

# Molecular processes from the AGB to the PN stage

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**Abstract.** Many complex organic molecules and inorganic solid-state compounds have been observed in the circumstellar shell of stars (both C-rich and O-rich) in the transition phase between Asymptotic Giant Branch (AGB) stars and Planetary Nebulae (PNe). This short ( $\sim 10^2$ - $10^4$  years) phase of stellar evolution represents a wonderful laboratory for astrochemistry and provides severe constraints on any model of gas-phase and solid-state chemistry. One of the major challenges of present day astrophysics and astrochemistry is to understand the formation pathways of these complex organic molecules and inorganic solid-state compounds (e.g., polycyclic aromatic hydrocarbons, fullerenes, and graphene in the case of a C-rich chemistry and oxides and crystalline silicates in O-rich environments) in space. In this review, I present an observational review of the molecular processes in the late stages of stellar evolution with a special emphasis on the first detections of fullerenes and graphene in PNe.

**Keywords.** Astrochemistry, molecular processes, planetary nebulae: general, stars: AGB and post-AGB, dust

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## 1. Introduction

At the end of the Asymptotic Giant Branch (AGB), low- and intermediate-mass stars experience strong mass loss that efficiently enriches the interstellar medium with gas and dust. The main processes of nucleosynthesis on the AGB are the production of carbon and of heavy s-process elements. AGB stars experience a different nucleosynthesis depending on the progenitor mass and metallicity (e.g., García-Hernández *et al.* 2007a and references therein). In our own Galaxy, low-mass ( $M < 1.5 M_{\odot}$ ) AGB stars remain O-rich and they probably do not form a Planetary Nebula (PN), while intermediate-mass ( $1.5 < M/M_{\odot} < 4$ ) turn C-rich and they produce s-process elements through the  $^{13}\text{C}$  neutron source. Finally, high-mass ( $M > 4 M_{\odot}$ ) AGB stars remain O-rich because of the Hot Bottom Burning (HBB) activation and they produce s-elements via the  $^{22}\text{Ne}$  neutron source (García-Hernández *et al.* 2006, 2009). Note that this AGB evolutionary scenario is strongly modulated by metallicity (e.g.,  $3^{\text{rd}}$  dredge-up efficiency, HBB activation). The more massive C-rich and O-rich sources are strongly obscured by the circumstellar dust at the end of the AGB and they experience a phase of total obscuration in their way to become PNe, being only accessible in the infrared and millimeter wavelength ranges.

More than 60 molecules have been detected in the circumstellar shells around AGB stars (e.g., Herbst & van Dishoeck 2009). Many gas-phase molecules such as inorganics (CO, SiO, SiS, NH<sub>3</sub>, etc.), organics (C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub>, etc.), radicals (e.g., HCO<sup>+</sup>), rings (e.g., C<sub>3</sub>H<sub>2</sub>), and chains (e.g., HC<sub>9</sub>N) have been detected around AGB stars. Gas-phase reactions cannot explain all of these molecules and solid-state chemistry has to be considered (e.g., molecules can form on dust grains). Indeed, amorphous silicates, weak crystalline silicates (olivine, pyroxene), refractory oxides (corundum, spinel) have been detected

around O-rich AGB stars. On the other hand, SiC and amorphous carbon are frequently observed in C-rich AGB stars, although other complex and disordered organic compounds (e.g., coal, kerogen, tholins) can provide the strong IR continuum and features observed. However, young and evolved PNe show strong Aromatic Infrared Bands (AIBs) - usually associated with Polycyclic Aromatic Hydrocarbons (PAHs) - and crystalline silicates in the case of a C-rich and O-rich chemistry, respectively. Mixed-chemistry (showing both C-rich and O-rich dust features) PNe are also observed. The aromatic (C-rich) and crystalline (O-rich) compounds are synthesized during the short ( $\sim 10^2$ - $10^4$  years) transition phase between AGB stars and PNe (e.g., García-Lario & Perea-Calderón 2003; Kwok 2004). Thus, post-AGB stars and proto-PNe are wonderful laboratories for astrochemistry, providing us with crucial information about the formation pathways of complex organic molecules and inorganic solid-state compounds. Here I present an observational review (both in C-rich and O-rich environments) of the molecular processes (i.e., gas-phase molecules and the dust grains that these molecules can form) from AGB stars to PNe as seen by the Infrared Space Observatory (ISO) and the Spitzer Space Telescope, which give us strong constraints to gas-phase and solid-state chemistry. Special attention is given to the first detections of fullerenes and graphene in PNe.

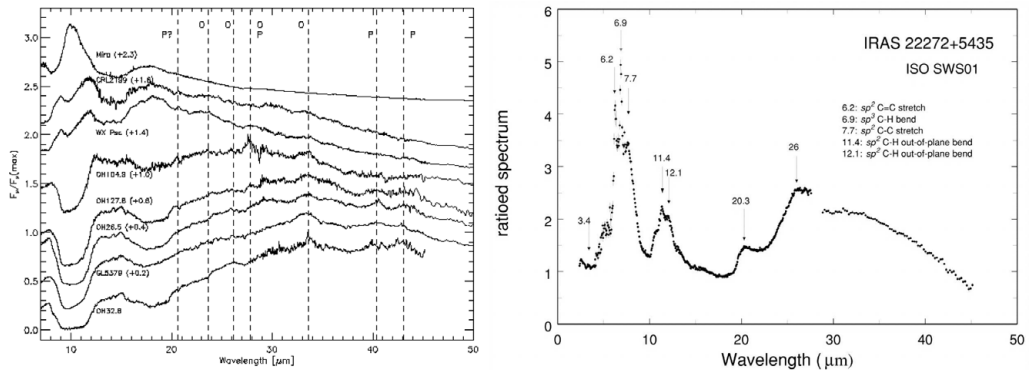
## 2. Molecular evolution from AGB to PNe as seen by ISO and Spitzer.

*O-rich chemistry.* ISO spectroscopy has revealed that weak crystalline silicate (olivine, pyroxene) and water ice features are only seen in high mass loss rate O-rich (C/O < 1) AGB stars - the so-called OH/IR stars (e.g., Sylvester *et al.* 1999; see Figure 1, left panel). Also, S-type AGB stars (with C/O  $\sim 1$ ) show a set of O-rich infrared features that are different to those seen in OH/IR stars (Hony *et al.* 2009). Another important result from ISO was the detection of strong crystalline silicates in O-rich post-AGB stars and PNe (e.g., Waters *et al.* 1996; Molster *et al.* 2002) as well as the identification of double-dust chemistry objects (e.g., cool WCPNe, Waters *et al.* 1998). Water ice features (both amorphous and crystalline) were also detected in some post-AGB stars (e.g., Manteiga *et al.* 2011 and references therein).

With the advent of the Spitzer Space telescope, it has been possible to study O-rich AGB stars in other galaxies as well as to study the relation between the dust properties and metallicity. It is found that O-rich AGBs are less obscured (a lower dust production) in low metallicity environments and the amorphous silicates are always seen in emission (e.g., Sargent *et al.* 2010). Another important Spitzer result was the identification of the (heavily obscured) high-mass precursors of PNe (the OHPNe). The latter sources showed unusual crystalline silicate features, likely due to the different nucleosynthesis in the previous AGB phase (García-Hernández *et al.* 2007b). In addition, Spitzer has permitted to study the total obscuration phase that could not be done by ISO (e.g., García-Hernández *et al.* 2007c). With regard to O-rich PNe, Spitzer found that O-rich PNe are less common at low metallicity such as in the Magellanic Clouds (MCs, Stanghellini *et al.* 2007). Also, many O-rich PNe showing amorphous silicates emission have been detected by Spitzer (e.g., Górny *et al.* 2010; Stanghellini *et al.* 2012 and these proceedings).

In short, the evolution of the O-rich dust features proceeds from amorphous (in the AGB phase) to crystalline silicates (in the PNe stage) (García-Lario & Perea-Calderón 2003). Two models for the crystallization of the silicates have been proposed: i) high-temperature crystallization at the end of the AGB as a consequence of the strong mass loss (Waters *et al.* 1996) or ii) low-temperature crystallization in long-lived circumbinary disks (Molster *et al.* 1999).

*C-rich chemistry.* Gas-phase organic molecules (e.g., C<sub>2</sub>H<sub>2</sub>, HCN, etc.) around the prototype C-rich AGB star IRC +10216 were first detected by ISO (Cernicharo *et al.*



**Figure 1.** *Left panel:* Weak crystalline silicate features from pyroxene (P) and olivine (O) found in OH/IR stars by ISO (Sylvester *et al.* 1999). *Right panel:* ISO spectrum of the proto-PN IRAS 22272+5435 showing the presence of aliphatic discrete features (e.g., at 3.4 and 6.9  $\mu\text{m}$ ) and the 8 and 12  $\mu\text{m}$  aliphatic plateaus together with AIBs (e.g., at 6.2 and 7.7  $\mu\text{m}$ ). The still unidentified 21, 26, and 30  $\mu\text{m}$  features are also seen (Kwok *et al.* 2001).

1999). These organic molecules are usually observed together with a strong dust continuum emission and a broad dust feature centered at  $\sim 11.5$   $\mu\text{m}$  (e.g., Yang *et al.* 2004). The strong dust continuum emission is usually attributed to amorphous carbon while the 11.5  $\mu\text{m}$  feature is believed to be produced by SiC (e.g., Speck *et al.* 2009). An unidentified broad feature at 25–35  $\mu\text{m}$  (the so-called 30  $\mu\text{m}$  feature; e.g., Volk *et al.* 2000) is already seen during the AGB phase. The 11.5 and 30  $\mu\text{m}$  features are also observed in the post-AGB and PNe phases (e.g., Hony *et al.* 2002; Morisset *et al.* these proceedings) but the still unidentified 21  $\mu\text{m}$  feature is genuine of the post-AGB stage (see Sect. 3).

The ISO detection of other C-bearing species such as polynes, benzene, etc. in post-AGB stars may be explained by the polymerization of  $\text{C}_2\text{H}_2$ , HCN, and carbon chains (Cernicharo 2004). Indeed, these small hydrocarbon molecules like  $\text{C}_2\text{H}_2$ ,  $\text{C}_4\text{H}_2$ ,  $\text{C}_6\text{H}_6$  have been suggested to be the building blocks of more complex molecules such as PAHs and that are known to show strong aromatic infrared bands (AIBs at 3.3, 6.2, 7.7, 8.6, and 11.3  $\mu\text{m}$ ; e.g., Allamandola *et al.* 1989) coincident with the unidentified infrared (UIR) emission observed in stars evolving from AGB stars to PNe. However, because of the low temperatures of the central stars, it is difficult to believe that the UIRs observed in proto-PNe are due to free-flying gas-phase PAHs (e.g., Kwok *et al.* 2001; Duley & Williams 2011). Interestingly, proto-PNe show aliphatic emission represented by the 8 and 12  $\mu\text{m}$  emission plateaus and the 3.4, 6.9, and 7.3  $\mu\text{m}$  features together with the classical AIBs (see Figure 1, right panel). This is a strong indication of the coexistence of aliphatic and aromatic structures in the circumstellar shells of these evolved stars. Thus, a better alternative to the PAH hypothesis is a solid material with a mix of aliphatic and aromatic structures such as hydrogenated amorphous carbon (HAC; e.g., Duley & Williams 2011), coal (e.g., Guillois *et al.* 1996), etc. Observationally, it seems clear that the aliphatic component decreases with the evolutionary stage, with the AIBs being stronger in the PN phase (Kwok *et al.* 2001; García-Lario & Perea-Calderón 2003). This change from aliphatic to aromatic structures was attributed to the photochemical processing by the UV photons from the central star (Kwok *et al.* 2001).

Our understanding of the C-rich chemistry in evolved stars has significantly improved with the more recent Spitzer data, permitting us to study extragalactic sources in the transition phase from AGB stars to PNe for the first time. Infrared features from gas phase molecules ( $\text{C}_2\text{H}_2$ , HCN,  $\text{C}_3$ ) are more common and strong in AGB stars of low

metallicity environments (e.g., Lagadec *et al.* 2007). Examples of truly extragalactic C-rich post-AGB stars were first detected by Bernard-Salas *et al.* (2006). More recently, Volk *et al.* (2011) have reported the Spitzer spectra of a significant sample of post-AGB stars in the MCs, finding that the unidentified 21  $\mu\text{m}$  feature is more common at low metallicity. The systematic study of heavily obscured post-AGB stars of our Galaxy show that aliphatic broad emissions (at  $\sim 10\text{--}15$ ,  $15\text{--}20$ ,  $25\text{--}35$   $\mu\text{m}$ ) as well as molecular absorptions from small hydrocarbons are typical during the total obscuration phase of the more massive C-rich post-AGB stars (García-Hernández *et al.* 2007c). As expected from the nucleosynthesis in the previous AGB phase, C-rich PNe were found to be more frequent at low metallicity, showing less processed dust grains (i.e., aliphatic dust dominates and AIBs are rare; Stanghellini *et al.* 2007).

In summary, the C-rich dust features seem to change from aliphatic (in the AGB phase) to mostly aromatic (in the PN stage) although a mix of aliphatic and aromatic features are observed in the post-AGB stage and still in some PNe. Several scenarios have been proposed to explain the aromatization from the AGB phase to the PNe stage: i) dust processing (change from aliphatic to aromatic structures) by the UV photons from the central star (e.g., Kwok *et al.* 2001; García-Lario & Perea-Calderón 2003; Kwok 2004); ii) acetylene ( $\text{C}_2\text{H}_2$ ) and its radical derivatives are the precursors of PAHs (e.g., Cernicharo 2004). The very recent detections of fullerenes and graphene in post-AGB stars and PNe have provided new valuable information about the dust processing in the circumstellar shells of evolved stars (see Sect. 4).

Mixed-chemistry sources. The mixed chemistry phenomenon (the simultaneous presence of both C-rich and O-rich chemistry and dust discovered by ISO) was found to be a common characteristic to cool Wolf-Rayet WCPNe, pointing to the presence of a long-lived circumbinary disk (Waters *et al.* 1998). More recent Spitzer observations show that the mixed-chemistry phenomenon is more common in the Galactic Bulge, being not restricted to cool WCPNe (Perea-Calderón *et al.* 2009). The binary hypothesis cannot explain the dual-dust chemistry phenomenon in the Galactic Bulge and a very late thermal pulse (Perea-Calderón *et al.* 2009) or hydrocarbon chemistry in an UV-irradiated, dense torus (Guzmán-Ramírez *et al.* these proceedings) have been invoked to explain the high detection rate of mixed-chemistry sources in the Bulge. In addition, mixed-chemistry has now been detected in some post-AGB stars (Cerrigone *et al.* 2009). Interestingly, the detection rate of mixed-chemistry PNe is strongly linked to the metallicity (Stanghellini *et al.* 2012 and these proceedings).

### 3. The unidentified 21, 26, and 30 $\mu\text{m}$ features

Apart from the aromatic and aliphatic features mentioned above, there is an interesting set of still UIR features located at 21, 26, and 30  $\mu\text{m}$  and that are usually observed in stars from the AGB to the PN phase.

The 21  $\mu\text{m}$  feature. This feature is only observed in post-AGB stars and their characteristics indicate a solid-state carrier with a fragile nature. Many different carriers of the 21  $\mu\text{m}$  feature have been proposed in the literature but it seems clear that the carrier should be a carbonaceous compound. Hydrogenated fullerenes, nanodiamonds, HAC, TiC nanoclusters, etc. are some examples among the proposed carbonaceous species. Amides (urea or thiourea) as the carrier of the 21  $\mu\text{m}$  emission is the more recent and exotic proposal (Papoular 2011).

The 26 and 30  $\mu\text{m}$  features. The 30  $\mu\text{m}$  feature, sometimes with substructure at 26  $\mu\text{m}$ , is seen from the AGB to the PN stage with an important fraction of the total energy output. This indicates that the carrier should be very abundant in the circumstellar shell.

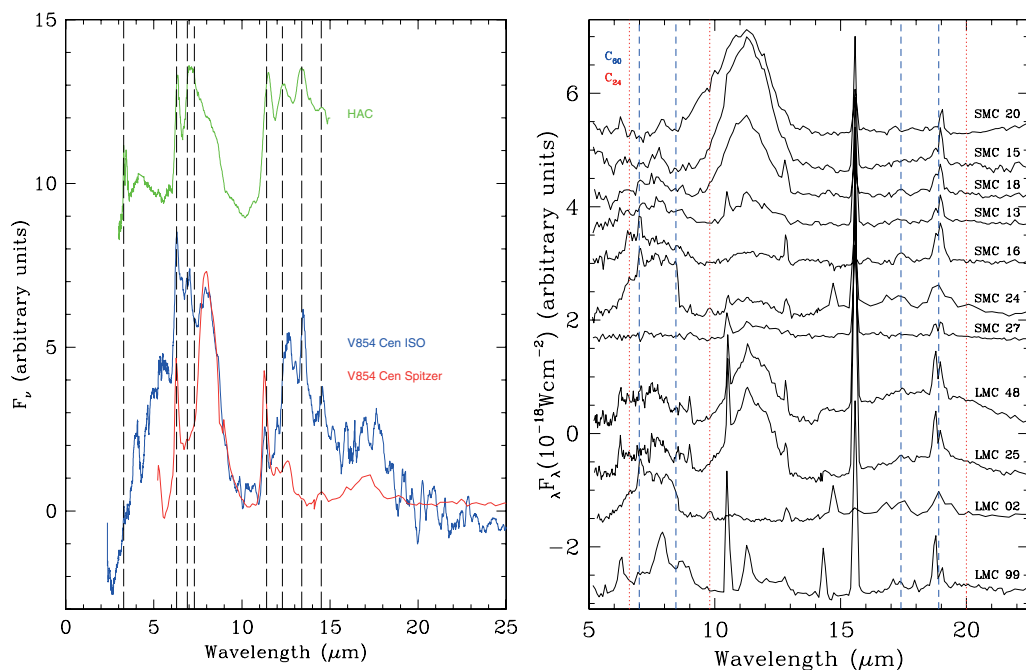
The carrier of the 30  $\mu\text{m}$  feature is usually assumed to be MgS (Hony *et al.* 2002) but Zhang *et al.* (2009) argue that MgS is very unlikely the carrier of the 30  $\mu\text{m}$  emission seen in C-rich evolved stars. Grishko *et al.* (2001) also show that HACs can explain the 30  $\mu\text{m}$  feature. The HAC identification can also explain the 21 and 26  $\mu\text{m}$  features. More recently, Papoular (2011) shows that aliphatic chains (CH<sub>2</sub> groups, O bridges and OH groups) can also explain the 30  $\mu\text{m}$  emission in sources evolving from AGB to PNe. Finally, it should be noted that other weaker UIR features at 15.8, 16.4, and 17  $\mu\text{m}$  are also seen in some proto-PNe (see e.g., Hrivnak *et al.* 2009).

#### 4. Fullerenes and graphene in circumstellar envelopes.

Fullerenes such as C<sub>60</sub> and C<sub>70</sub> are highly resistant and stable tridimensional molecules formed exclusively by carbon atoms. Fullerenes and fullerene-related molecules have attracted much attention since their discovery at laboratory (Kroto *et al.* 1985) because they may explain certain unidentified astronomical features such as the so-called diffuse interstellar bands (DIBs) (see e.g., Luna *et al.* 2008 for a review on interstellar/circumstellar DIBs). The remarkable stability of fullerenes against intense radiation, ionization, etc. reinforced the idea that fullerenes should be present in the interstellar medium with important implications for interstellar/circumstellar chemistry. Indeed, fullerenes were found on Earth on meteorites and several unsuccessful ISO attempts to look for the mid-IR signatures of fullerenes in circumstellar shells have been previously made, including R Coronae Borealis (RCB) stars (e.g., Lambert *et al.* 2001) and post-AGB stars (e.g., Kwok *et al.* 1999).

*Discovery of fullerenes in space.* The RCB stars have been considered to be the ideal astrophysical environments for the formation of fullerenes (Goeres & Sedlmayr 1992). This is because the H-deficiency together with the He and C-rich characters of RCBs resemble the experimental conditions on Earth, facilitating the formation of fullerenes (e.g., Kroto *et al.* 85). In late 2009 García-Hernández, Rao & Lambert looked for C<sub>60</sub> in a complete sample of 31 RCBs using Spitzer. They got the unexpected result that C<sub>60</sub> was only detected in the two RCBs (DY Cen and V854 Cen) with some H in their circumstellar shells. Interestingly, their detection of C<sub>60</sub> around RCBs occurred in conjunction with the presence of PAHs. In addition, they found that the V854 Cen's IR spectrum evolved from HACs (ISO 1996's spectrum) to PAHs and C<sub>60</sub> (Spitzer's 2007) (see Figure 2, left panel). These unique IR spectral variations prompted them to claim that the PAHs and fullerenes evolved from HAC grains. Because of the unexpected result in RCBs, they looked for fullerenes in ~240 PNe pertaining to very different environments and observed by Spitzer. The mid-IR signatures of the C<sub>60</sub> fullerenes were clearly found in five PNe with normal H abundances (including the PN Tc 1). The common presence of PAH features in fullerene-containing PNe confirmed them the unexpected results obtained in RCBs. Meanwhile, Cami *et al.* (2010) reported in *Science* the great discovery of the IR detection of C<sub>60</sub> and C<sub>70</sub> fullerenes in Tc 1 as due to the H-poor conditions in the inner core<sup>†</sup>. However, neither the central star, nor the inner core and the nebula are H-deficient and current understanding of stellar astrophysics does not allow for Tc 1 being a H-poor PN (see García-Hernández *et al.* 2010; García-Hernández, Rao & Lambert 2011). Thus, the detection of fullerenes in PNe and RCB stars have challenged the paradigm regarding fullerene formation in space, showing that, contrary to general expectation, fullerenes are

<sup>†</sup> García-Hernández, Rao & Lambert submitted their unexpected RCB results to *Science* on April 19th 2010 but their work was rejected; e.g., one reviewer was opposed to their work because it was “in the wrong direction with the least H-deficient stars showing the C<sub>60</sub> features”.



**Figure 2.** *Left panel:* Residual ISO and Spitzer/IRS spectra for the RCB star V854 Cen. The laboratory emission spectrum of HAC at 773 K is shown for comparison (García-Hernández, Rao & Lambert 2011). *Right panel:* Residual Spitzer spectra of fullerene-MCPNe. The band positions of C<sub>60</sub> (dashed) and planar C<sub>24</sub> (dotted) are marked (García-Hernández *et al.* 2011).

efficiently formed in H-rich circumstellar environments. In addition, C<sub>60</sub> has been recently detected in the proto-PN IRAS 01005+7910 (Zhang & Kwok 2011) and two binary post-AGB stars (Gielen *et al.* these proceedings), indicating that fullerene formation can occur just after the AGB phase.

*Formation of fullerenes in H-rich ejecta.* The simultaneous detection of PAH-like features and fullerenes toward C-rich and H-containing PNe indicates that modifications are needed to our current understanding of the chemistry of large organic molecules as well as the chemical processing in space (García-Hernández *et al.* 2010). The suggestion was made that both fullerenes and PAHs can be formed by the photochemical processing (e.g., as a consequence of UV irradiation or shocks) of HAC, which should be a major constituent in the circumstellar envelope of C-rich evolved stars. This idea is supported by the laboratory experiments on the decomposition of HAC, which show that the products of destruction of HAC grains are PAHs and fullerenes in the form of C<sub>50</sub>, C<sub>60</sub>, and C<sub>70</sub> molecules (Scott *et al.* 1997). More recently, García-Hernández *et al.* (2011) have presented new Spitzer detections of C<sub>60</sub> and C<sub>70</sub> fullerenes in PNe of the MCs (MCPNe), which have permitted an accurate determination of the C<sub>60</sub> and C<sub>70</sub> abundances (C<sub>60</sub>/C~0.07% and C<sub>70</sub>/C~0.03%) in space for the first time. The quantitative determination of fullerenes in space was possible thanks to the very recent laboratory studies of the C<sub>60</sub> and C<sub>70</sub> fullerenes (Iglesias-Groth *et al.* 2011; Cataldo *et al.* these proceedings). In addition, the new MCPNe studies show that neutral fullerenes are likely in solid-state and collisionally excited (i.e., they are not excited by the UV photons from the central stars) and that they probably evolved from the shock-induced decomposition of small solid particles similar to that of HAC dust (García-Hernández *et al.* 2011).

*First detection of graphene in space.* Interestingly, some of the fullerene-containing MCPNe display very unusual emission features at  $\sim 6.6$ ,  $9.8$ , and  $20 \mu\text{m}$  (see Figure 2, right panel) coincident with the theoretical transitions of planar  $\text{C}_{24}$  (García-Hernández *et al.* 2011). Planar  $\text{C}_{24}$  is a very stable molecule (more than the  $\text{C}_{24}$  fullerene) and can be viewed as a small fragment of a graphene sheet. The detection of these very unusual features in fullerene sources represents the first possible detection of graphene in space. However, a definitive confirmation has to wait for laboratory infrared spectroscopy of  $\text{C}_{24}$ , which is extremely difficult because of the high reactivity of  $\text{C}_{24}$ . The possible detection of graphene precursors ( $\text{C}_{24}$ ) opens the possibility of detecting other complex forms of carbon (e.g., carbon nanotubes, carbon onions, etc.) in space.

*UIR emissions in fullerene sources.* Remarkably, fullerenes and graphene have been detected in PNe whose IR spectra are dominated by aliphatic C-rich dust, represented by broad emissions such as those at  $6\text{--}9$ ,  $10\text{--}15$ ,  $15\text{--}20$ , and  $25\text{--}35 \mu\text{m}$ . The  $6\text{--}9 \mu\text{m}$  feature may be attributed to HACs or large PAH clusters. On the other hand, the broad  $10\text{--}15 \mu\text{m}$  (the  $11.5 \mu\text{m}$  feature) and the  $25\text{--}35 \mu\text{m}$  emission (the  $30 \mu\text{m}$  feature) are usually attributed to SiC (e.g., Speck *et al.* 2009) and MgS (e.g., Hony *et al.* 2002), respectively. However, the observed variability of these broad features is quite consistent with the variable properties of HACs (a material with mixed aliphatic and aromatic structures), which are able to provide a wide range of different spectra (e.g., the relative strength and position of the IR features) depending on their physical and chemical properties (e.g., size, shape, hydrogenation; e.g., Grishko *et al.* 2001). Indeed, these aliphatic emissions in low-metallicity extragalactic post-AGB stars and PNe are stronger and much more common than in the higher metallicity Galactic counterparts (Volk *et al.* 2011; Stanghellini *et al.* 2007, 2012). Because of the lower metal content (Si, Mg) of MC post-AGBs and PNe, the opposite is expected. Thus, it is very unlikely that the carriers of the broad  $11.5$  and  $30 \mu\text{m}$  emissions - usually seen in fullerene-containing PNe - are related with SiC and MgS, respectively, as it was suggested in the past. The carriers of the broad  $11.5$  and  $30 \mu\text{m}$  features (also the bump at  $15\text{--}20 \mu\text{m}$  and possibly the so-called  $21$  and  $26 \mu\text{m}$  features) are more likely related with other decomposition products of HACs or a similar material (e.g., fullerene and graphene precursors or intermediate products not yet identified) but a definitive answer requires further laboratory efforts.

## 5. Concluding remarks

In summary, the most likely explanation for the formation of fullerenes and graphene in H-rich environments is that these molecular species may be formed from the destruction of a carbonaceous compound with a mixture of aromatic and aliphatic structures - e.g., HAC - which should be widespread in space. In this context, the coexistence of a large variety of molecular species in H-rich circumstellar environments is supportive of a model in which non-equilibrium IR emission occurs from small solid particles containing aromatic, aliphatic, fullerene, and graphene structures similar to that of HAC dust. Indeed, Duley & Williams (2011) have recently suggested a model for the heating of HAC dust via the release of chemical energy that gives a natural explanation for the astronomical aromatic emission at  $3.3$  (and other UIR wavelengths) usually attributed to PAHs. Finally, it should be noted here that instead of HACs, other materials with a complex mix of aromatic and aliphatic structures (e.g., coal, kerogen, petroleum fractions, soot, quenched carbonaceous composites, carbon nanoparticles, etc.) can be present in astrophysical environments and they should be widely explored at laboratory. For example, coal and petroleum fractions may explain the great diversity of spectral features (aromatic and aliphatic) seen in proto-PNe (Guillois *et al.* 1996; Cataldo *et al.* 2002).

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