Astrochemistry

The origins of buckyballs in space

Alessandra Candian

The spectroscopic fingerprints of buckyballs have been observed in space, but questions remain about how these large molecules form. Laboratory experiments have revealed a possible mechanism.

A long-standing mystery in astronomical spectroscopy concerns diffuse interstellar bands, a family of absorption features seen in the spectra of the interstellar medium of the Milky Way and of other galaxies. First observed almost 100 years ago, the origin of any of the bands was unknown until 2015, when four of them were assigned[1] to the cation of buckminsterfullerene (C_{60}^{+}; the uncharged molecule is often referred to simply as fullerene, or colloquially as a buckyball). Fullerene and its analogue, C_{70}, are by far the biggest molecules detected in space, raising the question of how such large species can form in those rarified conditions. Researchers have suggested that fullerene forms in the outflows of old, carbon-rich stars known as asymptotic giant branch stars[2] – the temperatures and densities of these outflows promote chemistry similar to that of combustion. This could lead to the formation of soot, which can contain fullerene-like structures. Writing in *Astrophysical Journal Letters*, Bernal *et al.*[3] propose a very different formation route for fullerene.

The carbon atoms in fullerene are arranged in the shape of a football, a molecular structure that is remarkably stable but also difficult to construct. Fullerene has been made in the laboratory in experiments designed to probe the chemistry that occurs in carbon-rich stars: carbon in the form of graphite was vaporized into a high-density helium flow, producing carbon clusters[4]. The discovery that fullerene was among the reaction products led to the award of the Nobel Prize in Chemistry to Harry Kroto, Richard Smalley and Robert Curl in 1996.

However, the range of temperatures required to create fullerene in this way is quite specific[2]; outside that range, molecules known as polycyclic aromatic hydrocarbons (PAHs) are produced instead. These molecules are 2D sections of a single layer of graphite (a graphene sheet), decorated with hydrogen atoms. Subsequent experiments[5,6] have shown that PAHs that contain more than 60 carbon atoms are converted into fullerenes when exposed to sufficient ultraviolet irradiation.

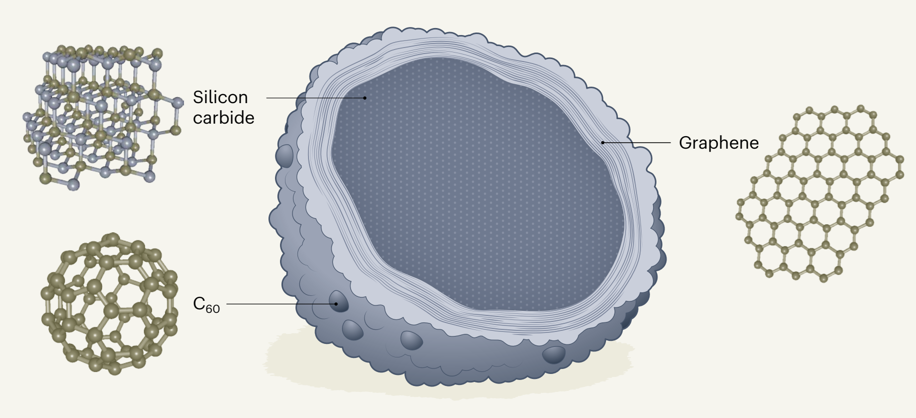

Figure 1 | Evidence of a mechanism for the formation of buckminsterfullerene in space. Bernal *et al.*[3] heated grains of silicon carbide (SiC) and bombarded them with ions, mimicking the conditions experienced by the dust around old stars. Using a transmission electron microscope, the scientists observed that the outer layers of SiC had transformed into graphene sheets, as shown in this idealized grain. They also observed the formation of hemispherical structures with diameters similar to that of buckminsterfullerene (C_{60}) on the surface of the grains. Their work thus reveals a convincing process through which C_{60} could form in the outflows of old stars.

The first astronomical source in which fullerene was detected was the star Tc 1 (ref. 7). Puzzlingly, however, the emission associated with fullerene came from a location far away from the star and its ultraviolet photons, whereas the PAH emissions were closer to the star. On the basis of the previously reported laboratory experiments, this is the opposite of what should happen if fullerene forms from PAHs in this source[8]. So how can the locations of the emissions be explained?

Bernal and co-workers now report that fullerene also forms readily from silicon carbide (SiC), which has been proposed to be the first carbonaceous material to condense out of old, carbon-rich stars[9]. The authors rapidly heated grains of the crystalline form of SiC that is found in highest abundance in meteorites[10], and irradiated them with xenon ions, mimicking the heating caused by shock waves around old stars.

Using a transmission electron microscope to image the surfaces of the samples down to the subnanometre scale, the scientists observed that the grain material had altered notably as a result of its treatment (Fig. 1). Silicon atoms had percolated to the outer layers of the grains, leaving behind what looked like sheets of carbon atoms in a hexagonal 'chicken-wire' arrangement – that is, graphene sheets.

The transformation of the outer layers of SiC into graphene sheets at high temperatures had been reported[11] previously for a different form of SiC from that studied by Bernal and colleagues. However, Bernal *et al.* also observed the formation of hemispherical structures with diameters similar to that of fullerene. Their work thus provides a convincing new mechanism for the formation of fullerene in evolved stars.

Bernal *et al.* report another piece of evidence supporting the idea that SiC grains are rapidly heated and bombarded with ions in evolved stars. They have identified a fragment of the Murchison meteorite – a highly studied meteorite that is rich in organic compounds – in which the ratio of carbon-12 to carbon-13 isotopes is typical of material from an old, carbon-rich star. This indicates that the fragment was not produced during or after the formation of the meteorite, but instead is stardust that originated in an old star. The fragment has a core of SiC surrounded by graphene sheets. However, previous analyses[12] of graphite-containing stardust found evidence only of titanium carbide cores, rather than SiC cores. This raises the question of how common SiC cores are in graphite-containing stardust.

The rapid heating of SiC grains in the presence of hydrogen can lead to the formation of PAHs[13]. Bernal and colleagues' findings therefore suggest that the thermal conversion of SiC to graphene sheets in evolved stars could be the first step in the formation of large carbon-containing molecules in general: subsequent (or simultaneous) exposure of the graphene to atomic hydrogen produces PAHs, whereas ion bombardment produces fullerene. Alternatively, PAH molecules might be molecular intermediates in the formation of carbon soot, which can then be broken down by ultraviolet irradiation to make PAHs again[14].

The efficiency of Bernal and colleagues' fullerene-forming mechanism is unknown, raising the question of how many SiC grains are needed to account for the observed abundance of fullerene molecules in space. If there aren't enough grains, then a further mechanism will be required to explain the abundance of fullerene. By contrast, if there are too many SiC grains, what happens to the 'excess' fullerene molecules produced, given that they are notoriously difficult to degrade? More experiments and detailed modelling of the formation of fullerene and of other carbon-containing large molecules from SiC grains are needed to understand this process, and to quantify its importance in old stars.

The launch of the James Webb Space Telescope in 2021 will provide powerful new tools for studying old stars, among other astronomical objects. Observations of fullerene-containing sources[7,8] such as Tc 1 will be able to constrain the regions in which SiC grains, fullerene and PAHs are present, providing more clues about how large molecules are actually formed. Further analysis and modelling of the routes involved will eventually allow astronomers to suggest the identities of the other mysterious molecules responsible for the diffuse interstellar bands.

Alessandra Candian is at the van't Hoff Institute for Molecular Sciences, University of Amsterdam, 1090 GD Amsterdam, the Netherlands, and at the Leiden Observatory, University of Leiden, Leiden, the Netherlands.
e-mail: a.candian@uva.nl

1. Campbell, E. K., Holz, M., Gerlich, D. & Maier, J. P. *Nature* **523**, 322–323 (2015).
2. Jäger, C., Huisken, F., Mutschke, H., Llamas Jansa, I. & Henning, T. *Astrophys. J.* **696**, 706–712 (2009).
3. Bernal, J. J. *et al. Astrophys. J.* **883**, L43 (2019).
4. Kroto, H. W., Heath, J. R., O'Brien, S. C., Curl, R. F. & Smalley, R. E. *Nature* **318**, 162–163 (1985).
5. Berné, O. & Tielens, A. G. G. M. *Proc. Natl Acad. Sci. USA* **109**, 401–406 (2012).
6. Zhen, J., Castellanos, P., Paardekooper, D. M., Linnartz, H. & Tielens, A. G. G. M. *Astrophys. J.* **797**, L30 (2014).
7. Cami, J., Bernard-Salas, J., Peeters, E. & Male, S. E. *Science* **329**, 1180–1182 (2010).
8. Cami, J., Peeters, E., Bernard-Salas, J., Doppmann, G. & De Buizer, J. *Galaxies* **6**, 101 (2018).
9. Frenklach, M., Carmer, C. S. & Feigelson, E. D. *Nature* **339**, 196–198 (1989).
10. Daulton, T. L. *et al. Science* **296**, 1852–1855 (2002).
11. Mishra, N., Boeckl, J., Motta, N. & Iacopi, F. *Phys. Status Solidi A* **213**, 2277–2289 (2016).
12. Croat, K. T., Bernatowicz, T. J. & Daulton, T. L. *Elements* **10**, 441–446 (2014).
13. Merino, P. *et al. Nature Commun.* **5**, 3054 (2014).
14. Cherchneff, I., Barker, J. R. & Tielens, A. G. G. M. *Astrophys. J.* **401**, 269–287 (1992).

Optical physics

Light trapping gets a boost

Kirill Koshelev & Yuri Kivshar

The ability of structures called optical resonators to trap light is often limited by scattering of light off fabrication defects. A physical mechanism that suppresses this scattering has been reported that could lead to improved optical devices. **See p.501**

Devices called optical resonators confine light, but for only a limited time because of unavoidable light emission. On page 501, Jin *et al.*[1] report that such emission can be greatly reduced by using the interference of light waves known as bound states in the continuum. Such waves are akin to exotic electron waves that were introduced in the theory of quantum mechanics almost a century ago[2]. The authors' finding could have many technological implications for nanophotonics, quantum optics and nonlinear optics – the study of how intense light interacts with matter.

Interference is a common wave phenomenon in physics, whereby two or more waves pass through one another to produce a combined waveform. Consider the case in which these waves are correlated with one another, either because they come from the same source or because they have almost the same frequency. If the crest of one wave coincides with the crest of another wave, the combined amplitude will be the sum of the individual amplitudes. And if the crest of one wave meets the trough of another wave, the combined amplitude will be the difference in the individual amplitudes. These two scenarios are called constructive and destructive interference, respectively.

The effects of interference can be observed for all waves, but interference associated with bound states in the continuum (BICs) has attracted much attention in photonics over the past few years[3]. BICs are formed by the destructive interference of several ordinary light waves that have a similar wavevector – a quantity that describes a wave's velocity and direction of propagation. This interference provides a means of achieving strong confinement of light and of increasing its amplitude through a phenomenon known as optical resonance. It can also be used to tune an optical resonator into the 'supercavity' regime, in which emission of light from the resonator is restrained[4]. Several approaches to realizing BICs have been suggested for waves in electronic, electromagnetic and acoustic systems.

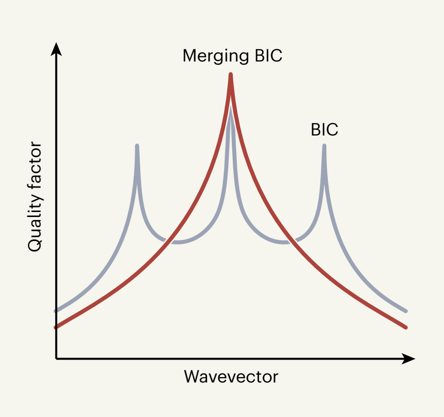

Figure 1 | Increasing the quality factor of an optical resonator. Jin *et al.*[1] report simulations of and experiments on a light-trapping device known as an optical resonator. The key characteristic of a resonator is the quality factor – a measure of the efficiency of light trapping. This quantity varies with the wavevector, which describes the velocity and propagation direction of a wave. The authors used their resonator to trap light in the form of waves called bound states in the continuum (BICs). They then combined these BICs into a single state: a merging BIC. As this graph shows, a merging BIC increases the quality factors of all waves that have similar wavevectors to it.

The concept of BICs was proposed for unusual states of electron waves by two pioneers of quantum mechanics, John von Neumann and Eugene Wigner[2]. They discovered that specific potentials (potential-energy profiles) could support spatially localized electron states that have energies larger than the maximum energy of the potential. In other words, the states could be confined even though their energies would normally allow them to escape. In photonics, a light wave that is trapped by an optical resonator can be converted to a BIC under certain conditions[3] – a discovery that was made only in 2008.

The main characteristic of an optical resonator is the quality factor – the ratio of the time over which the device can trap light to the period of the wave's oscillation. If the light waves destructively interfere to form BICs, the quality factor greatly increases. Moreover, in the BIC regime, the quality factor theoretically tends to infinity when one of the system parameters, such as the size of the resonator, is tuned. By contrast, the quality factor of a