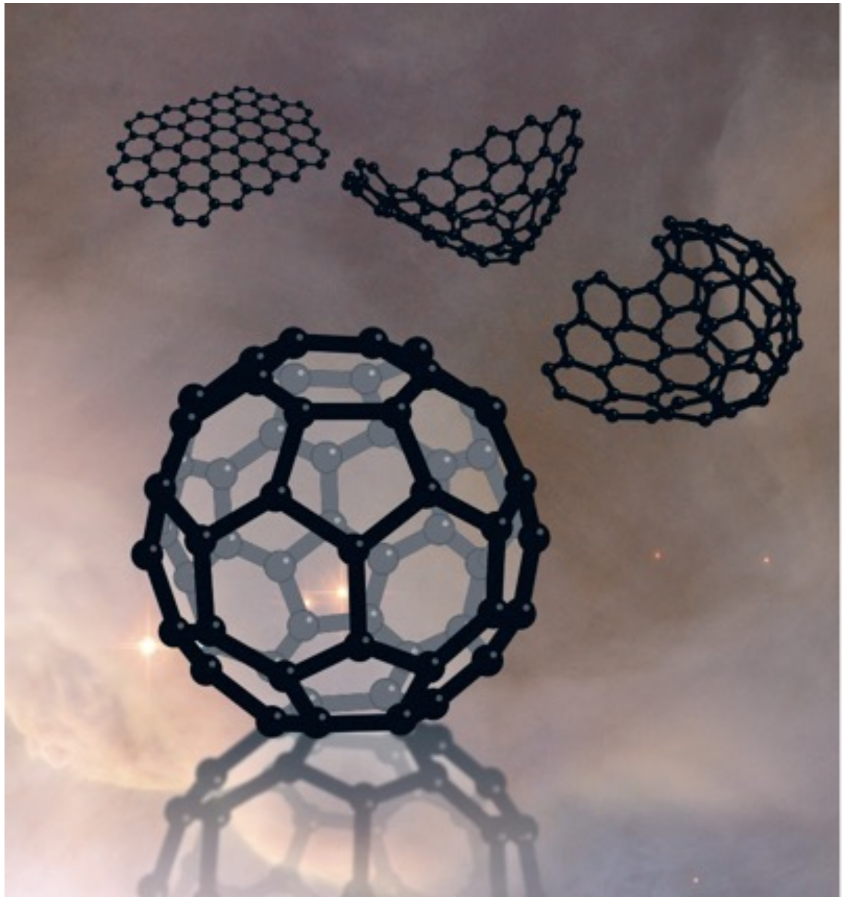
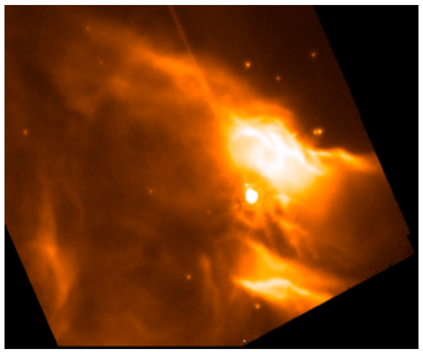
Cosmic fullerenes



O. Berné (IRAP / CNRS and Univ. Toulouse)

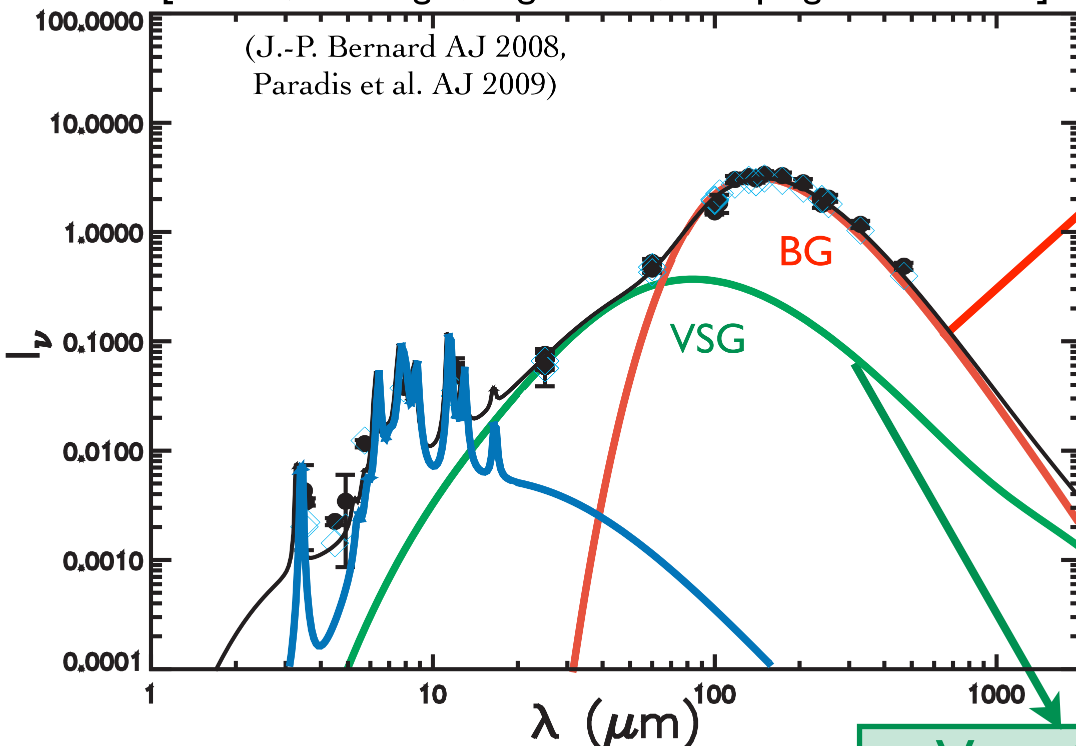
Contributors to the work presented today:
J. Montillaud (Obs. Besançon)
C. Joblin (IRAP / CNRS and Univ Toulouse)
G. Mulas (INAF Cagliari)
A. G. G. M. Tielens (Leiden University)
M. Rosenberg (Leiden University) **C. Boersma** (NASA Ames)

The infrared emission of dust in galaxies



NGC 7023, 8 μm

[Désert, Boulanger, Puget 1990, Compiègne et al. 2011]



Big Grains (BG)

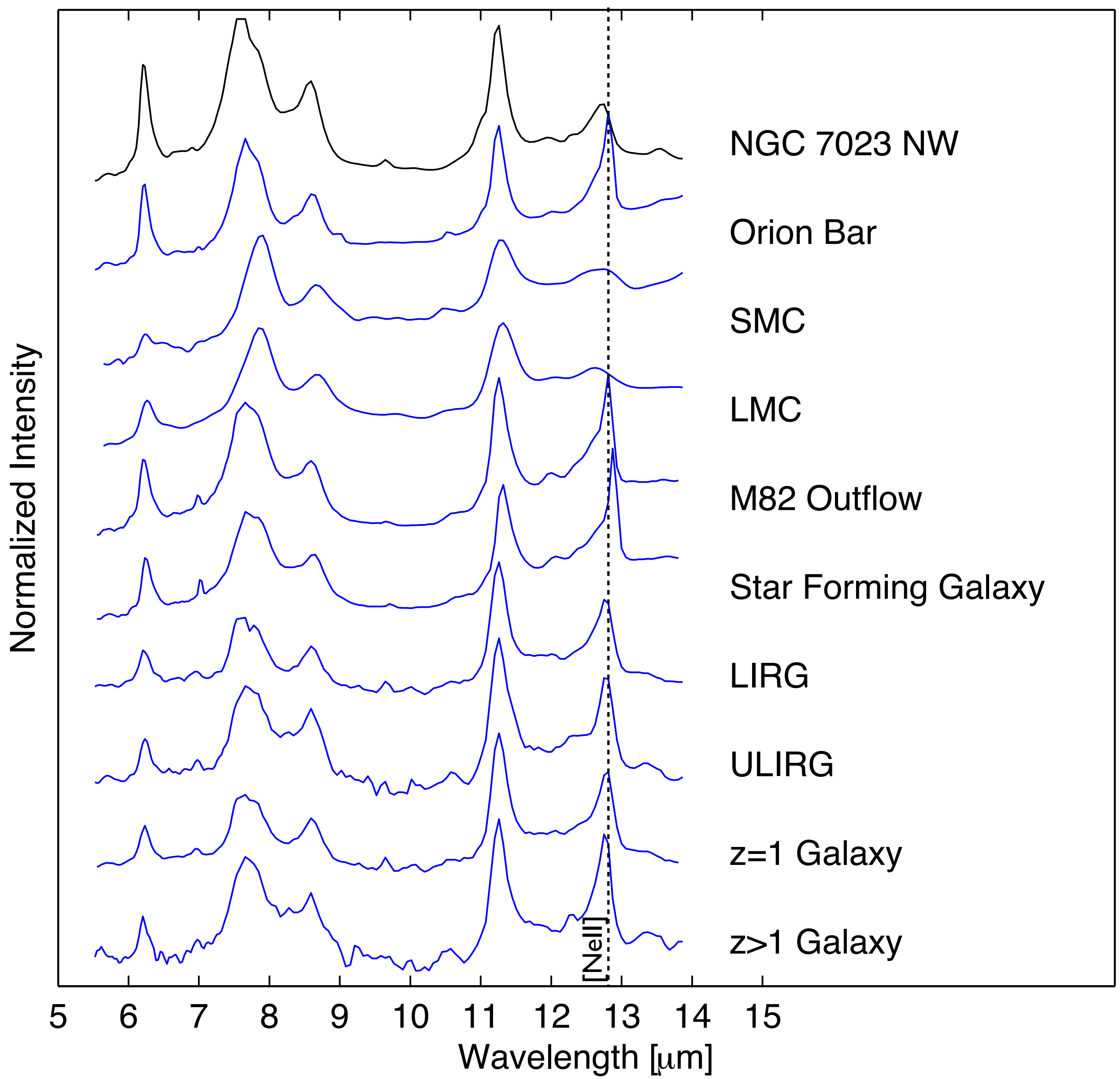
Silicate
size > 0.1 μm

Very Small Grains (VSGs)

carbonaceous,
10-100 nm...

(Désert et al. A&A, 1990; Draine & Li, ApJ, 2001)

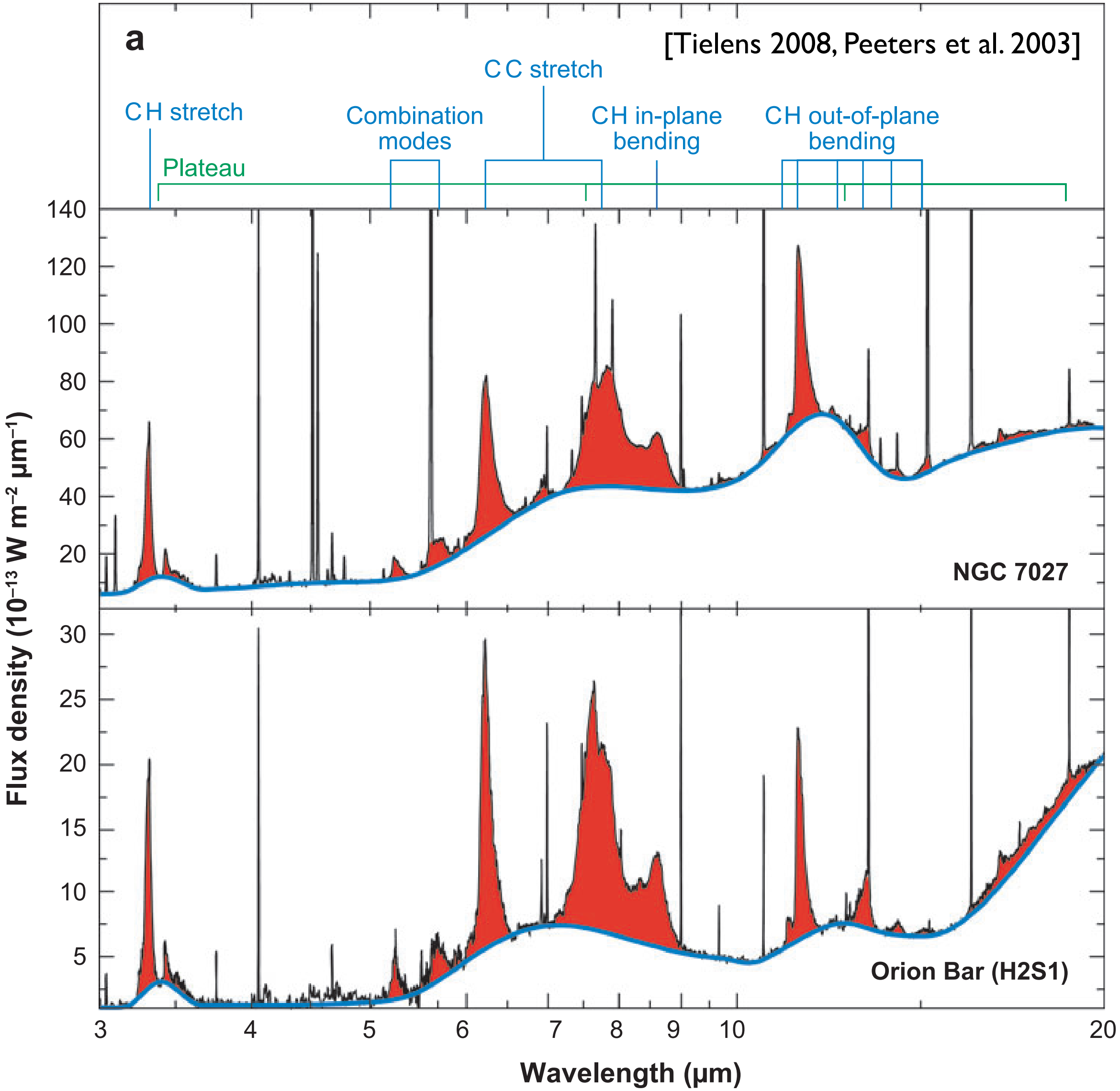
[Rosenberg, Berné, Boersma A&A 2014]



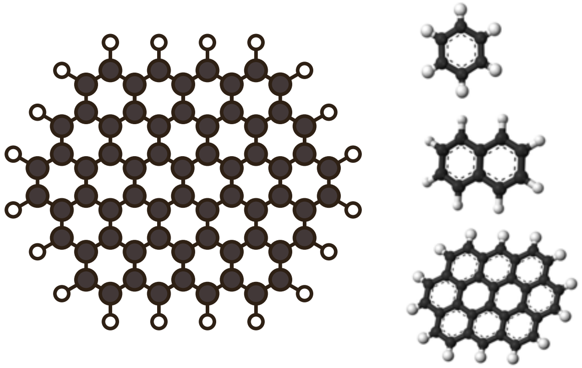
The PAH model

1984/1985 proposal that mid-IR bands are due to gas phase PAHs

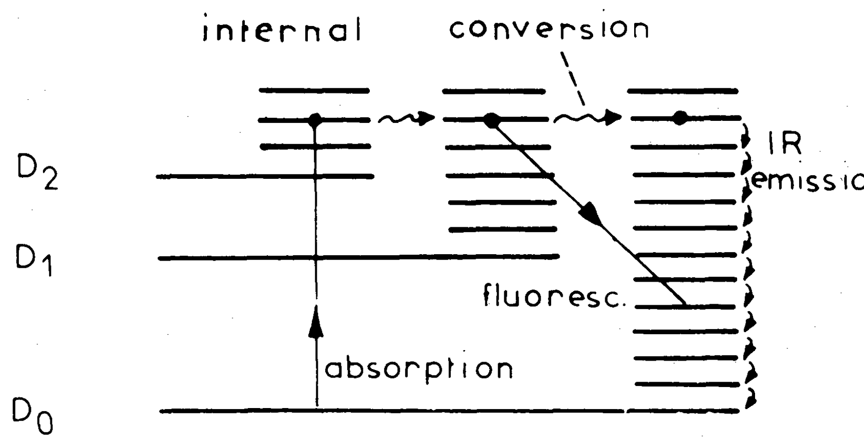
[Léger & Puget 1984] [Allamandola, Tielens, Barker 1985]



Polycyclic Aromatic Hydrocarbons (PAHs)



Emission by fluorescence (gas phase)



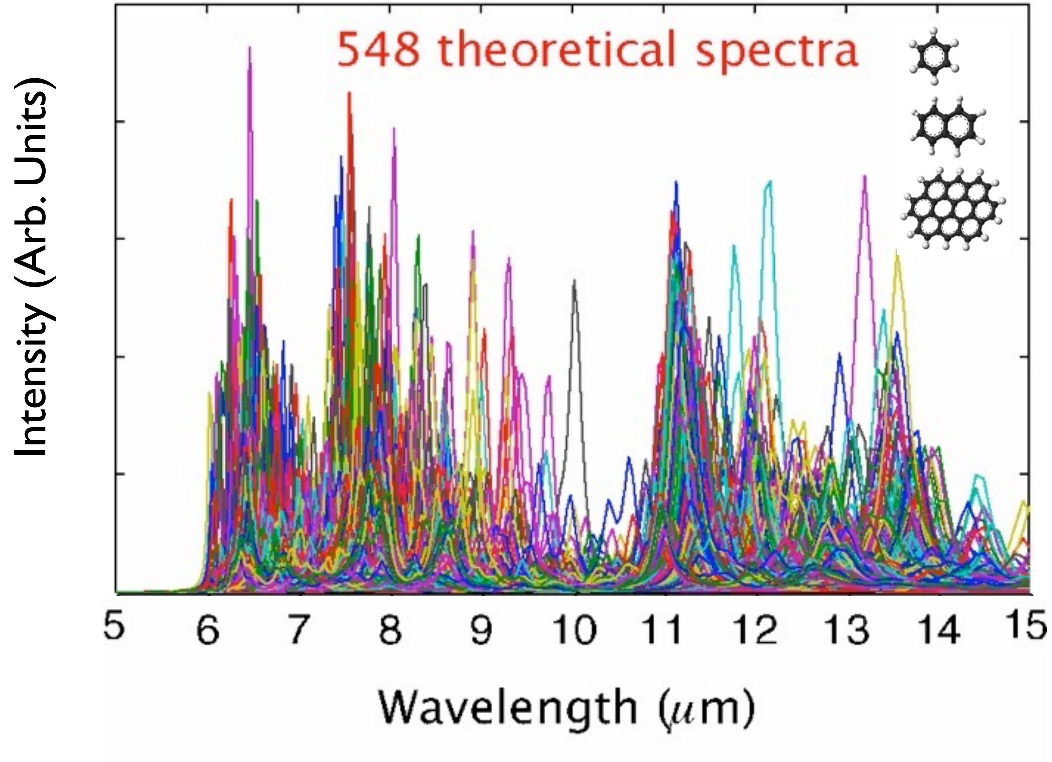
[Léger, d'Hendecourt, Défourneau, 1989]

No specific PAH molecule identified !

Random mixtures of PAHs

[Rosenberg, Berné, Boersma A&A 2014]

The NASA-Ames database: calculated spectra for more than 600 species, with a range of size and charge state http://www.astrochem.org/pahdb/ [Bauschlicher, Boersma et al. 2012] [Boersma et al. 2014]



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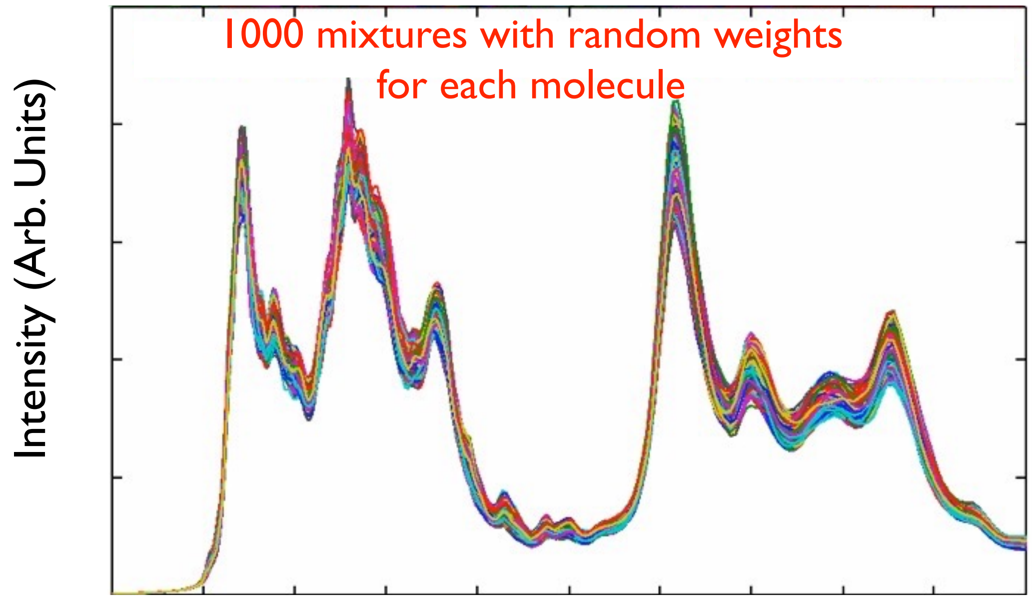

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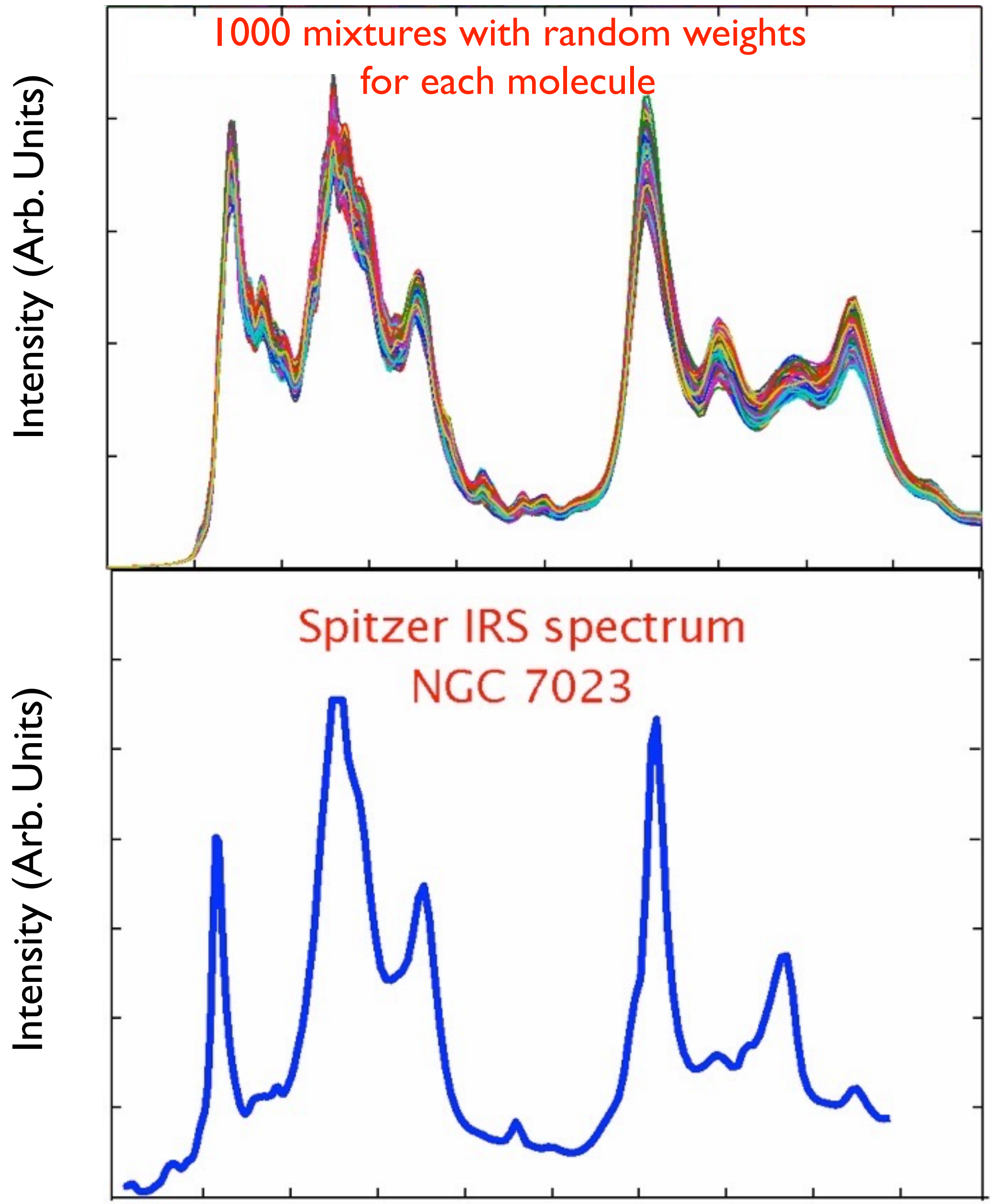
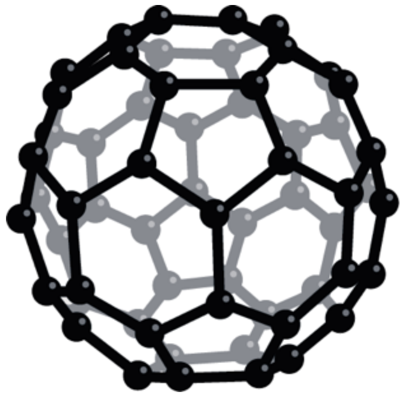


The serendipitous discovery of C_{60}



1985 Discovery of the C_{60} molecule in the lab

[Kroto, Heath, Obrien, Curl, Smalley, Nature, 1985]

162 LETTERS TO NATURE NATURE VOL. 318 14 NOVEMBER 1985

C_{60}: Buckminsterfullerene

H. W. Kroto*, J. R. Heath, S. C. O'Brien, R. F. Curl & R. E. Smalley

Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77251, USA

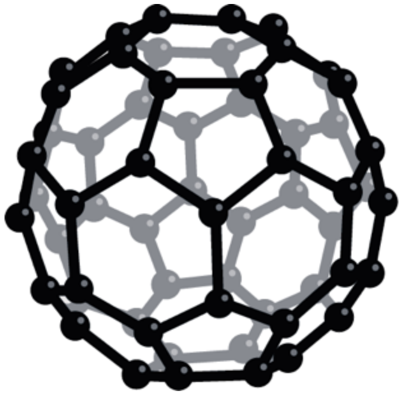
During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells[1], graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60-carbon atom structure might give rise to a superstable species, we suggest a truncated icosahedron, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. This object is commonly encountered as the football shown in Fig. 1. The C_{60} molecule which results when a carbon atom is placed at each vertex of this structure has all valences satisfied by two single bonds and one double bond, has many resonance structures, and appears to be aromatic.

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.

graphite fused six-membered ring structure. We believe that the distribution in Fig. 3*c* is fairly representative of the nascent distribution of larger ring fragments. When these hot ring clusters are left in contact with high-density helium, the clusters equilibrate by two- and three-body collisions towards the most stable species, which appears to be a unique cluster containing 60 atoms.

When one thinks in terms of the many fused-ring isomers with unsatisfied valences at the edges that would naturally arise

The serendipitous discovery of C_{60}



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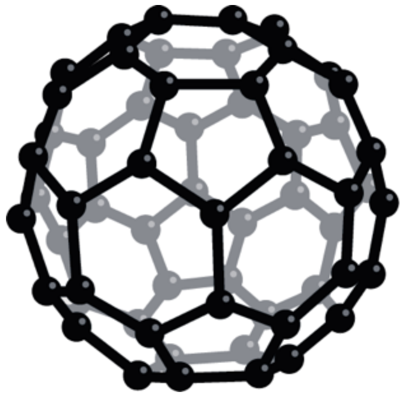
Richard Buckminster Fuller

The serendipitous discovery of C_{60}



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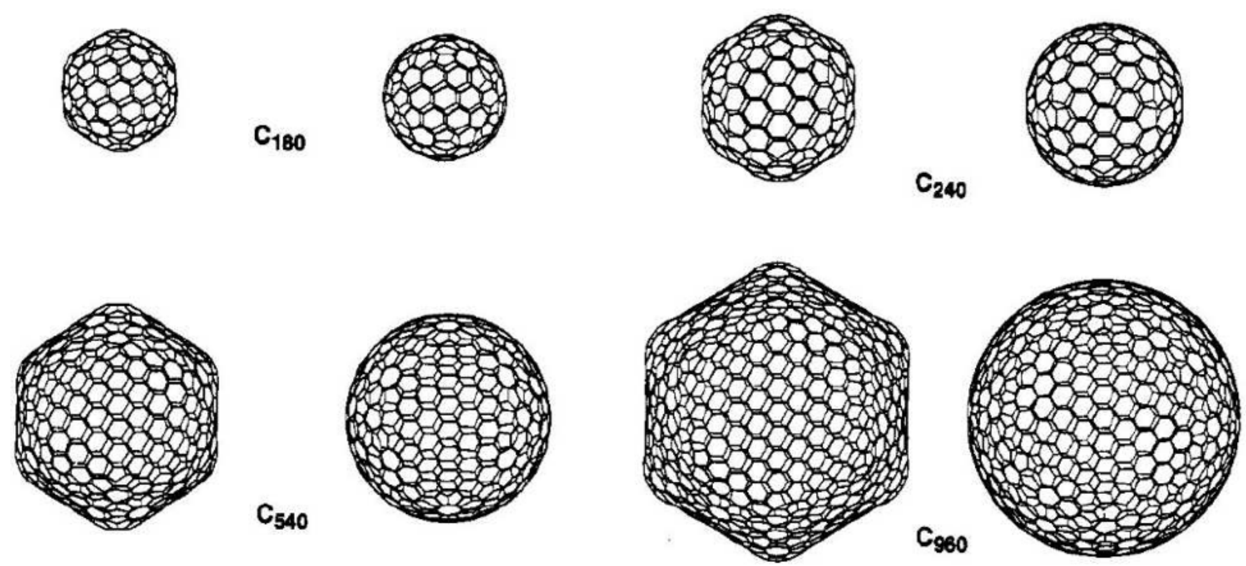
We are disturbed at the number of letters and syllables in the rather fanciful but highly appropriate name we have chosen in the title to refer to this C_{60} species. For such a unique and centrally important molecular structure, a more concise name would be useful. A number of alternatives come to mind (for

Fullerenes



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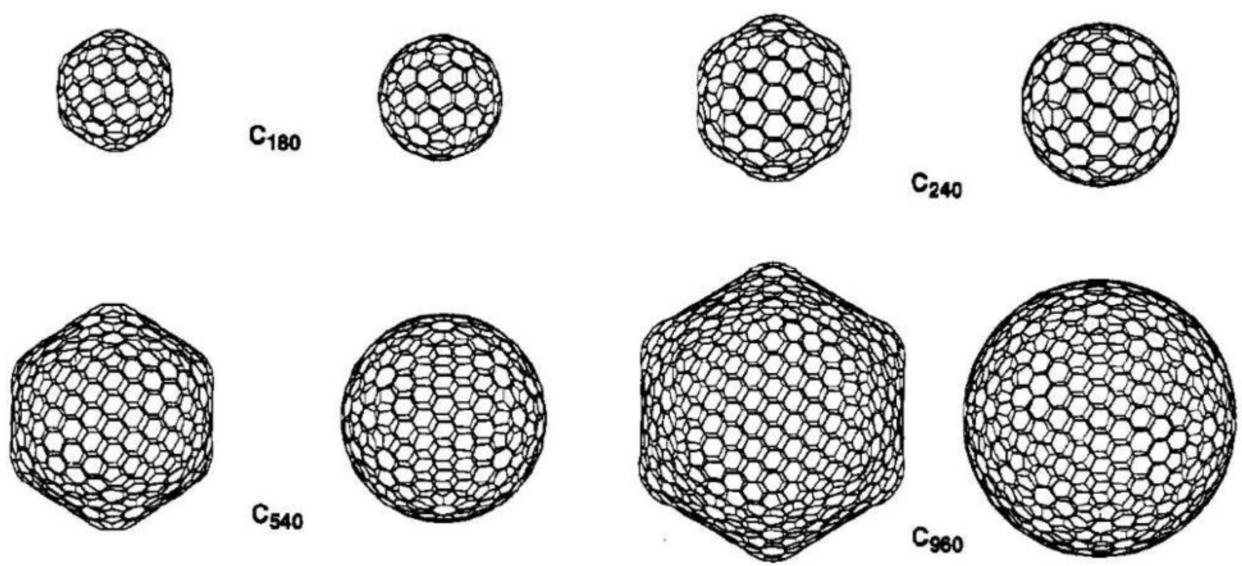

The serendipitous discovery of C_{60}

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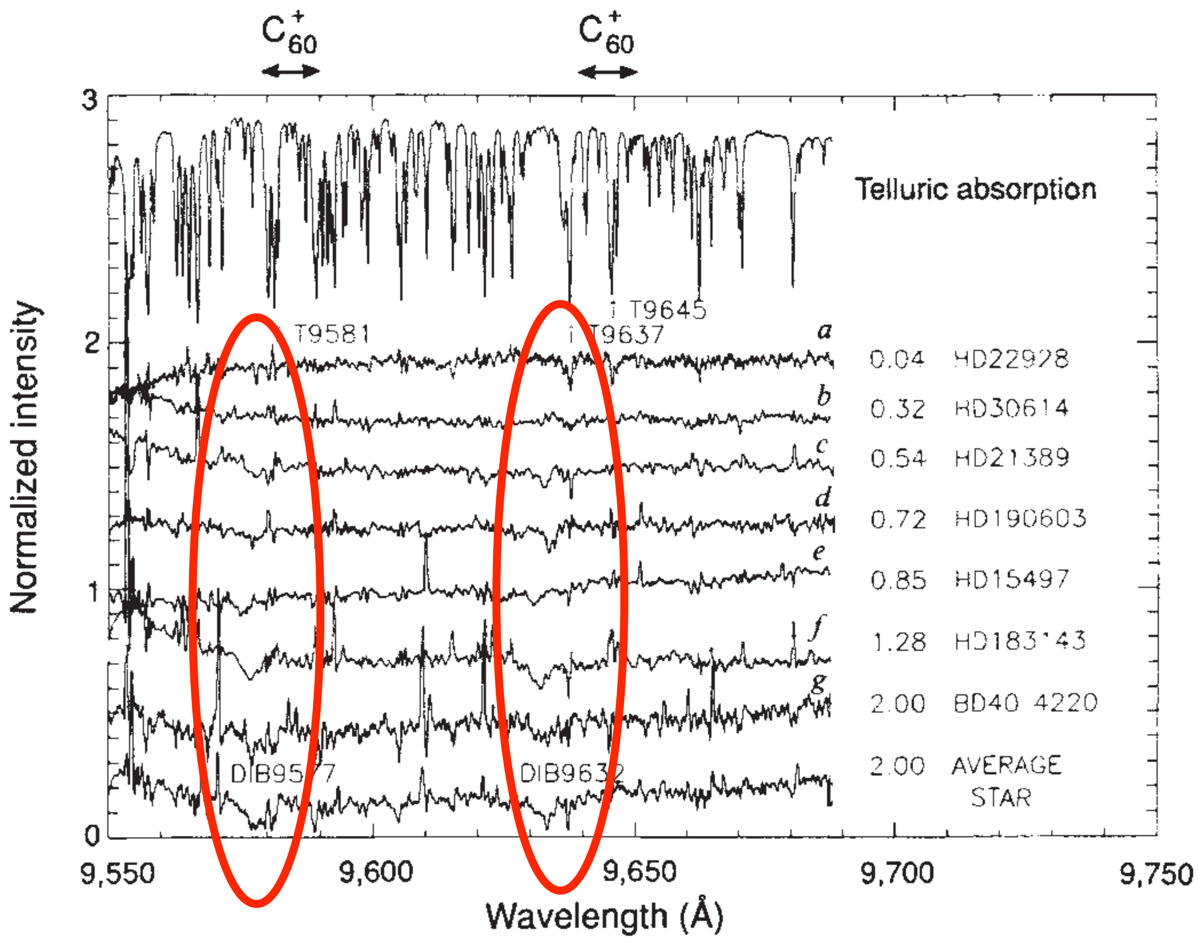
During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells[1], graphite has been vaporized by laser

C_{60} in space ?

1994

Detection of two interstellar absorption bands coincident with spectral features of C_{60}^{+}

B. H. Foing* & P. Ehrenfreund†

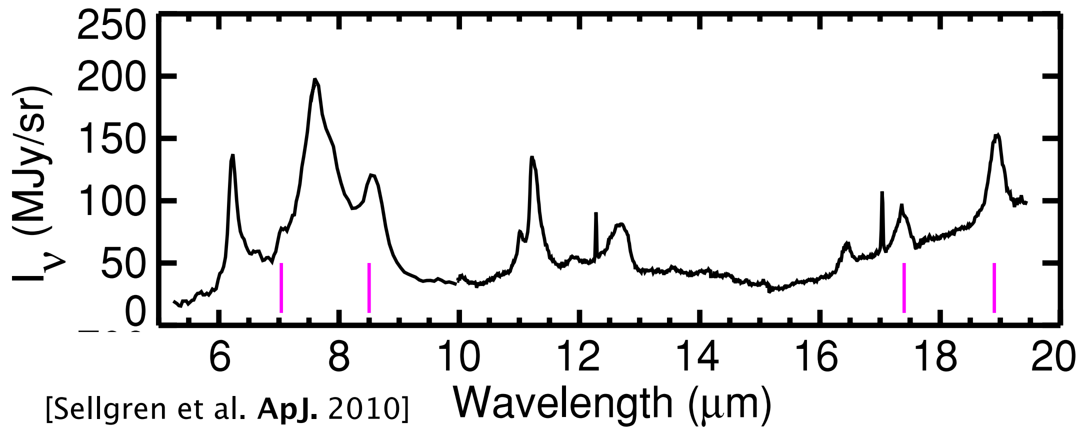


The identification of C_{60}^{+} based on coincidence of absorption bands with lab spectra is questioned by the fact that no cold, gas phase, spectroscopic data exist for this molecule

The existence of large gas phase carbon molecules

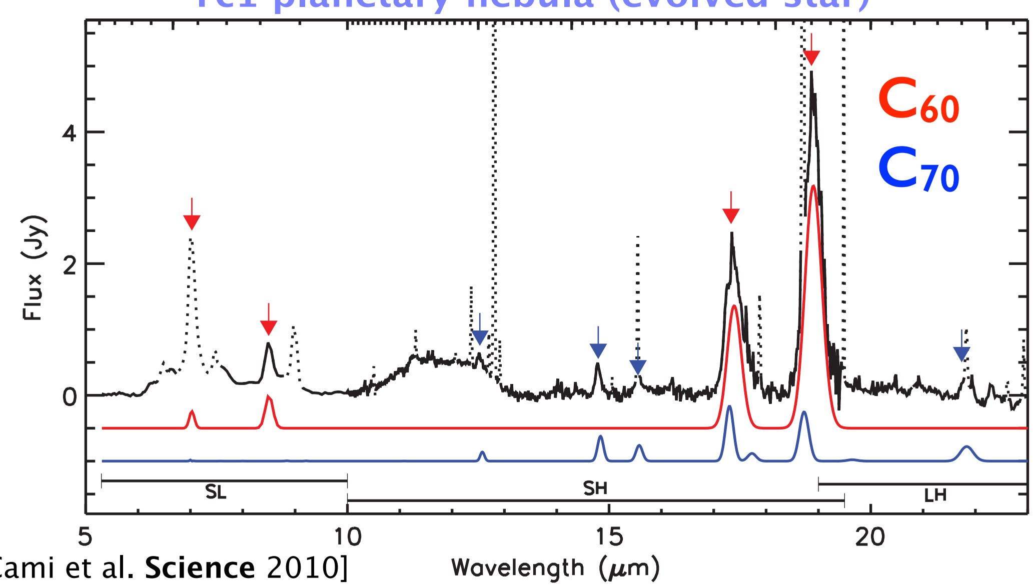
2010 Discovery of the C_{60} molecule in emission in space

NGC 7023 reflection nebula (interstellar medium)

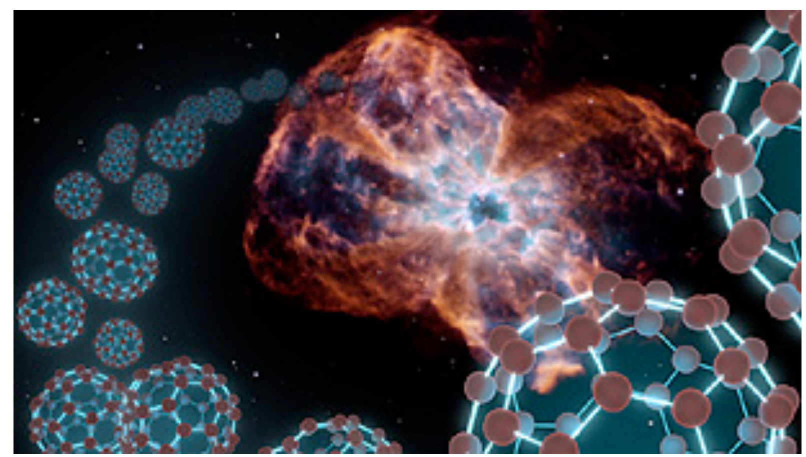


[Sellgren et al. **ApJ.** 2010]

Tc1 planetary nebula (evolved star)



[Cami et al. **Science** 2010]



Neutral form ! + Proposed to be in the solid phase by Cami et al. while Gas phase by Sellgren et al.

2010 summary of all the problems

On C_{60}

- How is C_{60} formed ?

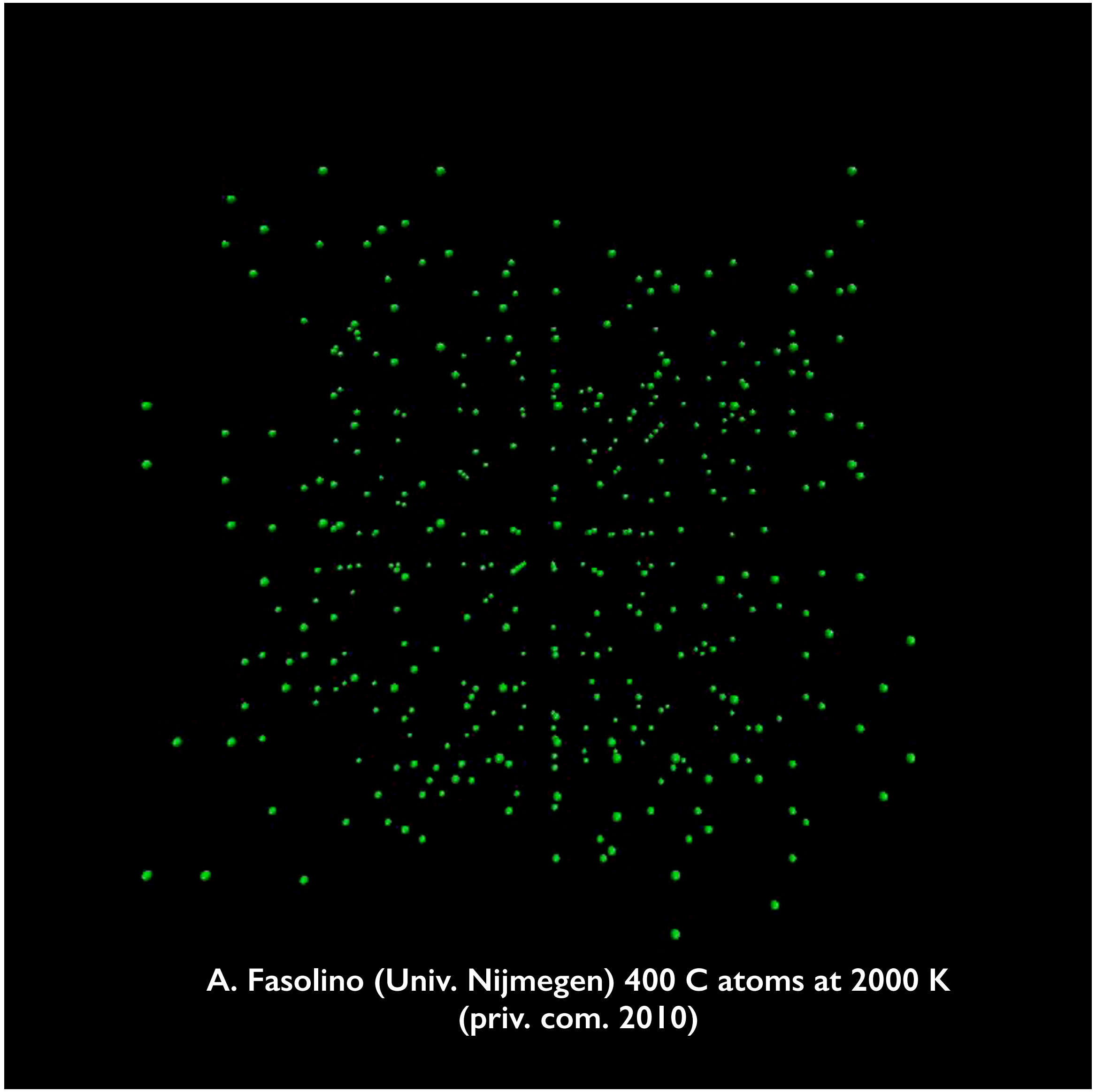
- C_{60} was detected, but it could not be proven that it is fluorescing

- C_{60} was detected, but given the harsh conditions in the ISM it should be ionized, in fact there is a claim of detection of C_{60}^{+} in absorption...

On the PAH model

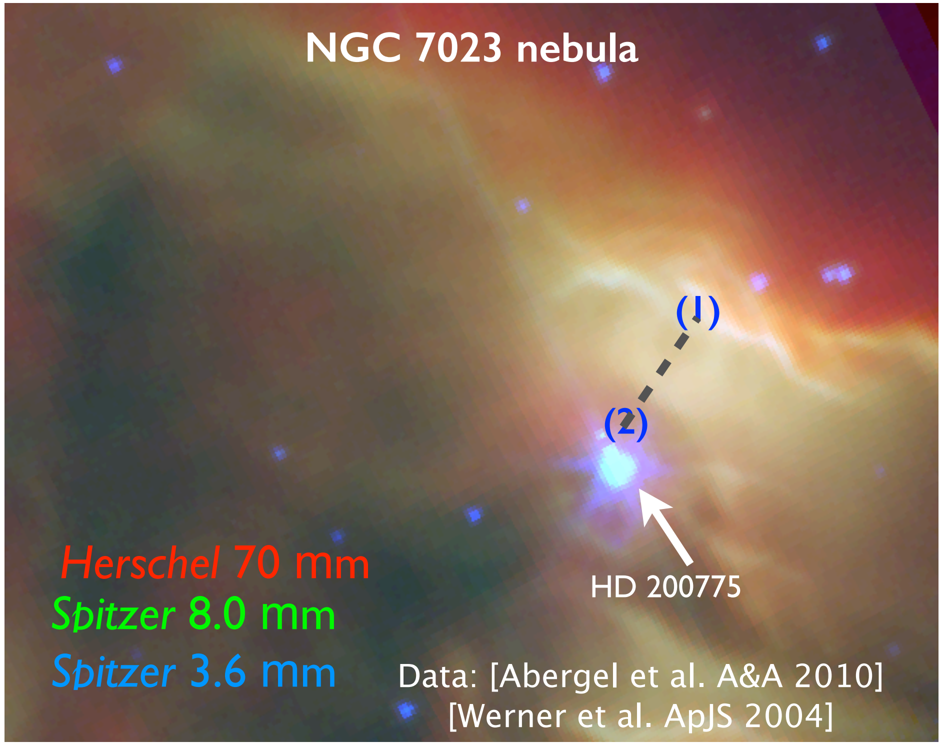
- The definitive proof of the existence of a specific gas phase carbon macro-molecule, heated to high T by individual UV photon has not been provided yet... for many astronomers this is a severe caveat of the PAH model (see dispute in the literature recently : Kwok & Zhang vs Li & Draine)

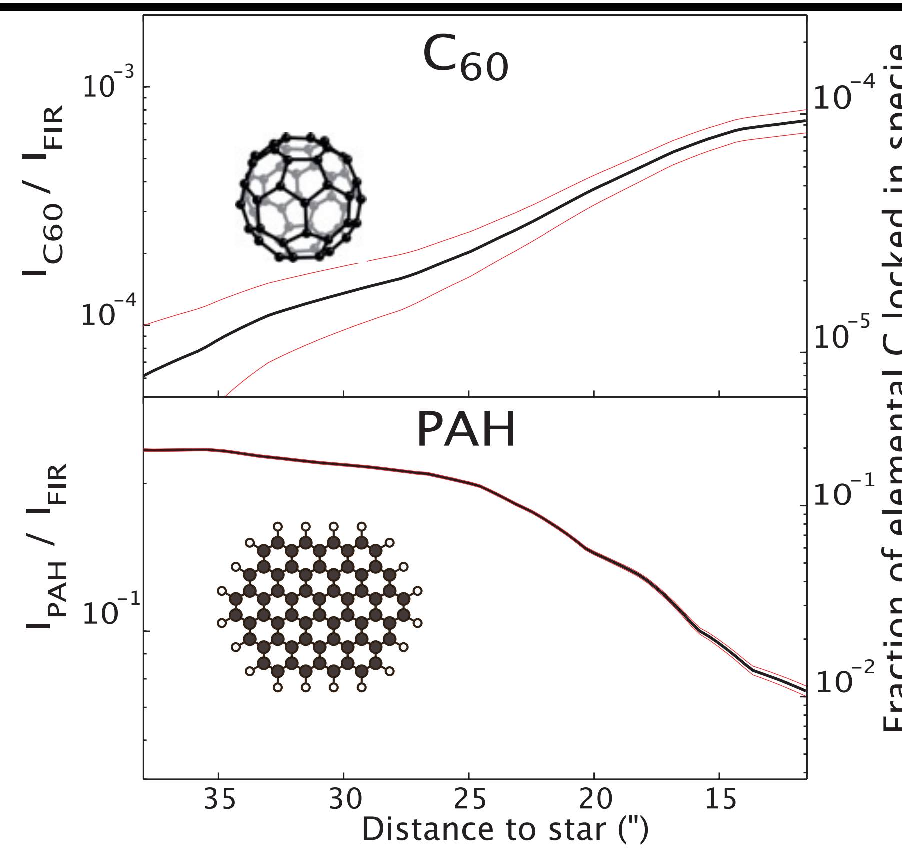
The formation of C_{60}

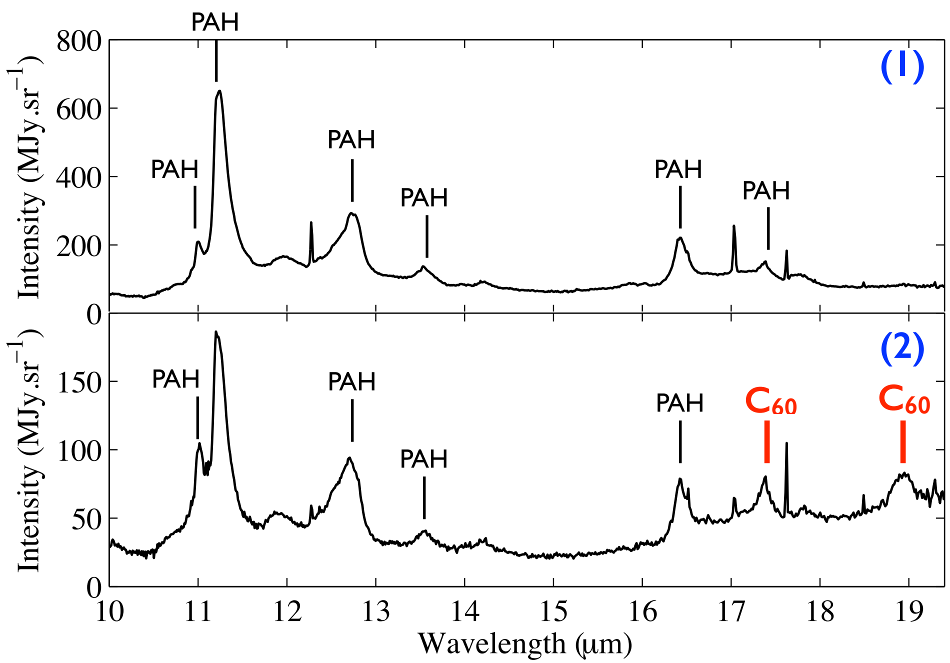


[Smalley 1992, Goroff 1996, Kroto & McKay 1988, Health 1991, Hunter et al. 1992, Rubin et al. 1991, Irle et al. 2006, Huang et al. 2007, Dunk et al. 2013]

Observational evidence of C_{60} formation in the ISM







C_{60} is formed in the interstellar medium, at low density (n_H=100 cm^{-3}) !

Aggregation (bottom up) process not possible !

C_{60} formation from photochemical PAH processing ?

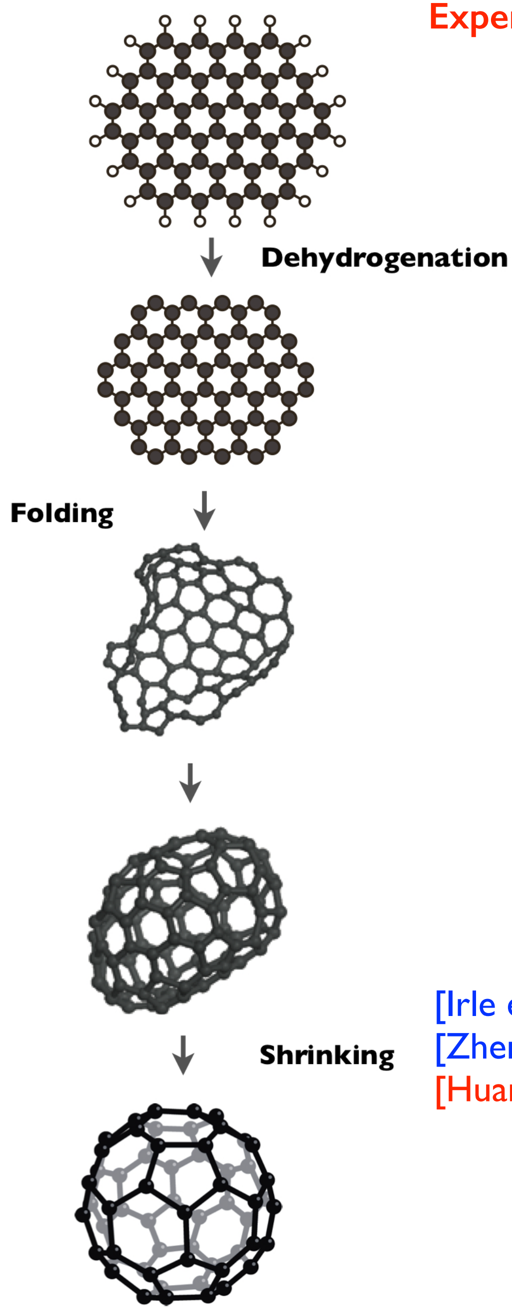
Conversion efficiency from PAHs to C_{60} ~0.1% at 15'' from the star in 10^5 years (age of the nebula)

[Berné & Tielens **PNAS** 2012]

Proposed scenario

Theoretical studies
Experimental studies

Increasing UV radiation field

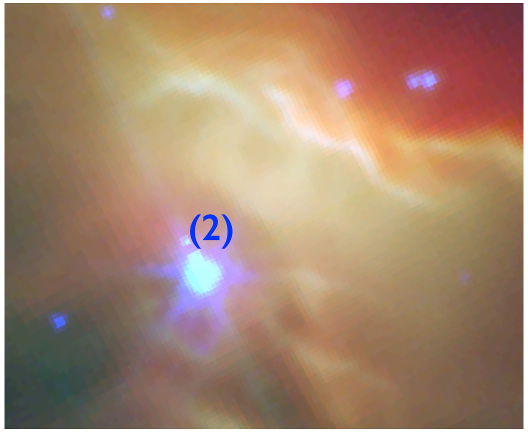


[Le Page et al. 2001]
[Montillaud et al. 2013]
[Lifshitz and co-workers, 199x]
[Jochims et al. 1994]
[Ekern et al. 1998]
[Szczepanski et al. 2001] ...

[Lebedeva et al. 2012]
[Chuvilin et al. 2010]

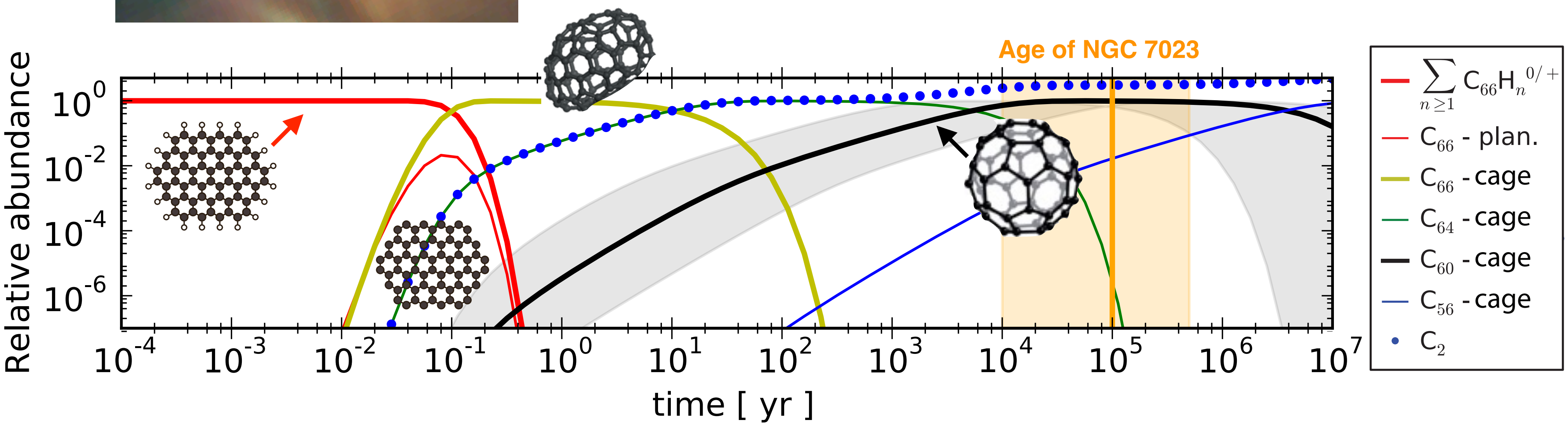
[Irle et al. 2006]
[Zheng et al. 2007]
[Huang et al. 2007]

Photochemical model for $C_{66}H_{20}$ to C_{60} in NGC 7023



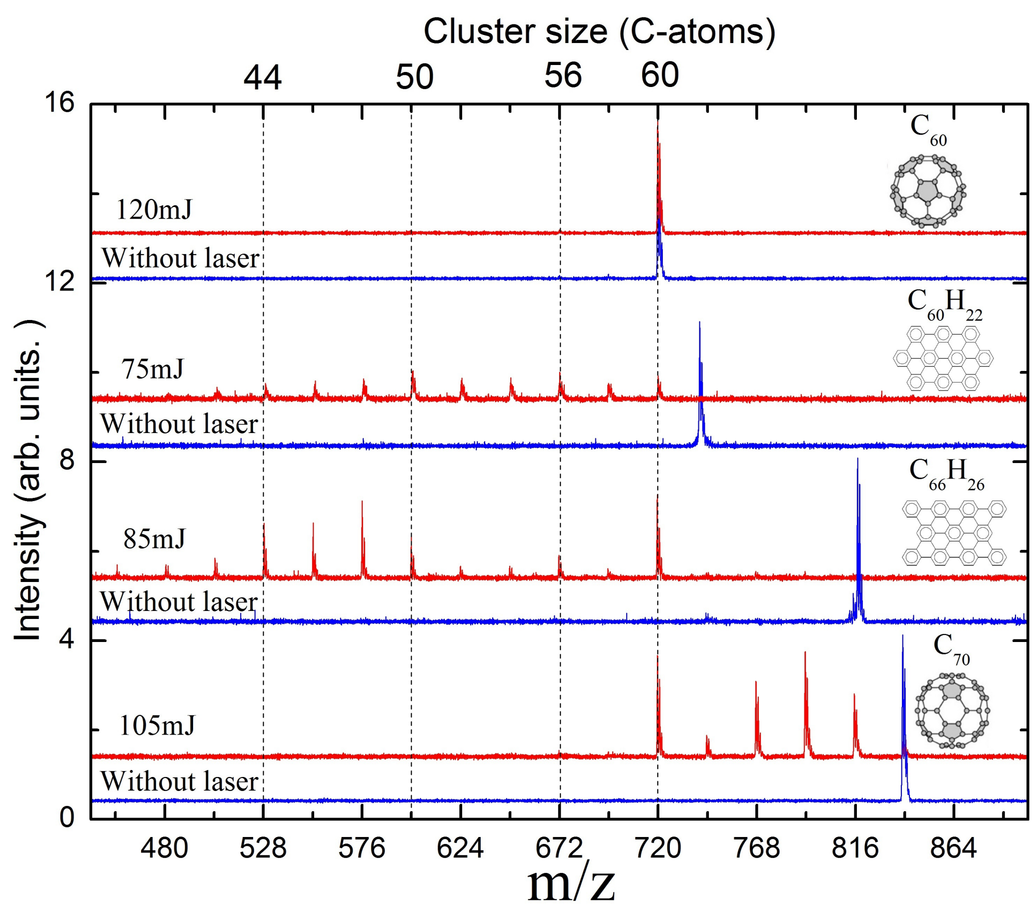
[Berné, Montillaud, Joblin, A&A 2015]

At 10” from the star
Go ~ 10^5
n_H ~ 500



- Circumovalene quickly dehydrogenated
- Graphene flakes (dehydrogenated PAHs) are unstable,
- Shrinking step takes typically 10^4 years,
- Yet we can reach C_{60} in about ~10^5 years a timescale comparable to the age of NGC 7023,
- C_2 molecules are formed from the destruction of cages but will likely be destroyed,
- Similarly, PAHs smaller than 60 C atoms will be destroyed (unless converted in something more stable),
- In the end, **only C_{60}** survives to this top down chemistry…

Laboratory confirmation



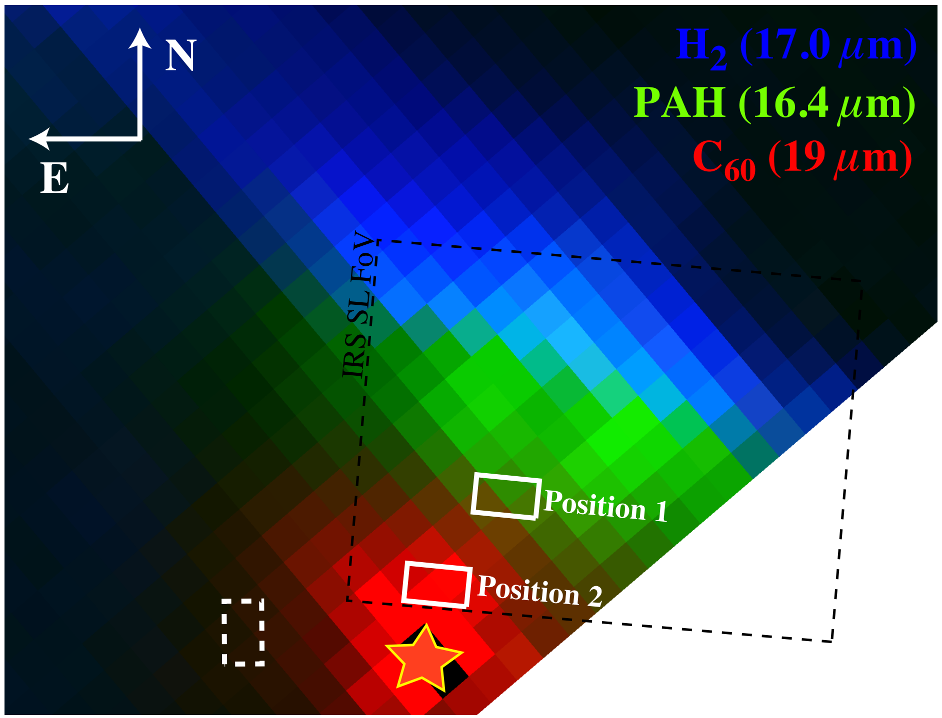
[Zhen et al. ApJ 2015]

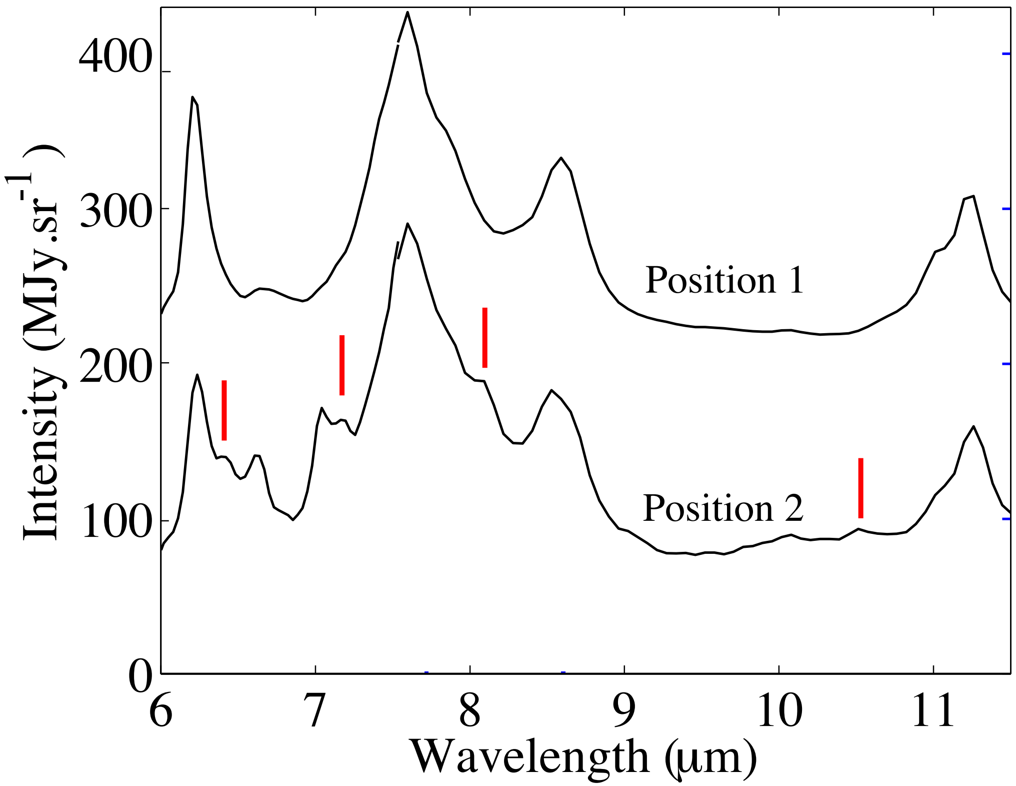
- Top down formation of C_{60} from PAHs confirmed in the laboratory

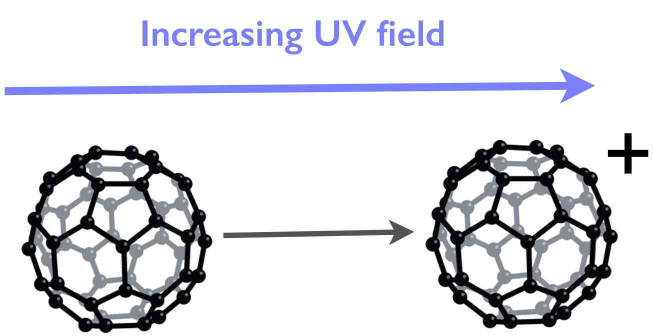
- However, pathway leading to C_{60} not clear, in particular the sequence folding vs C_2 loss

New bands in NGC 7023

Spitzer IRS long wavelength



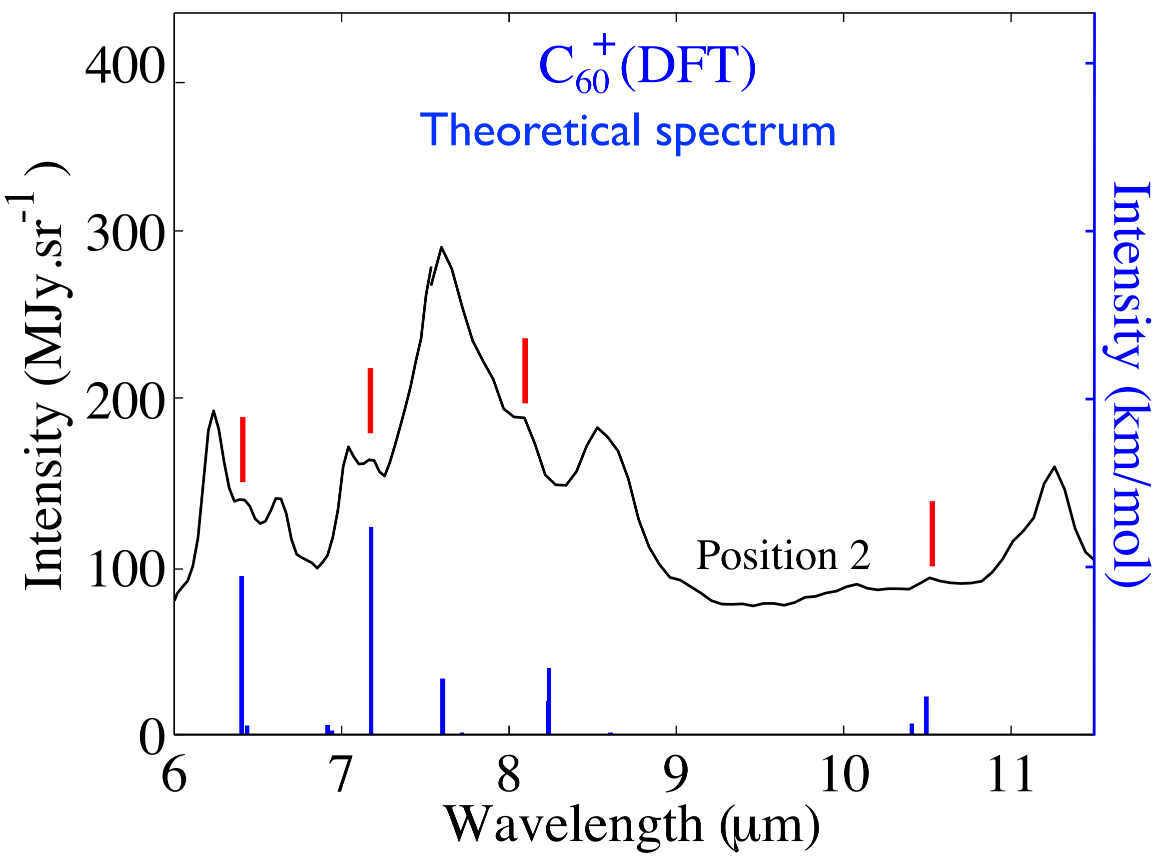




- Bands at 6.4, 7.1, 8.3 and 10.5 mm
- These bands are only present near the star
- Neutral C_{60} emission is more extended

Spectroscopy of C_{60}^+: theory vs observation

[Berné, Mulas, Joblin 2013]



Even without any emission model (which even for C_{60} is not available):

- Harmonic spectrum matches observed positions with 2% accuracy
- Bands with strongest intensities are strongest in observation

Ionization fraction and abundance:

- At observed position 38% of C_{60} is ionized
- Abundance : max 10^{-4} of the elemental C would be in C_{60}^+ (much smaller than F&E)

2015 remaining problems

On C_{60} fullerene

- C_{60} was detected, but it could not be proven that it is fluorescing
- The detection of C_{60}^+ suggests it is fluorescence

- C_{60} was detected, but given the harsh conditions in the ISM it should be ionized, in fact there is a claim of detection of C_{60}^+ in absorption...
- We detected the emission of C_{60}^+

- How is C_{60} formed ?
- We suggest it is formed from the photoprocessing of PAHs and it is confirmed in the lab that this is possible

On the PAH model

- The definitive proof of the existence of a specific gas phase carbon macro-molecule, heated to high T by individual UV photon has not been provided yet... for many astronomers this is a severe caveat of the PAH model
- C_{60}^+ is a counter example

Rugbene

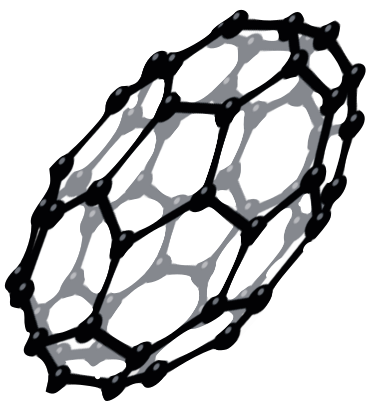
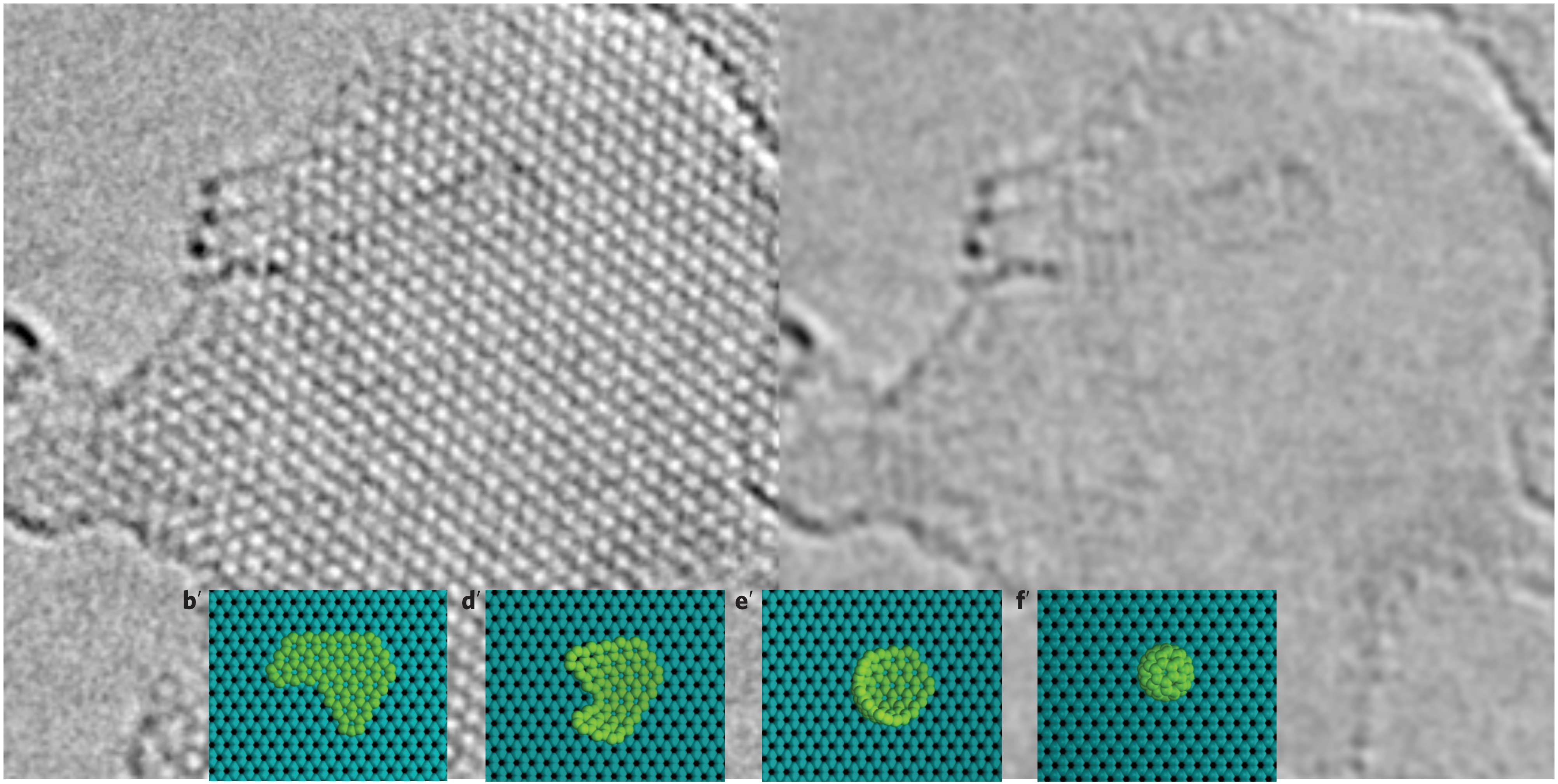


Fig. 1. a rugby ball on Toulouse grass.

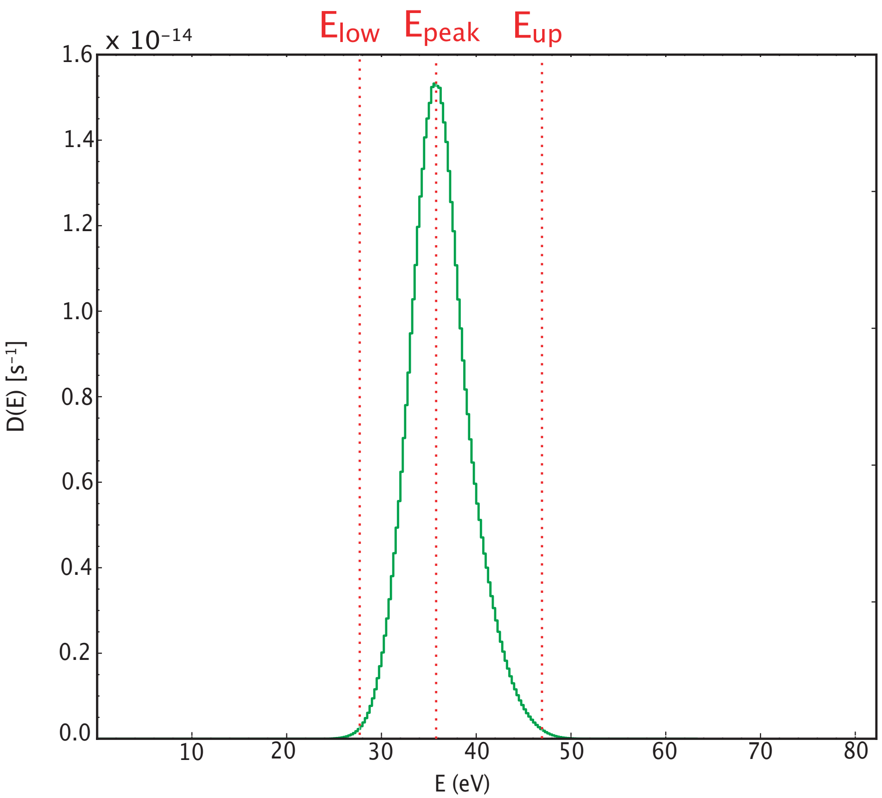
The roll up route

[Chuvilin et al. Nature Chem. 2010]



The remarkable stability of C_{60}

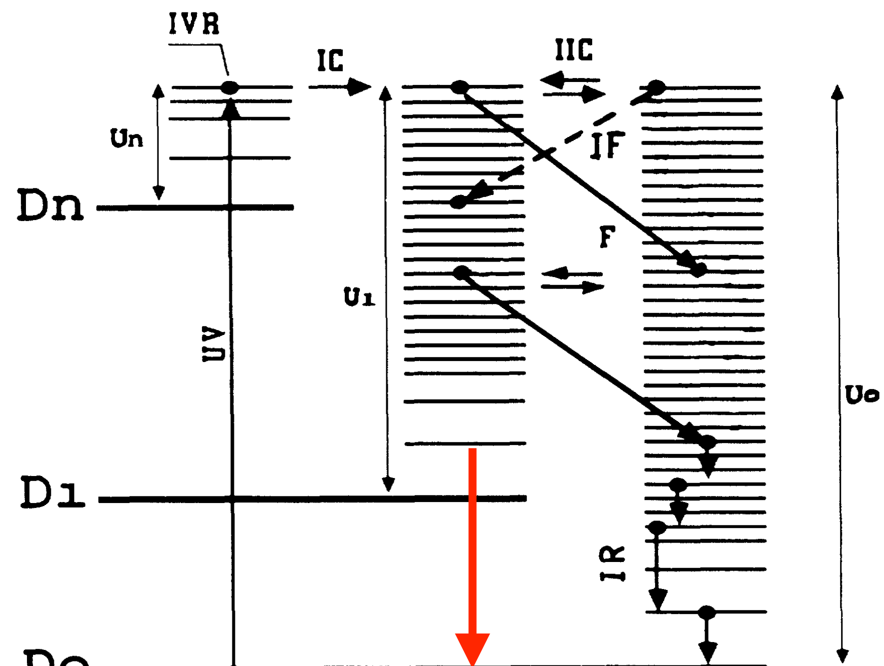
Probability of dissociation of C_{60} at 5” from the star, Go=2x10^5



Energies of dissociation for the cages

	a.		
Species*	E_{low}	E_{peak}	E_{up}
C_{66}	22	32	39
C_{64}	24	35	43
C_{62}	15	20	28
C_{60}	27	36	47
C_{58}	22	30	37

The energy required to break the cages is huge, hence these systems can survive at very high internal energies. In this case, emission from thermally excited electronic states a.k.a. Poincaré Fluorescence becomes important.



[Léger PRL 1988]