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Fullerene and graphene molecular nanostructures in evolved stars.

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Abstract

The detections of fullerenes and (possibly) planar C_{24} (a small fragment of a graphene sheet) in the H-rich circumstellar environments of evolved stars show that formation of these complex species does not require an H-poor environment contrary to general expectation. This together with the very recent identification of the fullerene cation C_{60}^+ as a diffuse interstellar band (DIB) carrier (the only DIB carrier known to date) reinforce the idea that these molecular nanostructures are ubiquitous in space. The understanding of the formation route of these complex organic species requires an interdisciplinary research, crossing the boundaries between astronomers, chemists, and physicists, with potential applications in nanotechnology and industry. Here, I review the main results of the interdisciplinary approach carried out at the Instituto de Astrofísica de Canarias (IAC) in order to learn about complex molecular nanostructures in evolved stars. Finally, I underline the main open questions and future directions like the expected observations on these complex organics in evolved stars from future facilities such as the James Webb Space Telescope.

1 Fullerenes in space: a brief history

Fullerenes such as C_{60} and C_{70} are very stable molecules very important for interstellar and circumstellar chemistry because they may explain many astrophysical phenomena like the diffuse interstellar bands (DIBs) or the ultraviolet bump. Fullerenes were discovered in the laboratory by [31] and they are also found on Earth and meteorites. The fullerene cation C_{60}^+ was also tentatively detected in the interstellar medium in the nineties ([15]) and this has been recently confirmed ([2], [3]). At laboratory, fullerenes are efficiently produced under H-poor conditions ([31], [11]) and fullerenes were expected to be detected in the extremely H-poor and so-called R Cor Bor (RCB) stars (e.g., [28]).

All previous searches of fullerenes in space have not detected them. This included searches in RCB stars ([10], [34]), post-AGB stars ([33]), and reflection nebulae ([36], [40]).



Figure 1: Left panel: Spitzer/IRS residual spectra in the wavelength range $\sim 5-20 \ \mu m$ of the RCB stars DY Cen (in red) and V854 Cen (in blue). The average residual spectrum of nine extremely H-deficient RCBs with little reddening (in black) is also shown. The expected temperature-dependent positions of the neutral C₆₀ features are marked with black dashed vertical lines. Right panel: Residual *ISO* 1996 September 9 (in blue) and Spitzer/IRS 2007 September 7 (in red) spectra in the wavelength range $\sim 2-25 \ \mu m$ for the RCB star V854 Cen. A blackbody of ~ 1000 K was subtracted from both spectra. The *ISO* spectrum (R ~ 1000) has been smoothed with a 13 box car in order to be compared with the Spitzer spectrum. The laboratory emission spectrum of HAC at 773 K (in green; [39]) is shown for comparison. The main laboratory HAC emission features ([39]) are marked with black dashed vertical lines (both figures adapted from [17]).

I started to be interested in fullerenes in space about ten years ago when I was doing a postdoc with Prof. David Lambert in Austin. He observed the three brightest RCB stars with the "Infrared Space Observatory" (ISO) ([34]) and I had experience with Spitzer, so we submitted a Spitzer proposal to get mid-IR spectra for a complete sample of 30 RCBs. One of the goals was to look for fullerenes in these fascinating stars. Once I was back to the Instituto de Astrofísica de Canarias (IAC) and after data reduction, we looked for C₆₀ in the full sample of RCBs and we got the unexpected result that C₆₀-like features were detected only in the two least H-deficient stars ([17]). This is shown in Fig. 1 (left panel) where we compare the average RCB spectrum with those of the two C₆₀-detected stars. Interestingly, for one of these stars, the infrared spectrum dramatically changed in a timescale of about ten years (Fig.1, right panel). The spectrum evolved from hydrogenated amorphous carbon (HAC)-like (with ISO) to policyclic aromatic hydrocarbons (PAH)- and C₆₀-like features with Spitzer.

Due to the unexpected result in RCB stars, we then looked for fullerenes in about 240 Planetary Nebulae (PNe) and we got 5 clear fullerene detections. Meanwhile, [1] reported the first IR detection of C_{60} and C_{70} in the young PN Tc 1. In [16], we show that all PNe with fullerenes (including Tc 1) are low-mass C-rich sources with normal hydrogen abundances. The *Spitzer* spectra of some of these PNe dispaly both the C_{60} and C_{70} features and some of them also display PAH-like features in their spectra (see e.g., [18], [20]).

Thus, we now know that fullerenes can be detected together with PAHs and that they are efficiently formed in H-rich circumstellar envelopes only. Fullerenes are detected in PNe with normal H abundances ([16]). This is confirmed by the independent detection of C₆₀ in only those RCB stars with some H ([17]) and mentioned above. Fullerene PNe display broad dust features at ~9–13 and 25–35 μ m, suggesting that both fullerenes and PAHs probably evolve from the photochemical processing of mixed aromatic/aliphatic nanoparticles similar to that of HAC-like dust ([16]), as suggested by some laboratory experiments ([39]). Fullerenes have also been detected in a proto-PN ([43]), reflection nebulae ([41]), and young stellar objects ([38]), and none of these space environments is H-poor.

Fullerenes have been detected in PNe of the Magellanic Clouds (MCPNe) and the first extragalactic detection of C_{70} was reported ([18]). The combination of the *Spitzer* information with laboratory data ([29]) permitted the determination of accurate abundances of C_{60} and C_{70} . The great variety of molecular species (HACs/PAHs clusters, fullerenes, etc.) observed in MCPNe seems to support the HACs scenario, where fullerenes may evolve from the UVinduced HACs decomposition ([20], [35]).

2 Fullerenes vs. metallicity and other C molecular nanostructures

Interestingly, the detection rate of fullerenes in C-rich PNe increases with decreasing metallicity, 5% of fullerene PNe are found in our Milky way, while it is 20% in the Large Magenallic Cloud and 44% in the Small Magellanic Cloud ([20]). This suggests a more limited dust processing (or the general presence of small dust grains) at low metallicity. Indeed, [37] have



Figure 2: Left panel: Spectra of Tc 1 (in black) and HR 6334 (in red) around the 4428 Å DIB. This DIB is found to be unusually strong in Tc 1 while HR 6334 - with a higher E(B-V) of 0.42 - does not show evidence of its presence (adapted from [12]). Right panel: The spectra of DY Cen (in red) and HD 115842 (in blue) around and 4000 Å where the eHe star BD -9° 4395 is also displayed (in green). The expected position and FWHM of the C₆₀ feature at 3980 Å are marked on top of the spectra; there is no evidence (additional absorption) in DY Cen for the presence of this neutral C₆₀ feature. However, there is an additional absorption band at 4000 Å in DY Cen, which is not present in HD 115842 neither in BD -9° 4395 (adapted from [19]).

shown that all Galactic fullerene PNe are subsolar metallicity low-mass PNe, which demonstrate that low-metallicity environments favours fullerene production and detection. Also, it is curious that the still unidentified 21 μ m feature is more common in the MCs than in the Galaxy ([42]) and the carrier could be related with the formation of fullerenes.

[42] reported an anti-correlation between the 30 μ m feature and the unidentified infrared (UIR) features for the Magellanic Cloud 21 μ m sources. Such an anti-correlation could result from radiation-induced decomposition of HAC-like grains into PAHs and fullerenes. Note that in the HACs scenario, the 21 μ m feature is also related with the formation of fullerenes and its carrier may be a fragile intermediate product from the decomposition of HACs or a similar material.

Unusual emission features at ~6.6, 9.8, and 20 μ m have been also detected in PNe ([18]). These features are coincident with the theoretical transitions of the planar C₂₄ molecule (just

a piece of graphene; [32]). However, a confirmation has to wait for laboratory spectroscopy, which is extremely difficult because of the high reactivity of C_{24} . The most interesting point here is that the possible detection of graphene precursors (C_{24}) opens the possibility of detecting other carbon molecular nanostructures such as nanotubes in space.

Sadjadi et al. (in preparation) have recently carried out density functional theory (DFT)-based couple-cluster calculations of the four C_{24} isomers (graphene, fullerene, ring, and bowl). They find the fullerene and graphene forms to be more stable but their simulated spectra show that only planar C_{24} displays features close to the astronomical bands. So, this new work also reinforces the idea of planar C_{24} being the most likely carrier of these IR features seen in space.

3 DIBs and fulleranes in fullerene environments

We have also done the first studies of DIBs in fullerene sources like PNe and RCB stars ([19], [21], [12]). The strongest electronic transitions of C_{60} are not detected in the optical and the DIBs are different for both types of stars (see Fig. 2). In particular, the 4428 Å DIB, shown in Fig.2 (left panel) for Tc 1, is found to be unusually strong in fullerene PNe, while a new DIB at 4000 Å was detected in the RCB star DY Cen (Fig. 2, right panel).

Regarding fulleranes (or hydrogenated fullerenes), the lab spectra of highly hydrogenated fullerenes like $C_{60}H_{18}$ and $C_{70}H_{38}$ show that the most intense transitions are found in the 3-4 μ m range. We looked for these species in two fullerene PNe but no features were found ([13]), likely indicating that if present in these objects, then they are by far less abundant than C_{60} and C_{70} . However, [44] have reported a tentative detection of hydrogenated fullerenes in a proto-PN, that would be consistent with $C_{60}H_{18}$ and $C_{60}H_{36}$. Both works suggest that hydrogenated fullerenes may be formed in the post-AGB phase but they are quickly destroyed by the ultraviolet radiation from the central star.

More recently, [45] have done DFT simulations of 5 isomers for a full set of hydrogenated fullerenes with very different hydrogen content (see Fig. 3). Interestingly, they find that hydrogenated fullerenes with very low H-content do not display IR features at $3-4 \mu m$ but still contribute to longer wavelengths. Thus, we cannot discard the presence of hydrogenated fullerenes with low H-content in space and they indeed could contribute to the 17.4 and 18.9 μm features seen in fullerene sources.

4 Fullerenes with GranTeCan

For the study of fullerenes, we have also used the mid-IR instrument Canaricam at the Spanish ten meter telescope GranteCan on the island of La Palma. In particular, we got mid-IR images (in the N and Q bands, covering several spectral features and their adjacent continua) of the brightest fullerene PN IC 418 ([14]).

The mid-IR images covered the dust continuum at 9.8 microns, the broad $\sim 9-13 \ \mu m$ feature, the C₆₀ feature at 17.4 μm , and the dust continuum around 20 μm . The emission



Figure 3: Local minimum geometries of $C_{60}H_m$ (m = 2, 4, 6, 8) isomers from model calculations. A total of 55 structures, 5 isomers for each of $C_{60}H_m$, m = 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 36, were included in [45]. The numbers of the isomers are assigned as 1 to 5 from left to right. The carbon cage is shown in grey and the C–H bonds are shown in blue. We can clearly see the geometric distortion of the C₆₀ cage when hydrogen atoms are attached (adapted from [45]).



Figure 4: Contour maps of the mid-IR GTC/CanariCam PAH2-Si3, SiC-Si3, PAH2-SiC, and Q1-Q4 images of IC 418 when calibrating with the standard stars (case i in [14]). Note that only two contours at 0.4 and 0.6 are displayed in the Q1-Q4 image, which also displays the *Spitzer* slit in red (adapted from [14]).

seen in these images is mainly coming from a ring-like structure that is seen in all filters, with the exception of the dust continuum emission at 9.8 μ m, which peaks near the central star (see [14]). The very similar spatial distribution seen in the Q1 and Q4 filters covering the C₆₀ feature and the dust continuum already suggests that both filters are dominated by the dust continuum emission. This is not strange if we take into account that IC 418 has a very low C₆₀ to continuum ratio.

We have subtracted the dust continuum emission from our images (see Fig. 4), recovering a nice ring-like structure for the broad $\sim 9-13 \ \mu m$ emission. We have tried to recover the spatial distribution of the weak PAH-like feature at 11.3 μm and it seems to be less well defined than for the broad $\sim 9-13 \ \mu m$ feature. However, only a residual C₆₀ emission (at about 5- σ from the sky background) is seen when subtracting the dust continuum emission at 20 μm . If real, this could explain why *Spitzer* clearly detected fullerenes in this PN, because *Spitzer* just observed this region.

The observed spatial distribution of C_{60} may have several interpretations and the data



Figure 5: Scheme of the addition reaction of anthracene to C_{60} fullerene. It is schematized the fact that initially anthracene forms a mono-adduct (#5) but in an excess of anthracene, a bis-adduct (#6) is obtained ([30]) (adapted from [30], [22]).

are not conclusive about fullerene formation and excitation. So, higher sensitivity observations (especially in the Q-band where water vapour severely limits the ground-based observations) are needed; for example by using the future James Webb Telescope (see [14] for more details).

5 Other fullerene compounds in the lab

Independently of the relevance of the laboratory induced reactions (e.g., Diels-Alder, the Scholl reaction) in circumstellar environments, the organic chemistry techniques are useful to synthesize/characterize some specific molecular nanostructures of our interest.

For example, we know that fullerenes and PAHs may coexist in fullerene PNe. C_{60} can react with a small PAH like anthracene via Diels-Alder reactions to form fullerene/anthracene mono-adducts or bis-adducts (see Fig. 5). Such fullerene/PAHs adducts display the same mid-IR features of isolated C_{60} molecules and we could not distinguish them via mid-IR spectroscopy only ([22]). Indeed, as for the case of hydrogenated fullerenes with low Hcontent, such fullerene adducts may contribute to the observed fullerene-like features observed in space.

Until now, we have synthesized and characterized adducts of C_{60} and C_{70} with small PAHs like anthracene, tetracene, and pentacene as well as adducts of fullerenes with iron penta-carbonyl ([22], [23], [24], [4], [5], [6]).

More recently, we have studied charge-transfer interactions between fullerenes and a series of alkylnapthnalenes, pinenes, and dienes like those shown in Fig. 6 ([25], [26]). We basically found that these interactions are rather weak.

In addition, we have recently obtained IR laboratory spectroscopy of several carbonized PAHs ([27]). The scheme displays the carbonization pathway for napthalene. Interestingly, such carbonized PAHs display infrared features coincident with the set of unidentified infrared bands (UIRs). The PAHs, if present in space, could experience carbonization under the action of shock waves, which are know to be very common in circumstellar and interstellar media.

It is to be noted here that in the lab, we have studied a new route towards graphene



SCHEME 1

Figure 6: Chemical structures of a series of alkylnapthnalenes, pinenes, and dienes used to study the $C_{60,70}$ charge-transfer interactions (adapted from [26]).

starting from heavily ozonided fullerenes (or C_{60} and C_{70} ozopolymers; [7], [8], [9]). This approach is found to be easier and more consistent preparation than the one for graphene oxide (GO).

6 Fullerenes with the James Webb Space telescope

Finally, the future James Webb Space telescope will be much more sensitive than Spitzer, with access to the near-IR range. This mission will permit near- and mid-IR spectroscopic and imaging studies of individual fullerene-containing sources. The James Webb will permit us to know the relative sub-arcsecond spatial distribution of the fullerenes, and other dust features and much higher spectral resolution to cleanly resolve the fullerene-like features. With such observations we will learn about fullerene formation and excitation, and we could detect other fullerene-based compounds in space.

7 Summary - open questions

In short, the knowledge of the chemical route to form fullerenes in space remains as the main open question. The astronomical observations suggest a top-down fullerene formation. Two main chemical routes starting from the photochemical processing of PAHs or HAC-like nanoparticles have been proposed to explain the detection of fullerenes in the interstellar medium and in evolved stars, respectively.

Another open questions are the following: i) What is the excitation mechanism of the fullerene emission? Thermal or fluorescence emission? Can the photo-switching give an extrastability to fullerene compounds ?; ii) Why DIBs are so different in the fullerene-containing environments around RCB stars and PNe?

What it seems to be clear is that a complex family of fullerene- and graphene-based molecules is very likely to be present in space but more laboratory, theoretical, and observational efforts are needed.

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