

ASTROCHEMISTRY

Fullerene solves an interstellar puzzle

Laboratory measurements confirm that a ‘buckyball’ ion is responsible for two near-infrared absorption features found in spectra of the interstellar medium, casting light on a century-old astrochemical mystery. SEE LETTER P.322

PASCAL EHRENFRUND & BERNARD FOING

More than 400 unidentified absorption features have been recorded in spectra of the interstellar medium of the Milky Way and other galaxies. The nature of these ‘diffuse interstellar bands’, which are present in spectra of the interstellar medium from the near-ultraviolet to the near-infrared domains, has evaded elucidation since their discovery nearly 100 years ago — one of the longest-standing mysteries of modern astronomy. Writing on page 322 of this issue, Campbell *et al.*¹ report laboratory spectra of the buckminsterfullerene, or ‘buckyball’, ion C_{60}^+ . The spectra provide an excellent match to two interstellar bands that we discovered and attributed to this ion², and securely identify C_{60}^+ as a component of the interstellar medium.

During the past 40 years, advances in astronomical instrumentation have enabled the detection of many weak diffuse interstellar bands (DIBs) (Fig. 1), and their various widths have been accurately measured^{3–5}. Numerous efforts have been made to identify the likely molecular group (the ‘carrier’) that causes the absorption bands through laboratory

studies, theoretical modelling and astronomical observations⁴. As a result, a host of candidate carriers has been proposed, ranging from dust grains to intriguing carbonaceous species, including fullerenes (a carbon allotrope)^{3,6}. High-resolution observations of fine spectroscopic details of certain DIBs^{7,8} have contributed to the consensus that polyatomic carbonaceous molecules in the gas phase are promising candidate carriers. The discovery and synthesis of fullerenes (including buckminsterfullerene) and of graphene in laboratories, have revolutionized our understanding of carbon chemistry and its applications ranging from astronomy and biotechnology to industrial processes.

In 1994, a search for the strongest signals of C_{60}^+ in interstellar-material spectra led to the discovery² of two absorption features (Fig. 1) at 9,577 and 9,632 Ångströms. These coincided with independent measurements of electronic transitions of C_{60}^+ in laboratory spectra using frozen-matrix techniques — in which the target species is diluted with an unreactive host species (such as neon) at very low temperatures, and is then spectrally analysed⁹. This preliminary match of two interstellar DIBs with C_{60}^+ showed wavelength shifts of 3–10 Å relative to the laboratory measurements; these

were attributed to known effects caused by the neon matrix. Nonetheless, the interstellar-medium study² estimated that about 0.6% of interstellar carbon may be in the form of C_{60}^+ , and proposed that fullerenes may have a significant role in interstellar chemistry. Arguments to support the C_{60}^+ match to the two strongest near-infrared DIBs also include the species’ extreme resistance to ultraviolet radiation, that the strengths and widths of the two DIBs were mutually correlated, and that their band widths were consistent with the spectrum of a rotating fullerene-like molecule^{2,10,11}. To provide unambiguous confirmation, laboratory gas-phase spectra of C_{60}^+ were called for.

In the current study, Campbell *et al.* report the laboratory synthesis of a complex of C_{60}^+ and helium at 5.8 kelvin, providing the best approximation so far of the gas-phase spectrum of C_{60}^+ . The laboratory measurements of C_{60}^+ band maxima at 9,632.7 and 9,577.5 Å show a stunning match to the observed wavelengths of the corresponding interstellar DIBs, with an accuracy of ± 0.1 Å. Moreover, the respective band widths of 2.2 and 2.5 Å are consistent with the 2.8-Å widths measured for these DIBs^{10,11}. Twenty-one years after the initial assignment, the authors’ superb laboratory results, which were achieved with a technically advanced set-up, have conclusively identified C_{60}^+ as the carrier of these two DIBs.

With the two strongest C_{60}^+ bands securely matched to DIBs, prospects are improving for the identification of the carriers of the more than 400 remaining DIB features, which have been recorded in a variety of astrophysical settings. In the past decade, observations across the entire optical range have established that diffuse band carriers are ubiquitous in space. DIBs have also recently been detected and mapped in the Magellanic Clouds (the Milky Way’s satellite galaxies) and in other galaxies. The carrier molecules may therefore constitute an important reservoir of organic material throughout the Universe.

The clear identification of additional DIB carriers could have a far-reaching impact on our understanding of astrochemical reaction networks. C_{60}^+ was possibly the easiest and most conspicuous molecule to identify owing to its signature of two strong bands in the near-infrared range that is clearly evident in interstellar-medium spectra, which have been corrected for atmospheric absorptions^{2,10,11}. The species’ cage-like symmetry and geometry⁶ (Fig. 1), as well as its chemical properties, increase its chances of survival in space and its expected natural formation in astrophysical environments^{4,10}. One possible approach to identify more DIB carriers would be to detect and quantify the presence in space of other fullerene compounds, which could be formed by the addition of hydrogen atoms, metals or other radicals in different charge or reactive states.

In previous analyses of mid-infrared

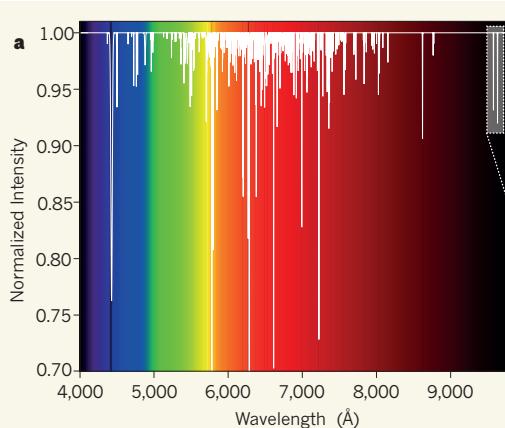


Figure 1 | Buckminsterfullerene in space. **a**, High-resolution absorption spectra of the interstellar medium, such as that shown here, include more than 400 unidentified diffuse interstellar bands (DIBs, white lines) spread across the optical and near-infrared domains^{3,5,10}. Fullerenes and other carbon-bearing molecules have been proposed as the absorbing species causing some of the interstellar DIBs, but conclusive identification had been elusive. **b**, Campbell *et al.*¹ now prove that the charged buckminsterfullerene ion C_{60}^+ is indeed responsible for the two strongest interstellar DIBs¹⁰ in the near-infrared at 9,577 and 9,632 Å (indicated by stars) discovered² in 1994.

emission spectra of a young planetary nebula (the ionized, ejected envelope of an old star) taken with NASA's Spitzer Space Telescope, researchers for the first time identified¹² specific molecular-vibration bands that were assigned to compounds of the fullerenes C₆₀ and C₇₀. Vibrational spectroscopy cannot perfectly distinguish between molecules of similar chemical bonds or between molecular excitation states, but it can provide a global inventory of molecular groups from the pool of organic materials in space. Electronic spectroscopy, such as that used by Campbell and colleagues, can pinpoint the fingerprints of individual molecules. Additional observations of circumstellar nebulae have shown that, under the right conditions, fullerenes can and do form efficiently in space⁴.

Other carbon-bearing molecules known as polycyclic aromatic hydrocarbons (PAHs) — fused benzene rings — have also been proposed^{13,14} as carriers of vibrational bands that are observed in the mid-infrared domain. These are estimated to be the most abundant complex organic molecules in space, comprising more than about 15% of cosmic carbon, and have also been proposed as potential DIB carriers. However, in contrast to C₆₀⁺, PAHs can undergo partial loss of hydrogen atoms (dehydrogenation), and would therefore exist in a large number of molecular isomers, diluting their spectral signatures¹⁵. This might explain why, despite several dedicated efforts¹⁶, no specific PAH electronic feature has been clearly associated with DIBs. Some metal-PAH complexes may eventually be shown to have special molecular configurations that have few isomers and strong oscillator strengths — these would have undiluted spectral features, which would permit their electronic spectroscopic identification and matching to astrophysical DIBs⁴.

The relationships between PAHs and fullerenes in space represent an intriguing puzzle. Laboratory studies have shown¹⁷ that C₆₀⁺ can form following sequential light-induced fragmentation of large PAH cations. Infrared observations obtained by the Spitzer and the European Space Agency's Herschel Space Observatory have also shown¹⁸ that C₆₀ can form in the tenuous and cold environment of an interstellar cloud illuminated by strong ultraviolet starlight — possibly as the product of the conversion of PAHs to graphene, and then to fullerenes.

As Campbell and colleagues' findings show, the identification of space molecules can be achieved only by measuring laboratory spectra under astrophysically relevant conditions, and the spectra must unambiguously match the astronomical data. This task requires theoretical modelling to determine other plausible fullerene- and PAH-candidate DIB carriers and a systematic programme of laboratory spectroscopy of these in frozen neon matrices (for screening) and in the gas phase (for identification).

Astronomical surveys of DIB strengths and profiles in different interstellar and circumstellar environments are needed to elucidate the formation and fate of carriers. All these research disciplines must be combined to provide further insights into the photochemistry, thermal conditions and integration in protoplanetary-disk material that affect the inventory and evolution of organic molecules from molecular clouds to star- and planet-forming regions. ■

Pascale Ehrenfreund is at the Space Policy Institute, George Washington University, Washington DC 20052, USA. **Bernard Foing** is at the European Space Research and Technology Centre of the European Space Agency, ESA-ESTEC, 2200 Noordwijk, the Netherlands.

e-mail: pehren@gwu.edu;
bernard.foing@esa.int

- Campbell, E. K., Holz, M., Gerlich, D. & Maier, J. P. *Nature* **523**, 322–328 (2015).
- Foing, B. H. & Ehrenfreund, P. *Nature* **369**, 296 (1994).

- Herbig, G. H. *Annu. Rev. Astron. Astrophys.* **33**, 19–73 (1985).
- Cox, N. L. J. & Cami, J. (eds) *Proc. Int. Astron. Un.* Vol. 9 (2014).
- Hobbs, L. M. et al. *Astrophys. J.* **705**, 32–45 (2009).
- Kroto, H. W. et al. *Nature* **318**, 162–163 (1985).
- Ehrenfreund, P. & Foing, B. H. *Astron. Astrophys.* **307**, L25–L28 (1996).
- Sarre, P. et al. *Mon. Not. R. Astron. Soc.* **277**, L41–L43 (1995).
- Fulara, J., Jakobi, M. & Maier, J. P. *Chem. Phys. Lett.* **211**, 227–234 (1993).
- Foing, B. H. & Ehrenfreund, P. *Astron. Astrophys.* **317**, L59–L62 (1997).
- Galazutdinov, G. A. et al. *Mon. Not. R. Astron. Soc.* **317**, 750–758 (2000).
- Cami, J., Bernard-Salas, J., Peeters, E. & Malek, S. E. *Science* **329**, 1180–1182 (2010).
- Leger, A. & Puget, J. L. *Astron. Astrophys.* **137**, L5–L8 (1984).
- Allamandola, L. J., Tielens, A. G. G. M. & Barker, J. R. *Astrophys. J.* **290**, L25–L28 (1985).
- Vuong, M. H. & Foing, B. H. *Astron. Astrophys.* **363**, L5–L8 (2000).
- Salama, F. et al. *Astrophys. J.* **728**, 154–162 (2011).
- Zhen, J., Castellanos, P., Paardekooper, D. M., Linnartz, H. & Tielens, A. G. G. M. *Astrophys. J.* **797**, L30–L34 (2014).
- Berné, O. & Tielens, A. G. G. M. *Proc. Natl. Acad. Sci. USA* **109**, 401–406 (2012).

SYSTEMS BIOLOGY

Network evolution hinges on history

The effects of mutations in proteins can depend on the occurrence of previous mutations. It emerges that such historical contingency is also important during the evolution of gene regulatory networks. SEE LETTER P.361

AARON M. NEW & BEN LEHNER

Anyone who has dealt with bureaucracy knows that the order in which events occur can be vital to achieving a given task. This is also true for evolution, in which certain mutations are sometimes beneficial, or even viable, only if other mutations have occurred first¹ — a phenomenon known as historical contingency. In this issue, Sorrells *et al.*² (page 361) show how historical contingency constrained the evolution of an entire gene regulatory network.

Historical contingency has long been thought³ to have a role in evolution, but only since the advent of large-scale DNA sequencing have we been able to peer back in time and replay the evolutionary tape to establish how the process works in biological systems. A wealth of DNA-sequence information means that we can now infer the sequences of extinct genes, allowing us to resurrect the proteins that they encoded⁴. Studying the role of these ancestral proteins in living cells has revealed that only certain paths can be taken during the evolution of protein functions⁵. But the part played by historical contingency in the

evolution of gene regulatory networks has not been well studied.

Budding yeasts, a group of fungi that includes the model organism *Saccharomyces cerevisiae* (brewer's yeast), have two mating types, 'a' and 'α'. When exposed to mating pheromone, both mating types switch on genes necessary for mating, and a cells also switch on genes specifically required for mating with α cells, referred to as α-specific genes (asgs). The identity of these asgs has changed little over hundreds of millions of years of evolution^{2,6,7}, but the way in which their expression is controlled has altered considerably.

Sorrells *et al.* reconstructed the evolution of asg regulation in *S. cerevisiae*. They showed that a regulatory protein, Ste12, initially activated asgs indirectly by binding to a DNA-binding protein called a2, and then evolved to bind directly to DNA. By constructing plausible evolutionary intermediates, the authors provide evidence that this change in Ste12 function was made possible by another change, in the way the two mating types are defined.

Previous work from this group^{6,7} found that, in ancestral species, a cells were defined by the presence of a2. But in *S. cerevisiae*, a cells are