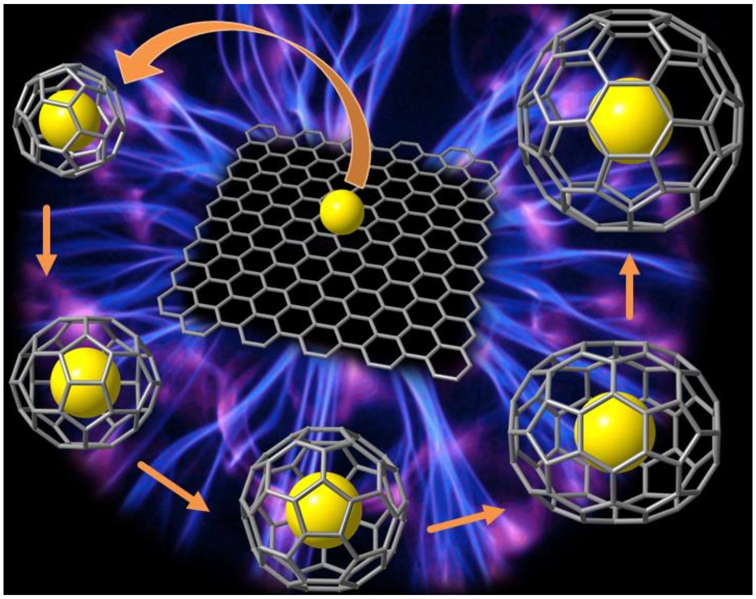
The Buckminsterfullerene Formation Process: New Revelations on the Origin of Nanocarbon and Insight into Fullerene Astrochemistry.

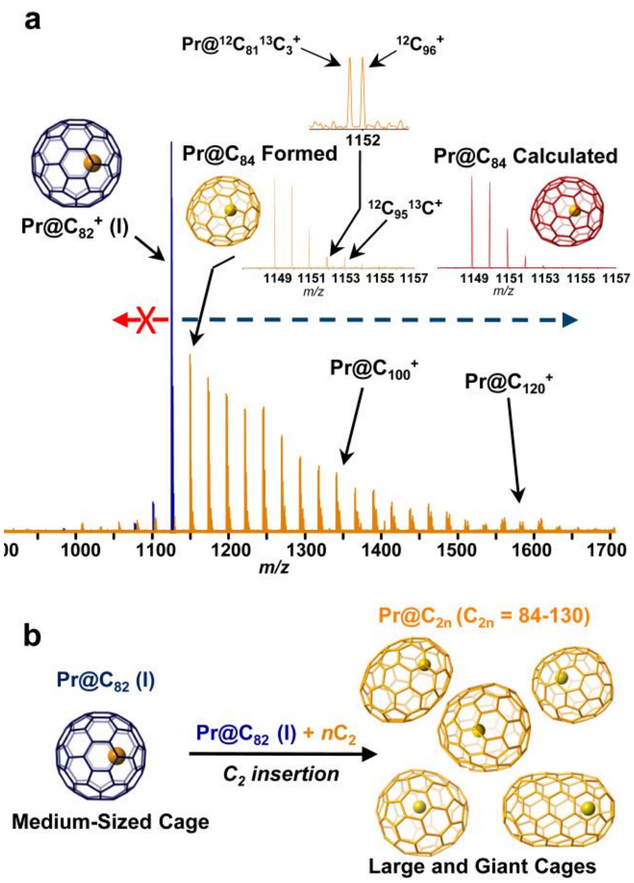
Fullerenes and metallofullerenes are exciting nanomaterials that attract wide attention for use as biomedical contrast agents, photovoltaics, and as materials for advanced technologies. They are also important cosmic molecules, forming in stellar/interstellar environments and stardust. Despite the many incredible findings that have changed our world since the discovery of Buckminsterfullerene in 1985, the most basic facts regarding how these beautiful molecules can even form in the first place has remained a long-standing mystery. Study of fullerene formation by has largely eluded experimental study for so long because the formation processes occur in the blink of an eye, under highly energetic conditions. We have overcome these problems by successfully devising experimental studies that use a laser to generate carbon vapor and detect the ultrafast and high energy reactions the result in fullerene formation, analyzed by the most powerful form of mass spectrometry. Fullerenes are discovered to grow by a bottom-up mechanism under the common, violent synthetic conditions of formation. Charge transfer is found to direct assembly of metallofullerenes. New elements and clusters are observed to be confined within unique cages, and new routes toward synthesis of heterofullerenes by atom exchange reactions are designed. For example, a tiny C_{28} cage can be grown around a single atom of titanium. These results are key to understanding fullerene formation, which should help to achieve targeted molecular synthesis and increased yields. Importantly, investigations are also performed that shed light into fullerene astrophysics and the origin of stardust.

Bottom-up formation of endohedral mono-metallofullerenes is directed by charge transfer

- Article link
    - Bottom-up formation of endohedral mono-metallofullerenes is directed by charge transfer
- Highlights
    - FSU researchers use MagLab’s unique 9.4 tesla ICR machine to make discovery
    - Promising nanomaterials origin revealed
- Abstract
    - An understanding of chemical formation mechanisms is essential to achieve effective yields and targeted products. One of the most challenging endeavors is synthesis of molecular nanocarbon. Endohedral metallofullerenes are of particular interest because of their unique properties that offer promise in a variety of applications. Nevertheless, the mechanism of formation from metal-doped graphite has largely eluded experimental study, because harsh synthetic methods are required to obtain them. Here we report bottom-up formation of mono-metallofullerenes under core synthesis conditions. Charge transfer is a principal factor that guides formation, discovered by study of metallofullerene formation with virtually all available elements of the periodic table. These results could enable production strategies that overcome long-standing problems that hinder current and future applications of metallofullerenes.



Metallofullerenes are found to assemble through a bottom-up formation mechanism from vaporized graphite doped with metals.

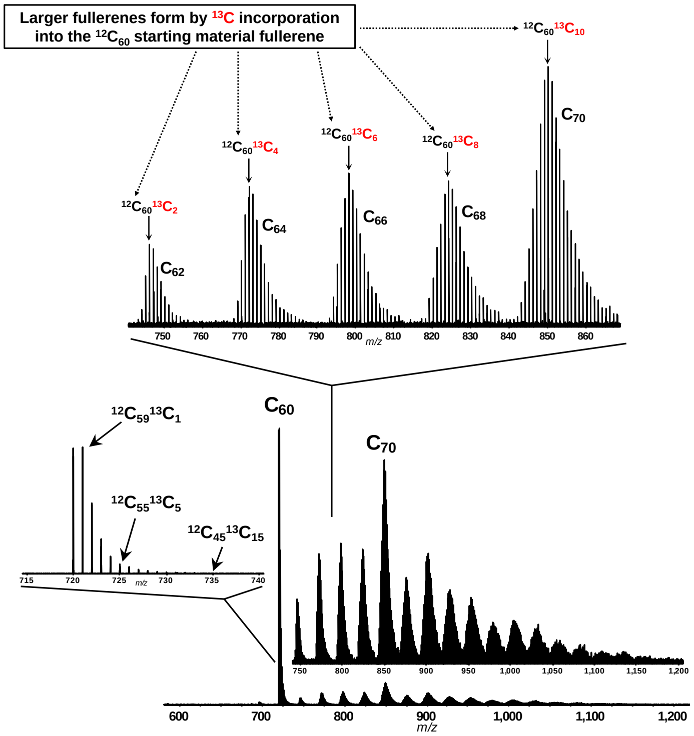


Bottom-up formation of large and giant mono-EMFs from Pr@C_{82}.

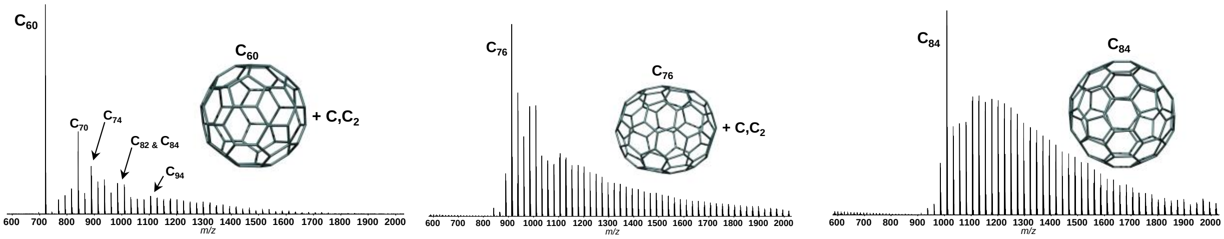
Closed network growth of fullerenes

- Article link
    - Closed network growth of fullerenes
- Highlights
    - Decades old mystery of Buckyballs cracked
    - Buckyballs grow by gobbling up carbon
- Abstract
    - Tremendous advances in nanoscience have been made since the discovery of the fullerenes; however, the formation of these carbon-caged nanomaterials still remains a mystery. Here we reveal that fullerenes self-assemble through a closed network growth mechanism by incorporation of atomic carbon and C_2. The growth processes have been elucidated through experiments that probe direct growth of fullerenes upon exposure to carbon vapour, analysed by state-of-the-art Fourier transform ion cyclotron resonance mass spectrometry. Our results shed new light on the fundamental processes that govern self-assembly of carbon networks, and the processes that we reveal in this study of fullerene growth are likely be involved in the formation of other carbonnanostructures

from carbon vapour, such as nanotubes and graphene. Further, the results should be of importance for illuminating astrophysical processes near carbon stars or supernovae that result in C_{60} formation throughout the Universe.



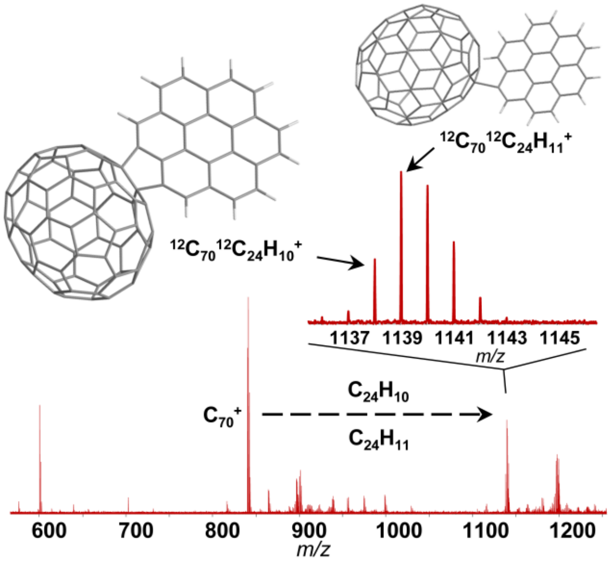
Exposure of C_{60} to pure ^{13}C vapor tracks growth; C_{60} is clearly shown to grow bottom-up into larger fullerenres by incorporation of C_2 and C.



Comparison of growth patterns after exposure of C_{60}, C_{76}, and C_{78} to carbon vapor, under optimal growth conditions. The same growth trends are observed indicating single mechanistic route. Importantly, absolutely no C_{60} forms via the growth processes of larger fullerenes. Thus, C_{60} forms by CNG from smaller fullerenes and is shown to be most resistant to carbon incorporation, further solving why C_{60} forms as the most abundant fullerene.

Metallofullerene and fullerene formation from condensing carbon gas under conditions of stellar outflows and implication to stardust

- Article link
  - Metallofullerene formation from condesning carbon gas under conditions of stellar outflows and implications to stardust
- Highlights
  - PNAS Science Sessions Interview Podcast (transcript)
  - Sodium aid metallofullerene formation in stellar outflows
- Abstract
  - Carbonaceous presolar grains of supernovae origin have long been isolated and are determined to be the carrier of anomalous ^{22}Ne in ancient meteorites. That exotic ^{22}Ne is, in fact, the decay isotope of relatively short-lived ^{22}Na formed by explosive nucleosynthesis, and therefore, a selective and rapid Na physical trapping mechanism must take place during carbon condensation in supernova ejecta. Elucidation of the processes that trap Na and produce large carbon molecules should yield insight into carbon stardust enrichment and formation. Herein, we demonstrate that Na effectively nucleates formation of $Na@C_{60}$ and other metallofullerenes during carbon condensation under highly energetic conditions in oxygen- and hydrogen-rich environments. Thus, fundamental carbon chemistry that leads to trapping of Na is revealed, and should be directly applicable to gas-phase chemistry involving stellar environments, such as supernova ejecta. The results indicate that, in addition to empty fullerenes, metallofullerenes should be constituents of stellar/circumstellar and interstellar space. In addition, gas-phase reactions of fullerenes with polycyclic aromatic hydrocarbons are investigated to probe “build-up” and formation of carbon stardust, and provide insight into fullerene astrochemistry.
- Significance
  - Fullerenes are now, without a doubt, an important cosmic molecule found across the universe. We experimentally study the processes that result in fullerene formation in oxygen- and hydrogen-rich carbon gas. Metallofullerenes are found to form as readily as empty cages and thus, like fullerenes, should be important constituents of (circum)stellar/interstellar space. Element trapping by metallofullerene formation is shown to be selective and rapid, which can explain long-standing astrophysical puzzles such as the anomalous element enrichment of stardust. Infrared spectroscopic signatures are simulated to provide an observational test for metallofullerenes in space. Further, energetic reactions between larger polycyclic aromatic hydrocarbons (PAHs) and fullerenes are established form stable classes of complex molecules that hold high astrochemical importance. Bottom-up fullerene growth is also demonstrated to result from PAH processing, another potentially important extraterrestrial formation mechanism.

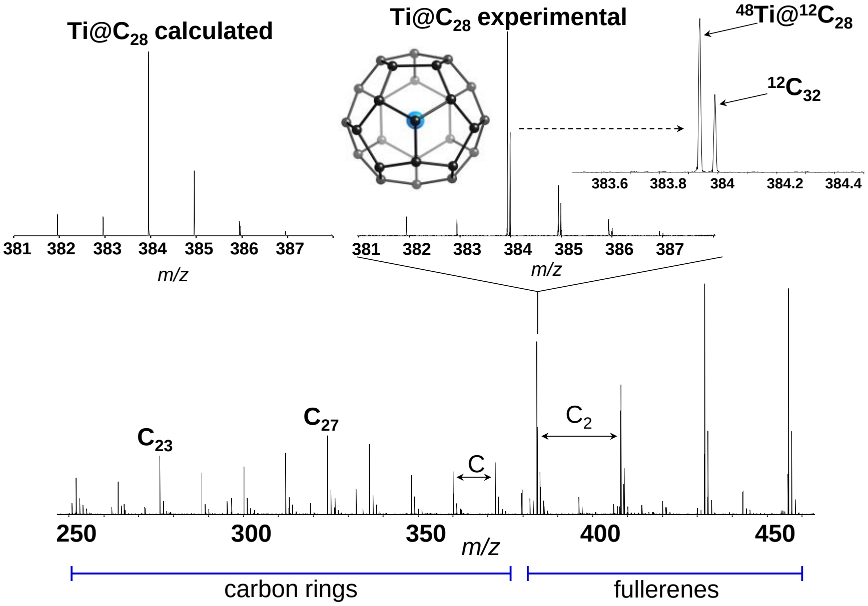
- 

- *Fullerenes and PAHs are often found in space together, and therefore, these fullerene-PAH products may reside in interstellar space. Bonding to and within metals are also likely very important.*

The smallest stable fullerene, M@C_{28} (M = Ti, Zr, U): stabilization and growth from carbon vapor

- Article link
  - The smallest stable fullerene, M@C_{28}
- Highlights
  - Tiny buckyball grown around metal atom
- Abstract
  - The smallest fullerene to form in condensing carbon vapor has received considerable interest since the discovery of Buckminsterfullerene, C_{60}. Smaller fullerenes remain a largely unexplored class of all-carbon molecules that are predicted to exhibit fascinating properties due to the large degree of curvature and resulting highly pyramidalized carbon atoms in their structures. However, that curvature also renders the smallest fullerenes highly reactive, making them difficult to detect experimentally. Gas-phase attempts to investigate the smallest fullerene by stabilization through cage encapsulation of a metal have been hindered by the complexity of mass spectra that result from vaporization experiments which include non-fullerene clusters, empty cages, and metallofullerenes. We use high-resolution FT-ICR mass spectrometry to overcome that problem and investigate formation of the smallest fullerene by use of a pulsed laser vaporization cluster source. Here, we report that the C_{28} fullerene stabilized by encapsulation with an appropriate metal forms directly from carbon vapor as the smallest fullerene under our conditions. Its stabilization

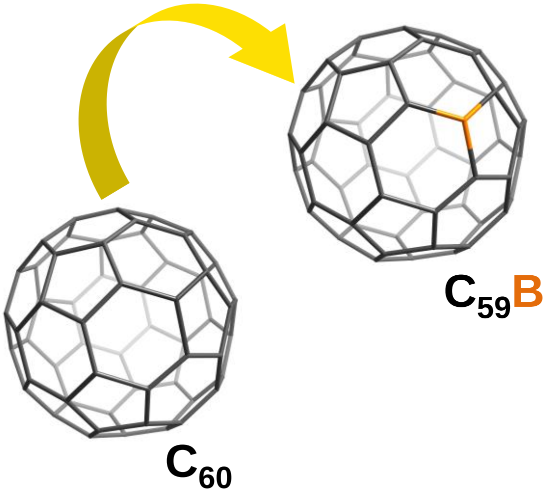
is investigated, and we show that $M@C_{28}$ is formed by a bottom-up growth mechanism and is a precursor to larger metallofullerenes. In fact, it appears that the encapsulating metal species may catalyze or nucleate endohedral fullerene formation.



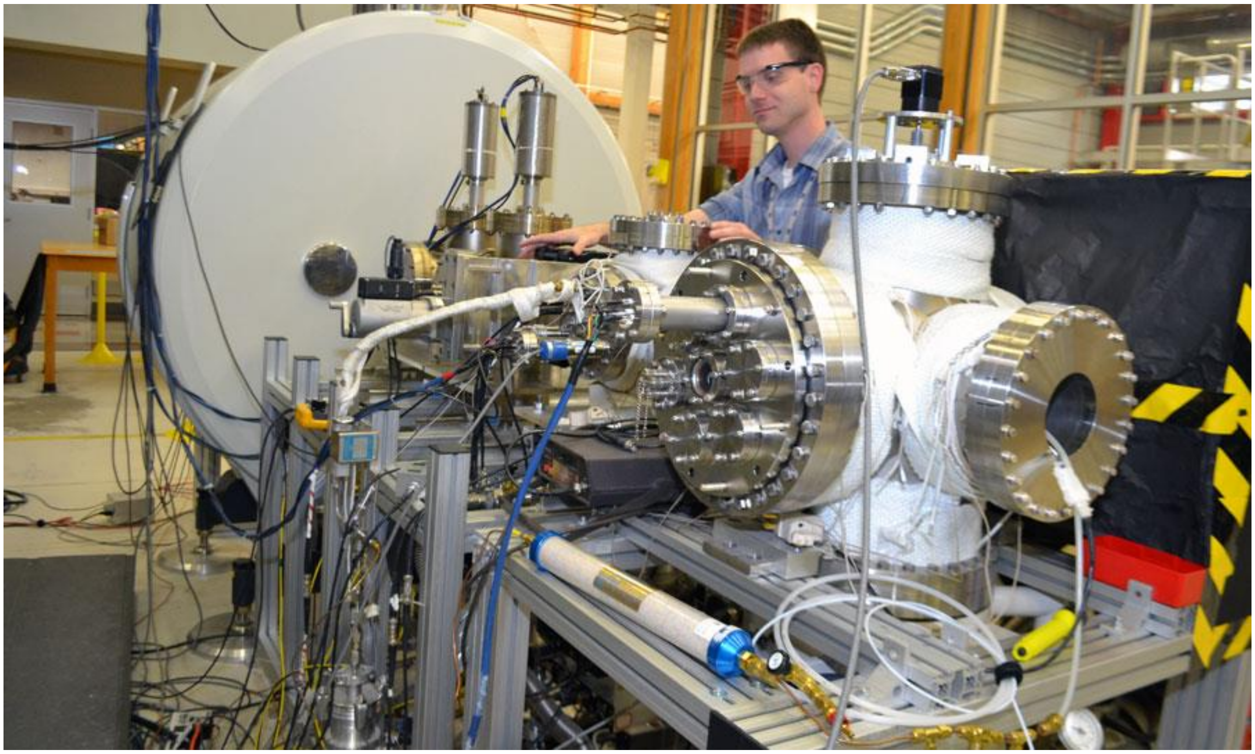
The tiny T_d-C_{28} fullerene is grown a titanium atom.

Formation of heterofullerenes by direct exposure of C_{60} to boron vapor

- Article link
    - Formation of heterofullerenes by direct exposure of C_{60} to boron vapor
- Highlights
    - Boron vapour trail leads to heterofullerenes
- Abstract
    - **Introducing boron**: Heterofullerenes that incorporate boron have been scarcely studied because a formation route from C_{60} is not known. It is now reported that $C_{59}B^-$, an electronically closed-shell species, is formed directly from pristine C_{60} in the gas-phase by facile atom exchange reactions.



The heterofullerenes, $C_{59}B$, is directly synthesized from pristine C_{60} by atom exchange reactions with B.



Paul Dunk working on the cluster instrument at the National High Magnetic Field Laboratory in Tallahasee, FL.