The Role of Cosmic Fullerenes

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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 $\rightarrow$ $C_{60}$ 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 $\rightarrow$ evolution into..?
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

- Processing
- Destruction
- Processing
- Formation
- Processing
- Delivery

- POLYynes
- PAHs
- DIMethyl Ether
- FULLEREnes
- ACETYLENE
- Amino Acids
- RNA
Main Sequence

Core H burning
H $\rightarrow$ He
Hydrogen Mantle

$t \sim 10$ billion yr
Main Sequence
Core H burning
Hydrogen Mantle
$t \sim 10$ billion yr
Red Giant Branch
Contracting He core
$H$ shell burning
Expanding envelope
Mass loss
Horizontal Branch
Core He burning
$He \rightarrow C \rightarrow O$
Inactive $H$ shell
$t \sim 100$ million yr
Asymptotic Giant Branch
Degenerate CO core
He shell burning
$H$ shell burning
Thermal Pulses / Dredge–up
Expanding envelope
Severe mass loss
$t \sim 10$ million yr
Main Sequence
Core H burning
H \to He
Hydrogen Mantle
t \sim 10 \text{ billion yr}

Red Giant Branch
Contracting He core
H shell burning
Expanding envelope
Mass loss
t \sim 1 \text{ billion yr}

Horizontal Branch
Core He burning
He \not\to C \not\to O
Inactive H shell
t \sim 100 \text{ million yr}

Asymptotic Giant Branch
Degenerate CO core
He shell burning
H shell burning
Severe mass loss
Expanding envelope
Thermal Pulses / Dredge-up
Expanding envelope
Degenerate CO core
= White Dwarf
Expanding envelope
might become PN

post–AGB – Planetary Nebula

Degenerate CO core = White Dwarf
Expanding envelope might become PN

t \sim 10,000 \text{ yr}
In the surroundings: Warm Molecules and Dust grains

- AGB star
- Pulsations
- "Extended atmosphere"
- Molecular bands
- "Primitive" dust seeds
- Dust forming layer
- "Primitive" dust seeds
- Dust–driven outflow

Molecular bands in photosphere and extended atmosphere
Structure of extended atmosphere
Connection with pulsations
Identification of possible "primitive" dust species
All stars O-rich initially
- Fusion + dredge-up
- C abundance ↑
- If \([C/O] > 1 \rightarrow \text{Carbon star}\)
- Also CS abundance C-rich
- Totally different chemistry in circumstellar matter

Yamamura et al. (1999)
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.
A Fullerene Family

$C_{60}$  $C_{240}$  $C_{540}$  $C_{960}$
“BuckyOnion”
Single water molecule trapped in stoppered molecular cage.
“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 unratinalizable.... War is obsolete.”
Full geodesic domes from hexagons and pentagons – the pentagons cause the “rounding” of the dome.
Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C\textsubscript{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\textsubscript{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\textsubscript{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.
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 $C_{70}$

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

Widespread and abundant in space?

Graphite vaporization.

Kroto et al. 1985

Time of flight mass spectra.

High He pressure

Low He pressure

No. of carbon atoms per cluster
SPECTROSCOPISTS

DO IT WITH FREQUENCY AND INTENSITY
**Early Searches**

- Electronic transitions.
- **neutral C\textsubscript{60}** in ISM: not found (overview: Herbig, 2000).
- **C\textsubscript{60}**\textsuperscript{+}: 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\textsubscript{60}**\textsuperscript{+}.

![Graph showing normalized intensity vs wavelength for C\textsubscript{60}^+ ions with peaks at 9.58 and 9.64 Å.](image)
\textbf{C}_{60} \text{ & } \textbf{C}_{70} \text{ vibrational modes}

- Neutral \textbf{C}_{60}: 4 IR active modes: 7.0, 8.5, 17.4, 18.9 \mu m.
- 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 \textbf{C}_{70}: 32 IR active modes.

\textit{Menéndez \& Page (2000)}
Wavelengths, widths & relative strengths match measured (lab) values.

Buckyballs In A Young Planetary Nebula
NASA / JPL-Caltech / J. Cami (Univ. of Western Ontario/SETI Institute)

Spitzer Space Telescope • IRS
ssc2010-06a

Cami et al. (2010)
More C\textsubscript{60} Detections

- Evolved stars:
  - R Cor Bor: García-Hernández et al. 2011, Clayton et al. 2011.
  - Post-AGB (O-rich?): Gielen et al. 2011.

- ISM:

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

PAHs $\rightarrow$ Fullerenes?

Berné & Tielens (2011)
For (small) dPAHs: Expect specific features around 5.5, 10.6 and 19\(\mu\text{m}\).

Consistent with larger PAHs.

Mackie et al. (2014)
Dehydrogenated PAHs

Mackie et al. (2014)

dPAHs in NGC 7023?
Meanwhile at the lab

\[ C_{66}^+ \]

\[ C_{66}H_{26}^+ \]

Zhen et al (2014)
266 nm

Zhen et al (2014)
Meanwhile at the lab (III)

532 nm

Cluster size (C-atoms)

Intensity (arb. units.)

m/z

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. C60 'Buckyball' is at the lower right. Credit: Leiden University Linnartz/Tielens
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.*
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 $T_{\text{eff}}$

- Fullerene and Mixed Big-11
- PNe with normal PAHs
- PNe with no dust features

Sloan et al. (2014)
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

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 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?
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.
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!
- $C_{60}$ ring: edge of ionized zone / PDR?
- $\rightarrow$ Determine $G_0$, $n$, $T$ with $[\text{OI}]$ and $[\text{CII}]$ cooling lines and far-IR continuum.
- FIFI-LS and HAWC will observe all $C_{60}$-Pne.
Metallofullerenes: form as easily as fullerenes in “dirty” atmospheres.

Dunk et al., 2013, PNAS.
Dunk et al., 2013, PNAS.

Symmetry breaking activates silent modes: e.g. feature at ~6.5 micron
Fullerene-rich post-AGB stars exhibit additional features as well!

Could these be the silent modes?

Sloan et al. (2014).
- In RNe: *peak* abundance $\sim 10^{-4}$ of cosmic C.
- In PNe: uncertain estimates; range from $\sim 10^{-5}$ to $\sim 1.5\%$. 
Laboratory confirmation of $\text{C}_{60}^+$ as the carrier of two diffuse interstellar bands

E. K. Campbell¹, M. Holz¹, D. Gerlich² & J. P. Maier¹

Implies $\sim 0.5\%$ of C in $\text{C}_{60}^+$
\[
\frac{W}{E_{B-V}} = 3 \ [\text{mÅ}] \left( \frac{\chi_{DIB}}{10^{-4}} \right) \left( \frac{60}{N_C} \right) \left( \frac{\lambda}{5000 \text{Å}} \right)^2 \left( \frac{f}{10^{-2}} \right)
\]

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