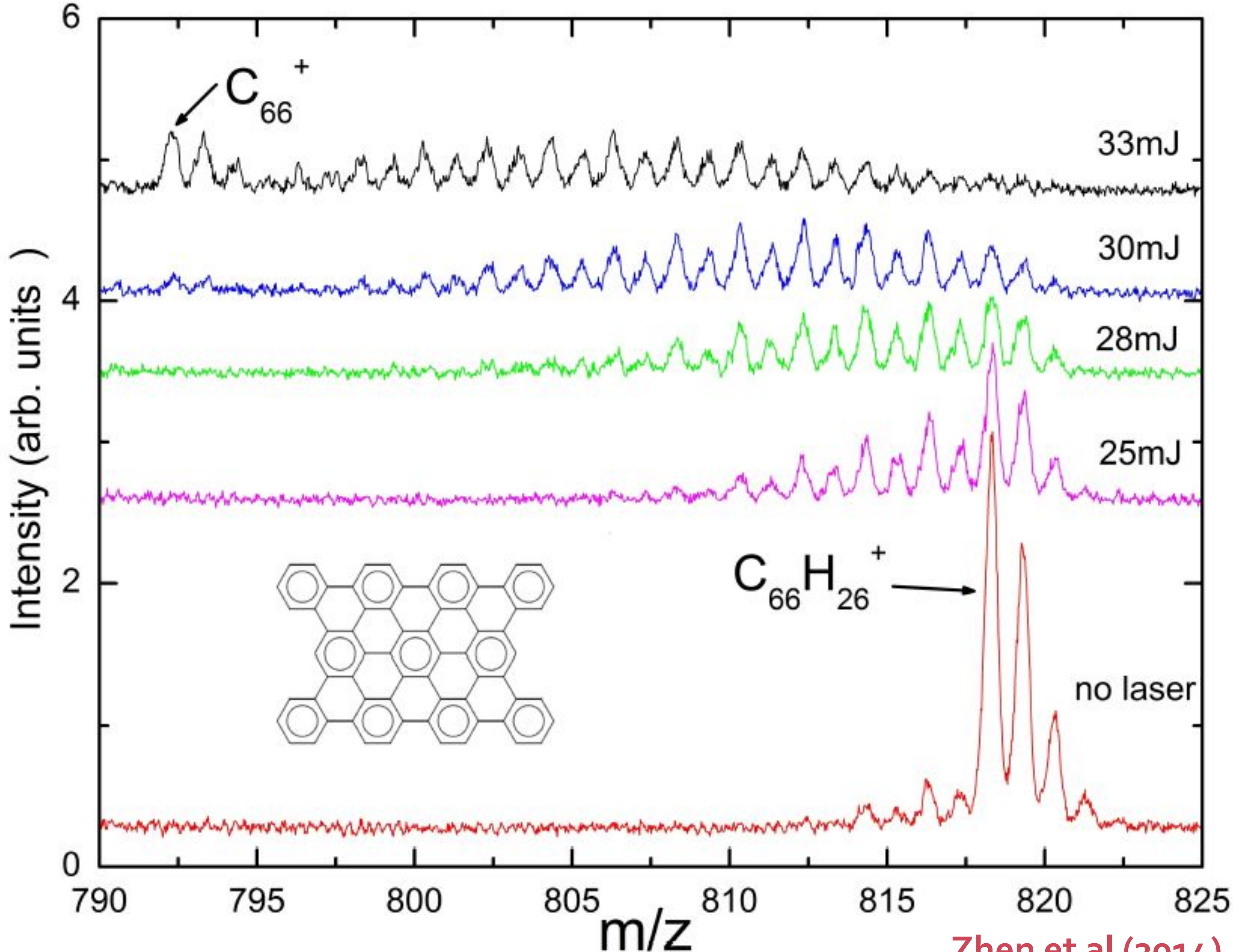
Mackie et al. (2014)

Dehydrogenated PAHs



Mackie et al. (2014)

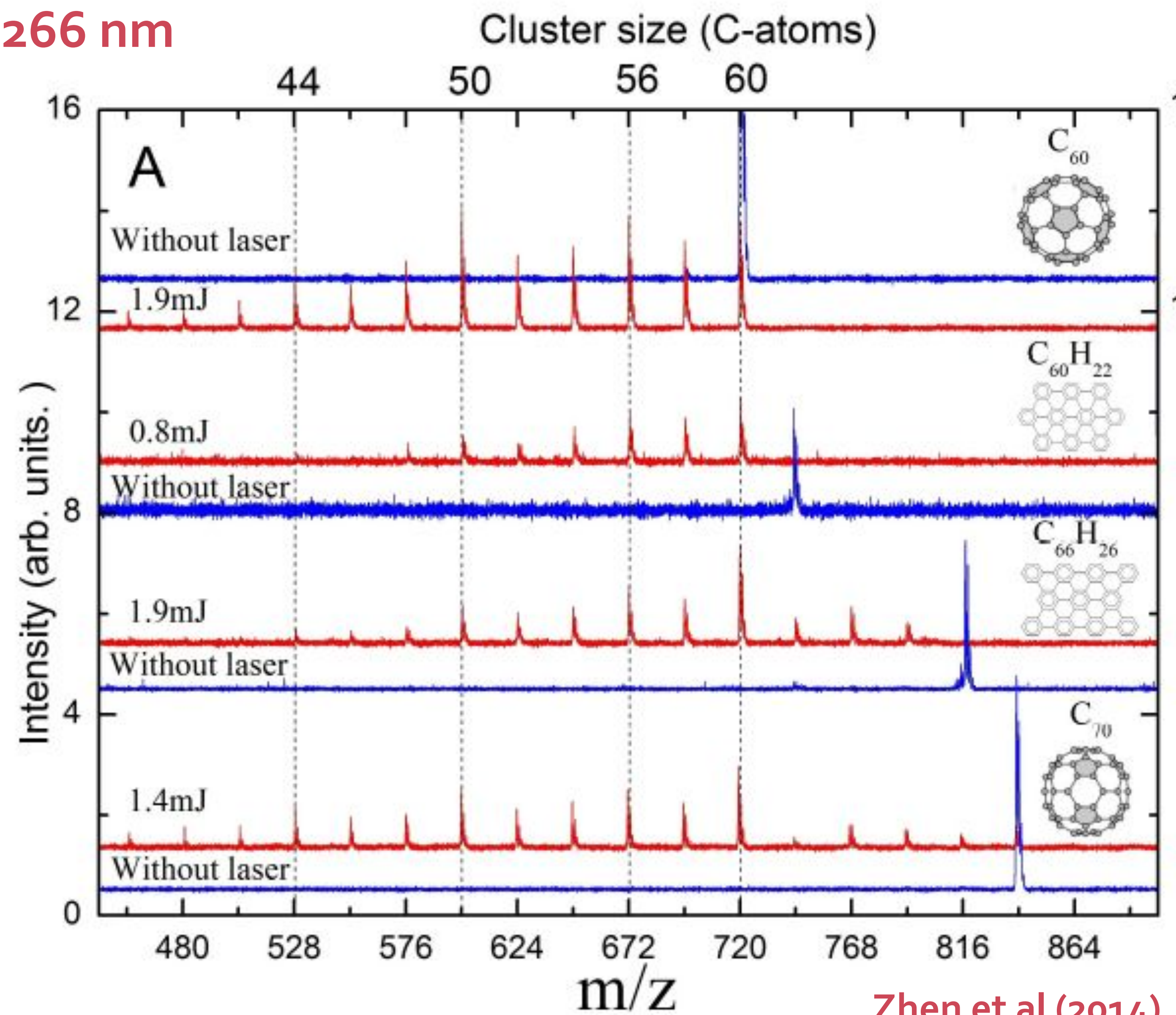
Meanwhile at the lab



Zhen et al (2014)

Meanwhile at the lab (II)

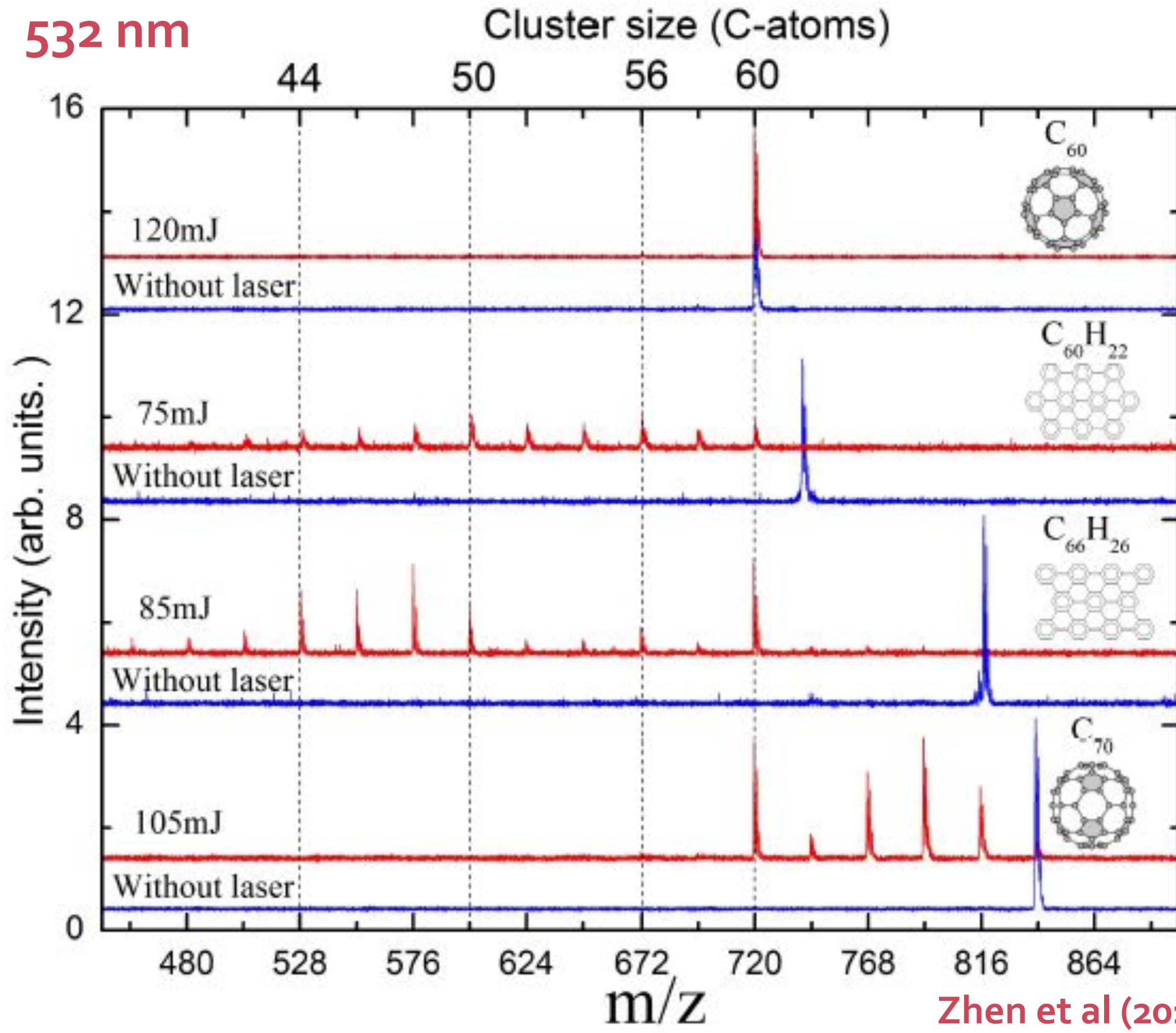
266 nm



Zhen et al (2014)

Meanwhile at the lab (III)

532 nm



Zhen et al (2014)

Molecular striptease explains Buckyballs in space

Dec 09, 2014

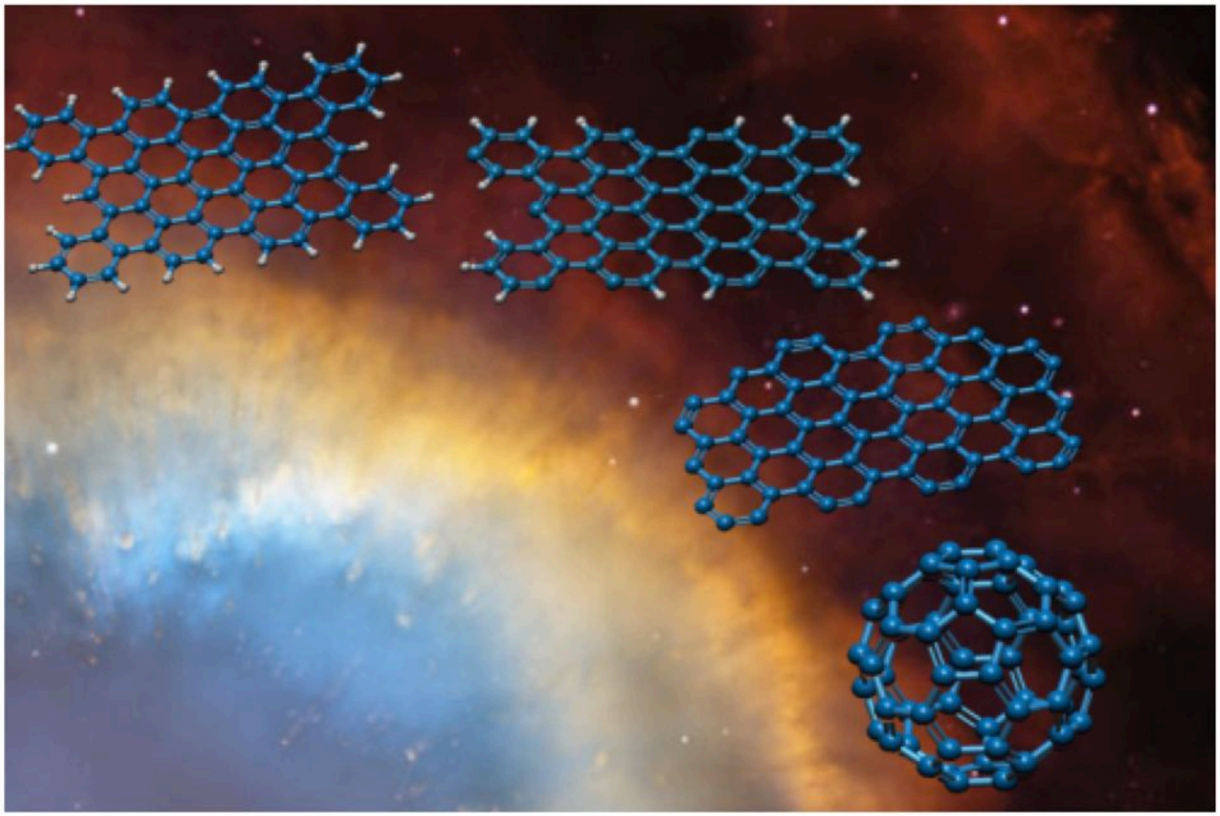


Illustration of how a big PAH (upper left) starts with a molecular striptease, stripping off H-atoms one by one, until the naked carbon skeleton is left over. De C60 'Buckyball' is at the lower right. Credit: Leiden University Linnartz/Tielens

Fullerene Formation in Evolved Stars

- On first sight, this scenario is promising for evolved stars as well:
  - PAHs are often seen in PNe.
  - Hot central stars → lots of UV photons!

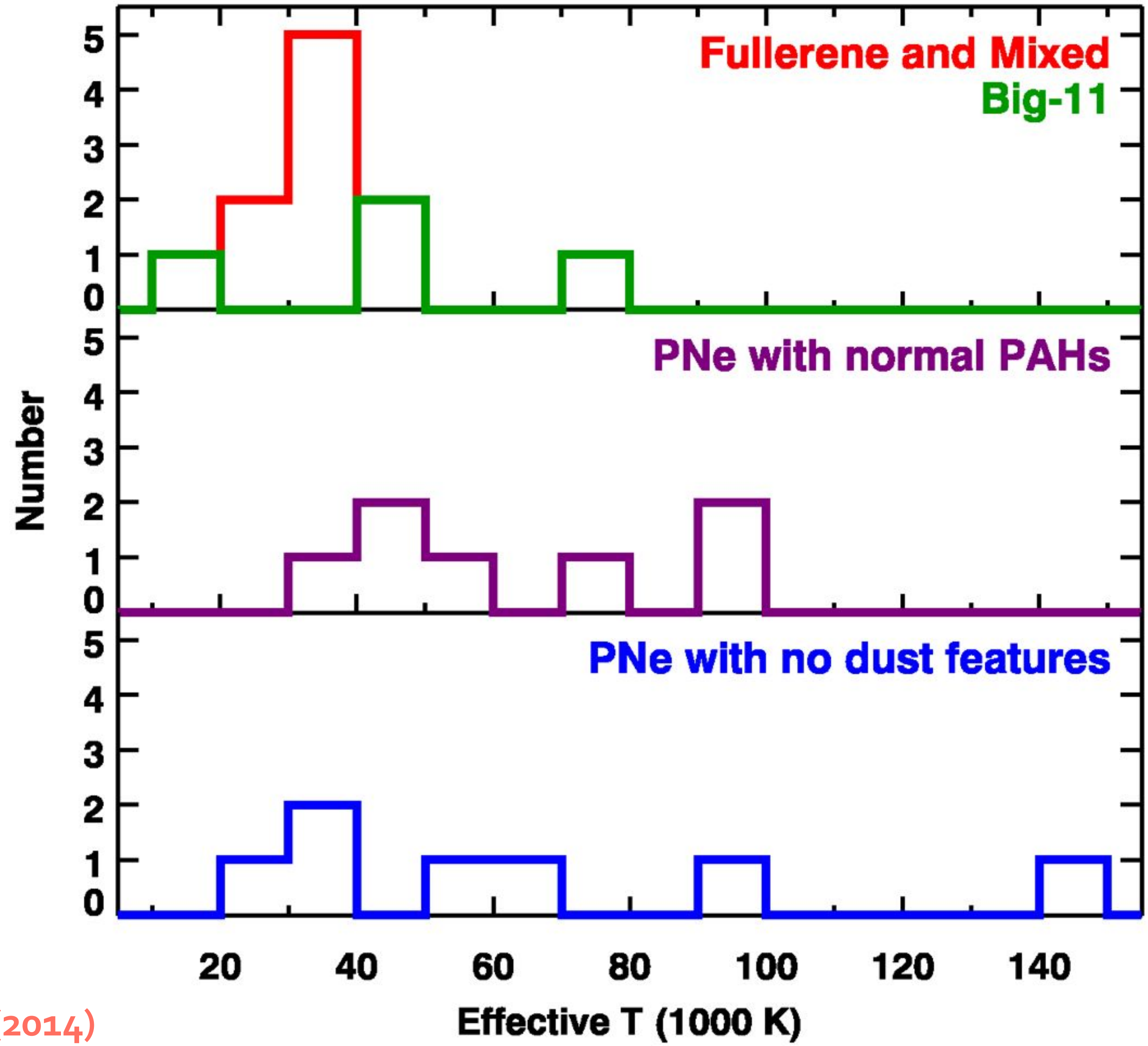
When you have a good idea, there's always observations to prove you wrong.

Fullerenes in evolved stars

To figure out the formation of fullerenes in evolved stars, we should consider that:

★ Fullerenes are ***not*** common in evolved stars:
only 3% of a sample of galactic PNe show 17.4/18.9 micron bands (Otsuka et al. 2014).

Fullerenes and T_{eff}

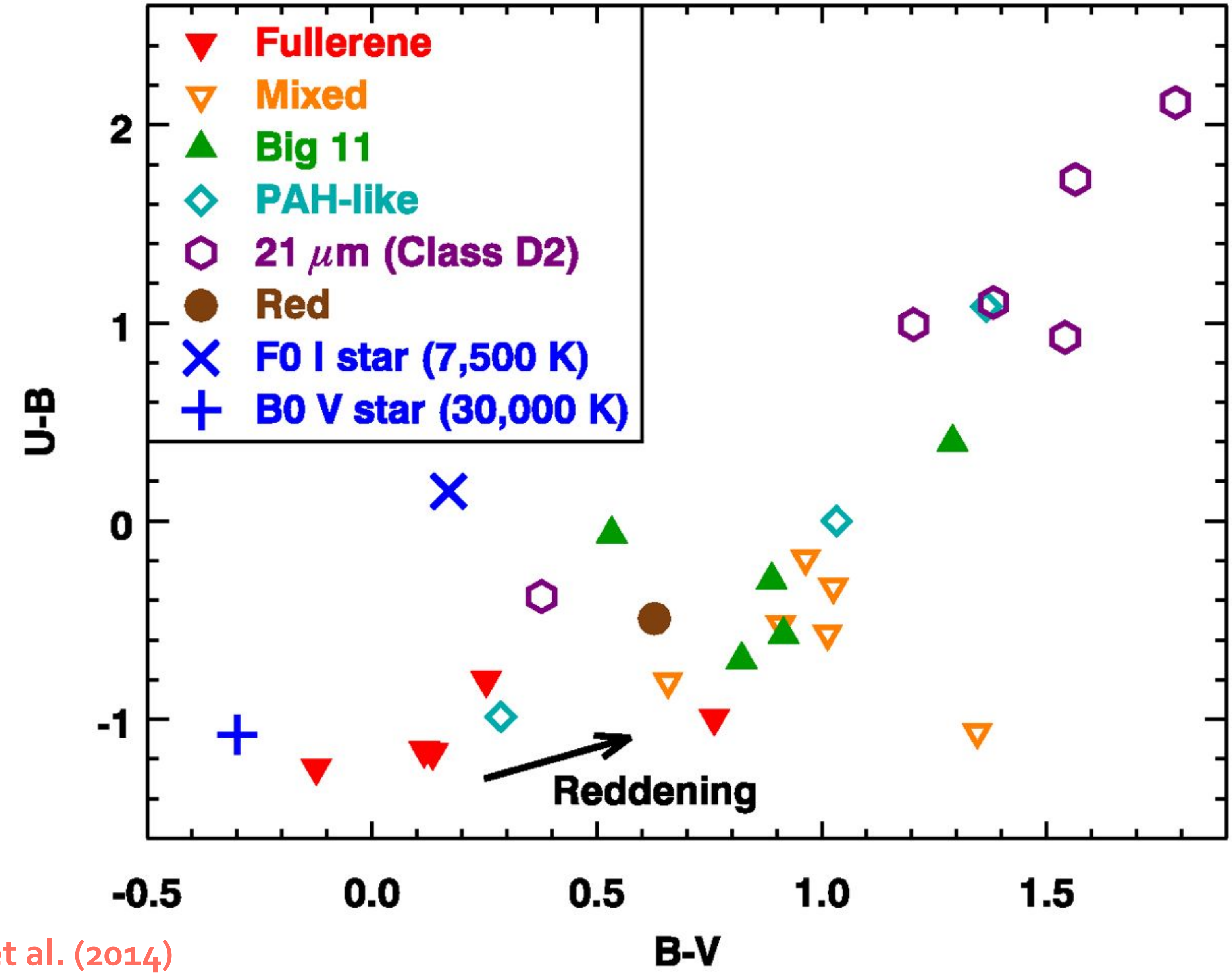


Sloan et al. (2014)

Fullerene Evolution

- Although fullerenes are extremely stable, they are not seen in more mature PNe, even those where PAHs *are* seen.
- What happens to the fullerenes as the young PNe evolve, and PAHs start appearing?
- → Fullerenes should not be destroyed... Maybe turned into fullerene derivatives?

Fullerenes in clear lines of sight?



Sloan et al. (2014)

Fullerenes in evolved stars

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★ Fullerenes are ***not*** common in evolved stars:
only 3% of a sample of galactic PNe show 17.4/18.9 micron bands (Otsuka et al. 2014).

★ Fullerenes do ***not*** require the strongest or hardest UV fields; in fact fullerenes are generally seen in the somewhat more mild environments (Sloan et al., 2014). Note: in Tc 1, fullerenes much further from star than PAHs, and in different geometry!

★ Fullerenes are seen in the least reddened sources.

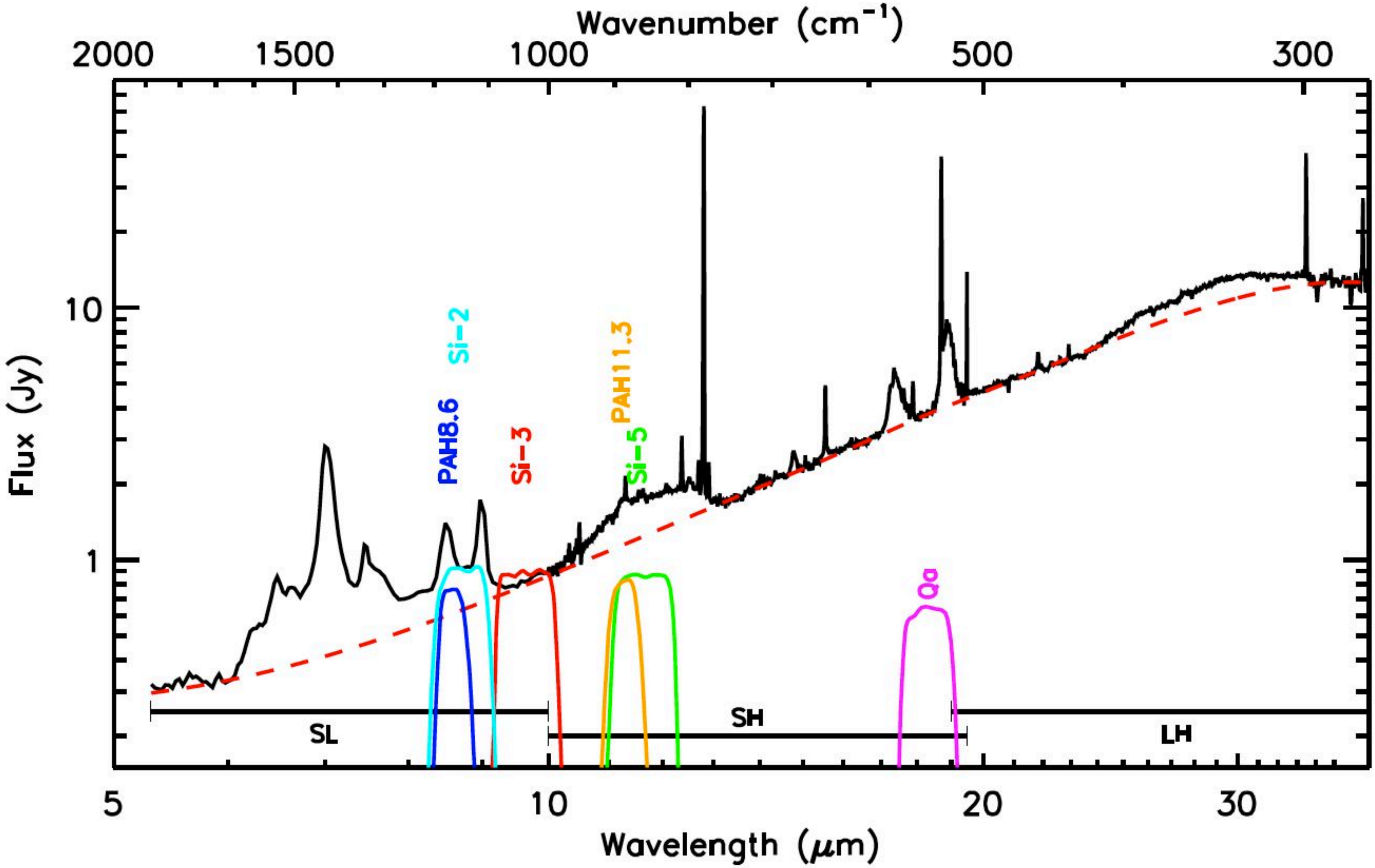
Shocks, maybe associated with developing ionization front?
"Special" objects?

Studying the fullerene nest

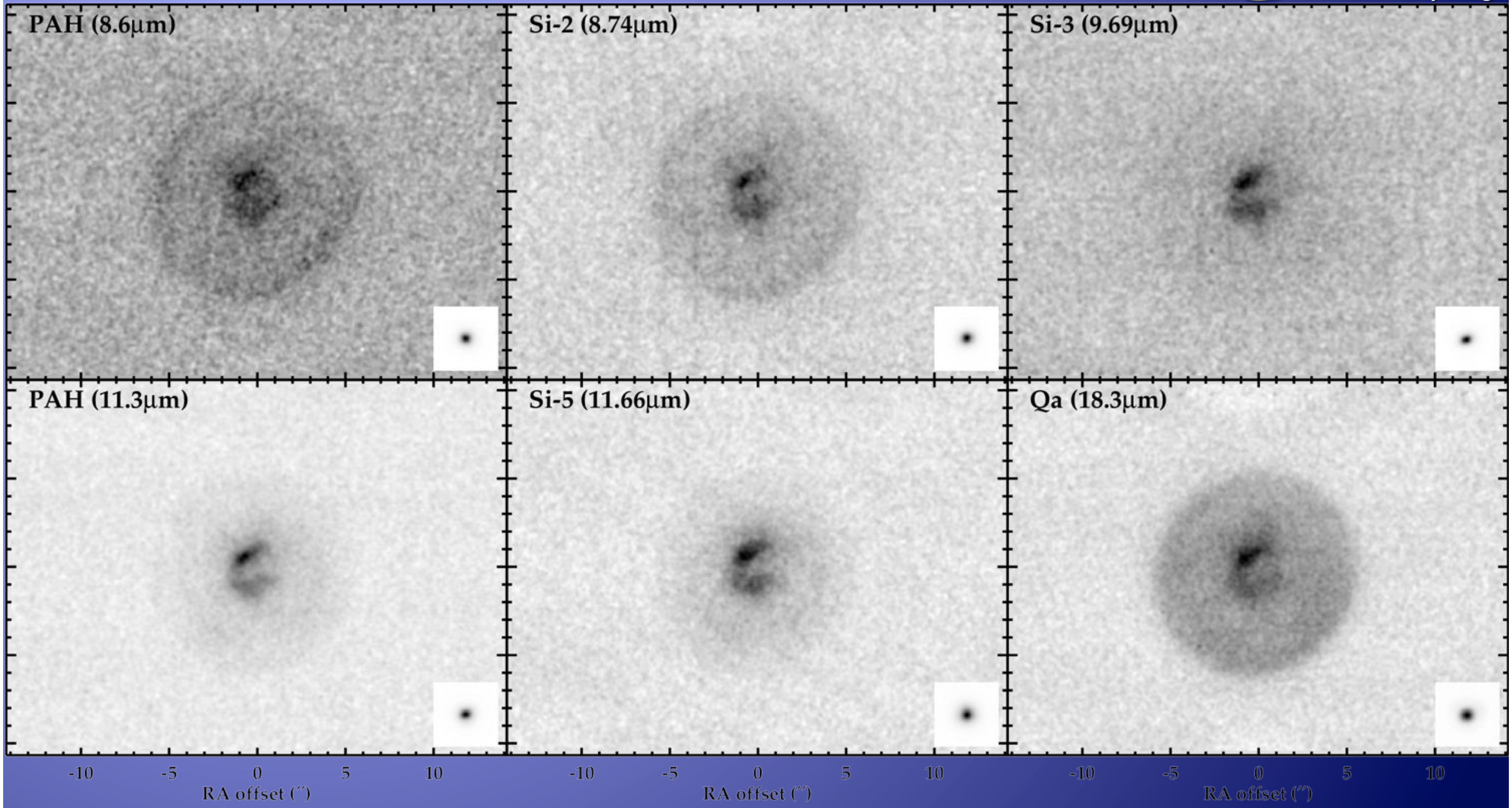
To figure out the formation of fullerenes in evolved star environments, we are currently carrying out:

- Spatial studies of C_{60} PNe.
- Optical spectroscopy: properties of the central stars; physical conditions and elemental abundances in the (ionized) nebula.
- IR spectroscopy: use SOFIA to determine the properties of the PDR around the ionized zone.
- Need UV spectroscopy for C abundance.

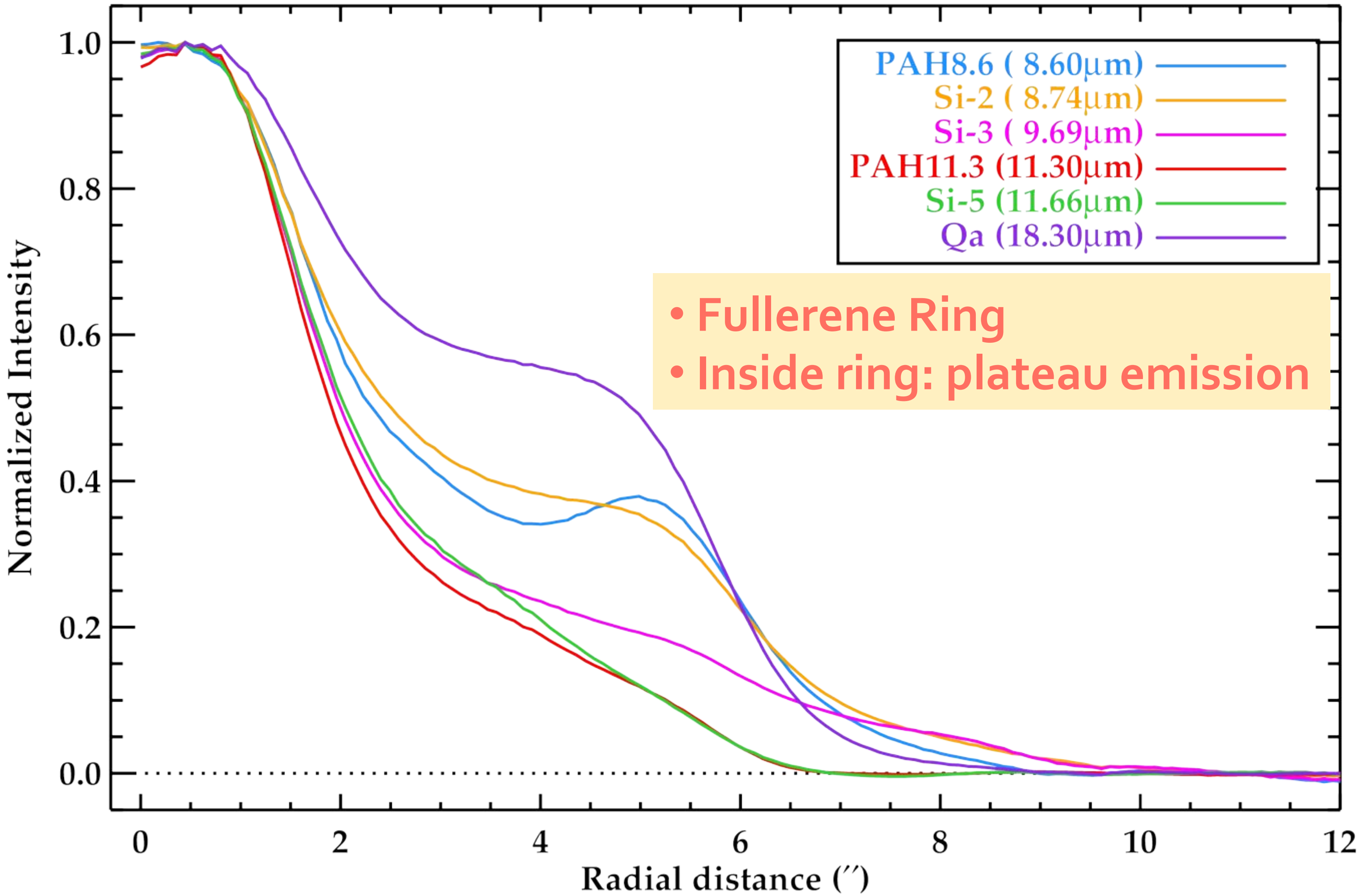
Gemini T-ReCS observations



Tc1: Lord of the Fullering

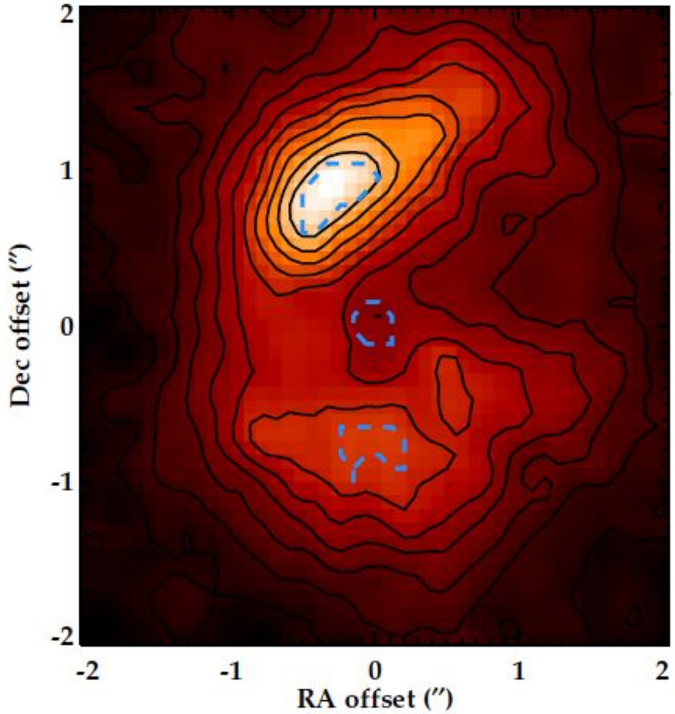


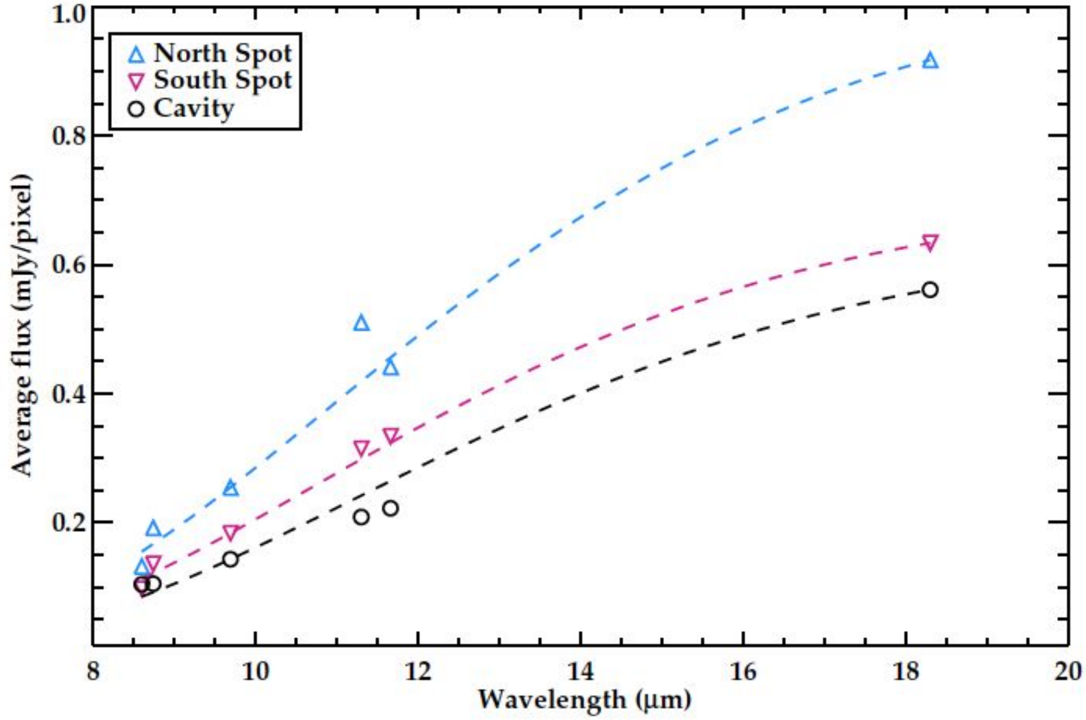
Radial Profiles



- Fullerene Ring
- Inside ring: plateau emission

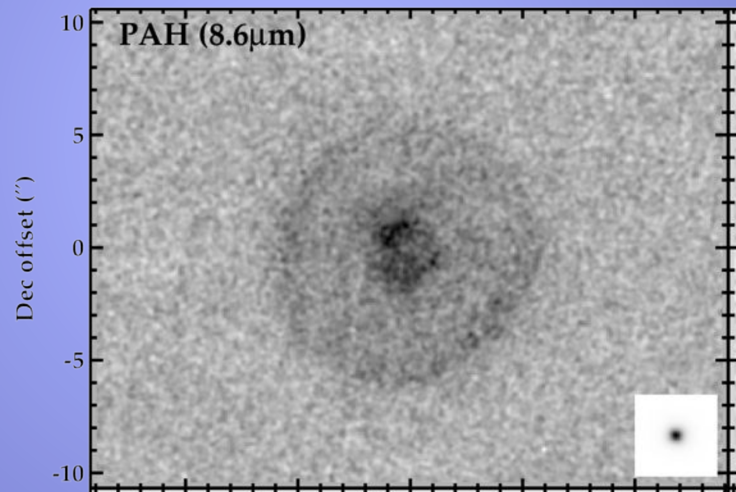
Where are the PAHs?

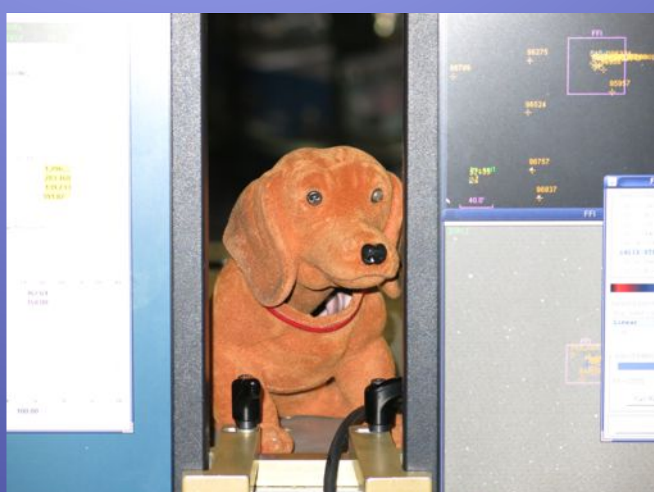




- …. In a tiny spot in the central structure → Far away from the fullerene ring!

SOFIA & C_{60}-PNe



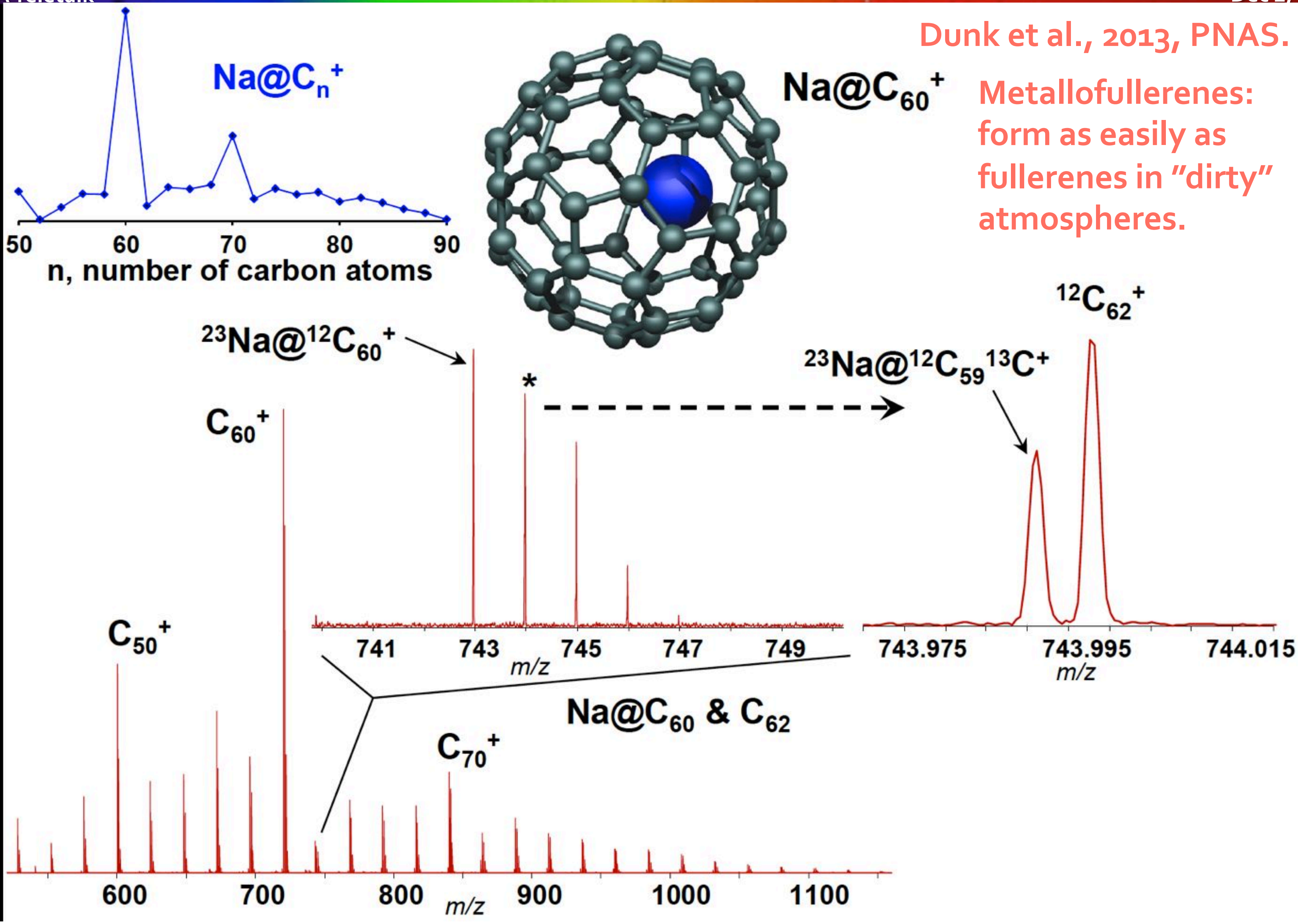


- C_{60} ring: edge of ionized zone / PDR?
- → Determine Go, n, T with [OI] and [CII] cooling lines and far-IR continuum.
- FIFI-LS and HAWC will observe all C_{60}-Pne.

Metallofullerenes

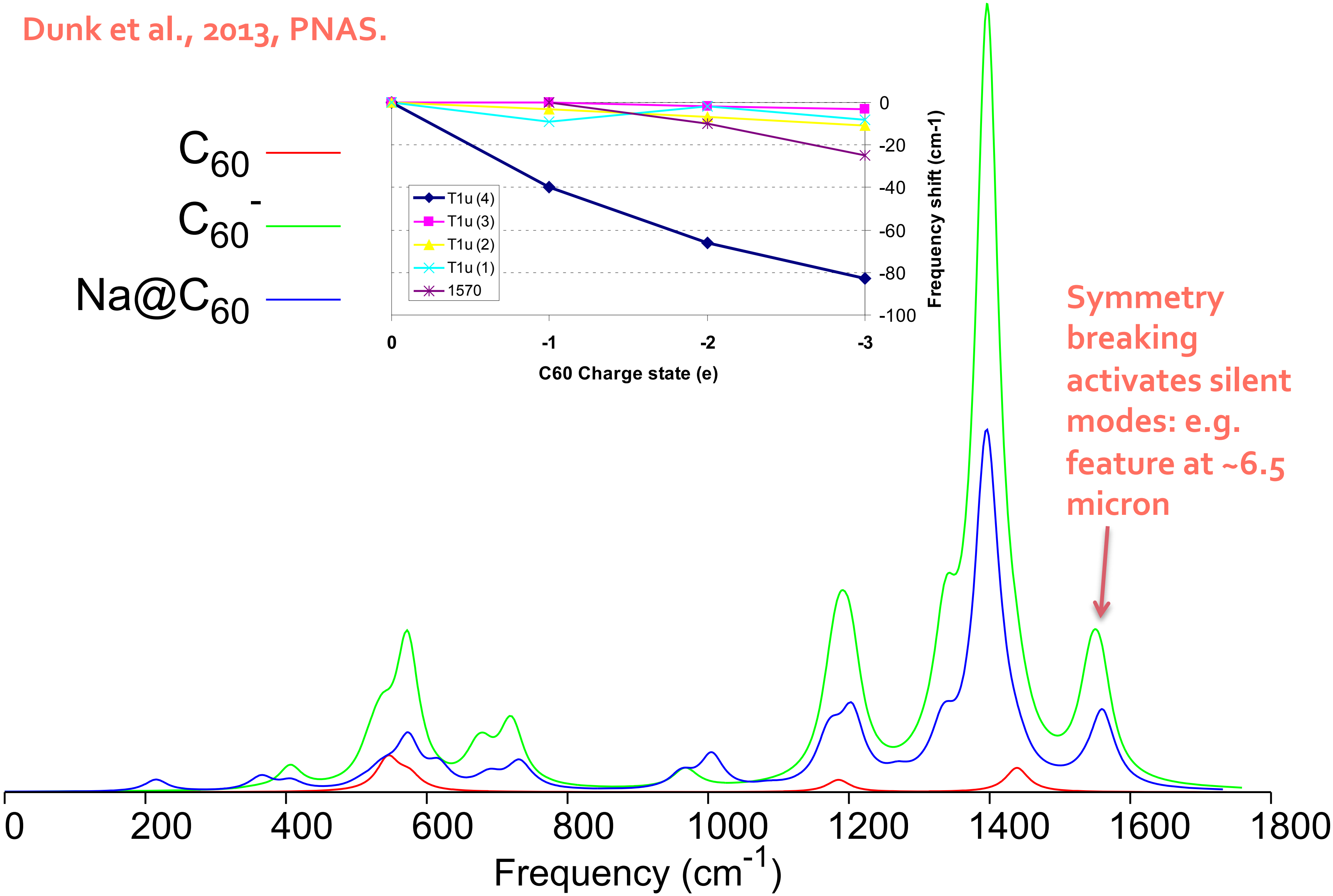
Dunk et al., 2013, PNAS.

Metallofullerenes: form as easily as fullerenes in "dirty" atmospheres.

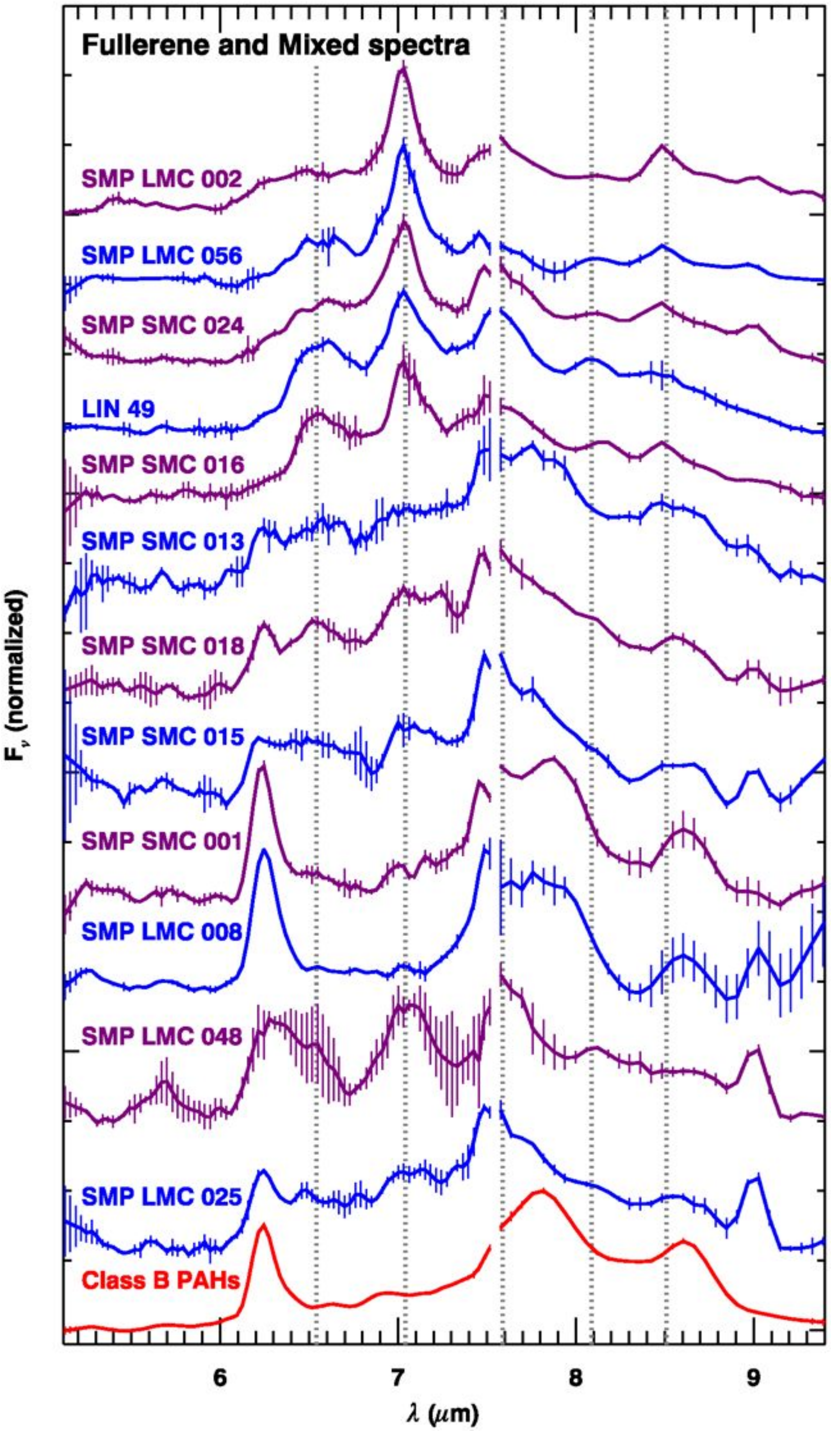


IR metallofullerenes

Dunk et al., 2013, PNAS.



Symmetry breaking activates silent modes: e.g. feature at ~6.5 micron



IR post-AGB

Dec 2, 2015

Fullerene-rich post-AGB stars exhibit additional features as well!

Could these be the silent modes?

Sloan et al. (2014).

How much C_{60} is there?

- In RNe: *peak* abundance ~10^{-4} of cosmic C.
- In PNe: uncertain estimates;
  range from ~10^{-5} to ~1.5%.

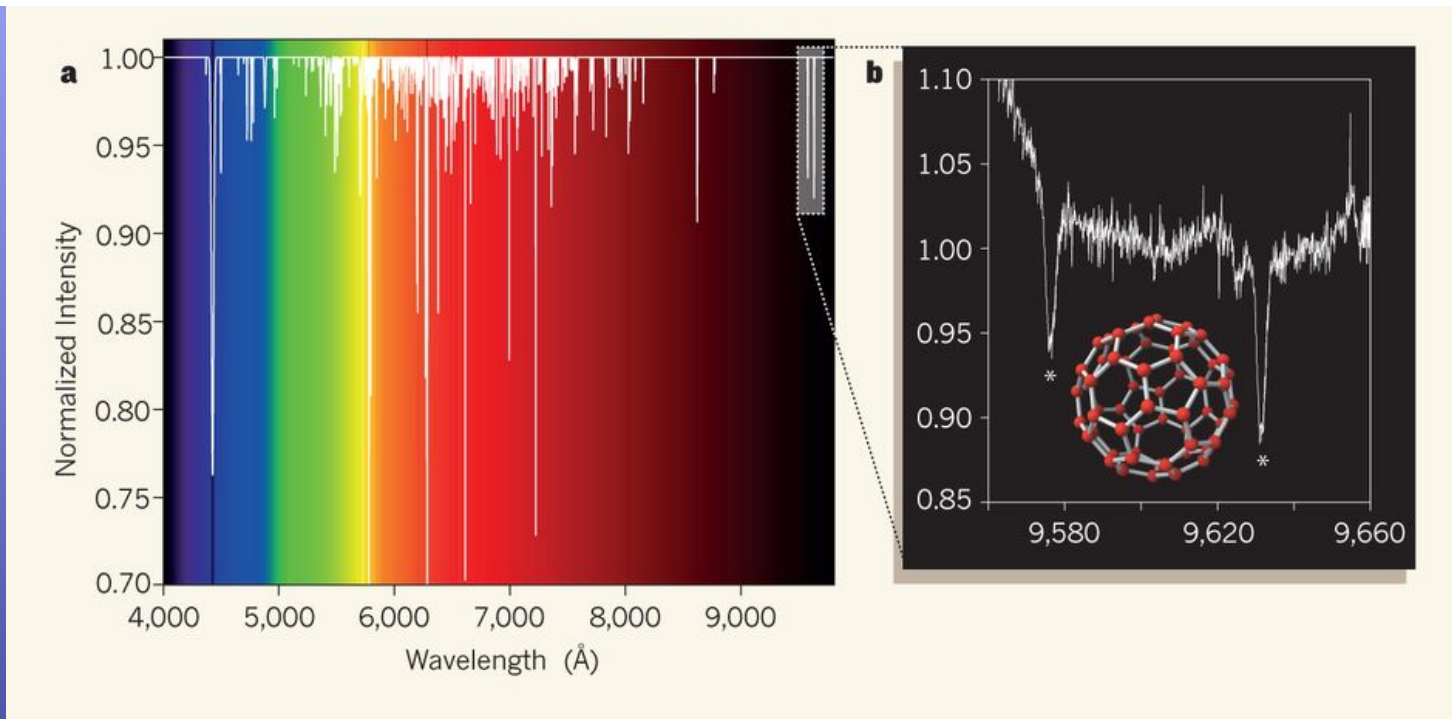
LETTER

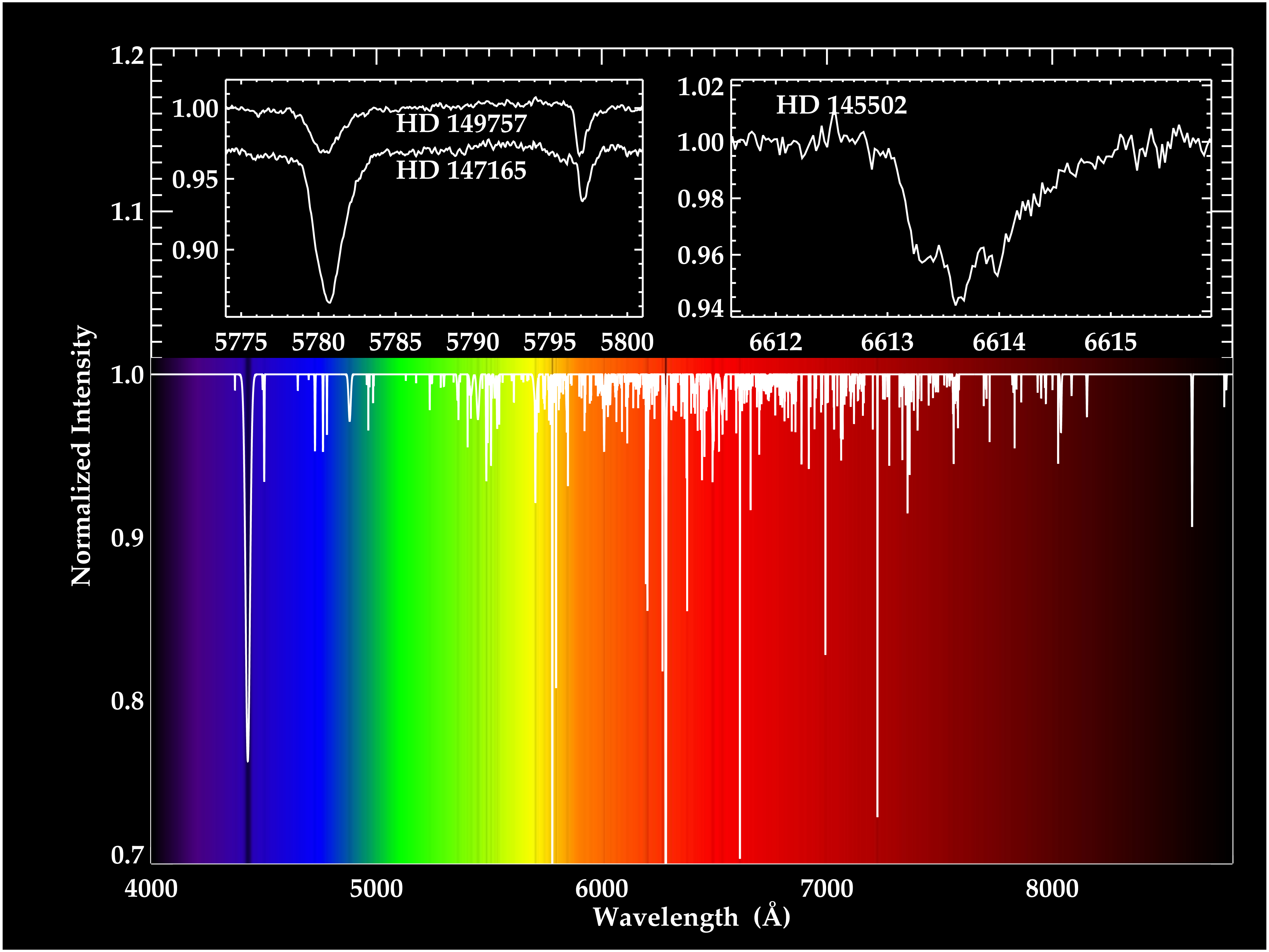
doi:10.1038/nature14566

Laboratory confirmation of $C_{60}{}^{+}$ as the carrier of two diffuse interstellar bands

E. K. Campbell[1], M. Holz[1], D. Gerlich[2] & J. P. Maier[1]

Implies ~0.5% of C in $C_{60}{}^{+}$





HD 149757
HD 147165
HD 145502
Normalized Intensity
Wavelength (Å)
1.2
1.1
1.0
0.9
0.8
0.7
1.00
0.95
0.90
5775
5780
5785
5790
5795
5800
1.02
1.00
0.98
0.96
0.94
6612
6613
6614
6615
4000
5000
6000
7000
8000

Abundances / Strengths

$$\frac{W}{E_{B-V}} = 3\ [\mathrm{m}\mathring{A}] \left(\frac{\chi_{DIB}}{10^{-4}}\right)\left(\frac{60}{N_C}\right)\left(\frac{\lambda}{5000\mathring{A}}\right)^2\left(\frac{f}{10^{-2}}\right)$$

χ_{DIB} **Fraction of C in DIB carrier**

- Medium / strong DIBs require:
  - **High Abundance** and/or
  - **Small**(er) **size** and/or
  - **Large** Oscillator **strength**: can we find species (or mechanisms) with much stronger transitions?

DIBs & Fullerenes

- C_{60}^{+} bands seen in UV-dominated environments (e.g. Orion).
- What happens to fullerenes in less extreme diffuse clouds?
- → chemical evolution, with great potential for DIB carriers, given C_{60}^{+} abundance!

The Fullerene Future

- Study detailed (spatially resolved) physical conditions and abundances for the PNe to figure out fullerene formation (and dust processing).
- Study physical and spectral characteristics of fullerene derivatives.
- What is the overall fullerene abundance?
- What happens to the cages? Can they survive and play a role in the DIBs?
- Big picture: formation, processing and destruction of carbonaceous dust.

Key Points

Fullerene family is present in space

In evolved stars, ISM, YSOs.
Mostly neutral C_{60}, some C_{70}, but also fullerene derivatives.

Formation: PAHs → C_{60} in Reflection Nebulae

Planetary Nebulae may require other route.
Possibly closed network growth in SNe.

Something happens to the fullerenes

Fullerene signature disappears in PNe → evolution into.. ?

Credits to the Cast

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