A search for hydrogenated fullerenes in fullerene-containing planetary nebulae

J J Díaz-Luis¹, ², D A García-Hernández¹, ², A Manchado¹, ², ³ and F Cataldo⁴, ⁵

¹ Instituto de Astrofísica de Canarias, C/ Via Láctea s/n, E–38205 La Laguna, Spain
² Departamento de Astrofísica, Universidad de La Laguna (ULL), E–38206 La Laguna, Spain
³ Consejo Superior de Investigaciones Científicas, Madrid, Spain
⁴ INAF- Osservatorio Astrofisico di Catania, Via S. Sofia 78, Catania 95123, Italy
⁵ Actinium Chemical Research srl, Via Casilina 1626/A, 00133 Rome, Italy

E-mail: jdiaz@iac.es, agarcia@iac.es

Abstract. Detections of C₆₀ and C₇₀ fullerenes in planetary nebulae (PNe) of the Magellanic Clouds and of our own Galaxy have raised the idea that other forms of carbon such as hydrogenated fullerenes (fulleranes like C₆₀H₃₆ and C₆₀H₁₈), buckyonions, and carbon nanotubes, may be widespread in the Universe. Here we present VLT/ISAAC spectra (R ≈ 600) in the 2.9-4.1 μm spectral region for the Galactic PNe Tc 1 and M 1-20, which have been used to search for fullerene-based molecules in their fullerene-rich circumstellar environments. We report the non-detection of the most intense infrared bands of several fulleranes around ~3.4-3.6 μm in both PNe. We conclude that if fulleranes are present in the fullerene-containing circumstellar environments of these PNe, then they seem to be by far less abundant than C₆₀ and C₇₀. Our non-detections together with the (tentative) fulleranes detection in the proto-PN IRAS 01005+7910 suggest that fulleranes may be formed in the short transition phase between AGB stars and PNe but they are quickly destroyed by the UV radiation field from the central star.

1. Introduction

Fullerenes and fullerene-based molecules such as hydrogenated fullerenes and buckyonions may explain some astrophysical phenomena like the intense UV absorption band at 217 nm (e.g., [1]) or the so-called diffuse interstellar bands (DIBs; see e.g., [2, 3]). Their presence in astrophysical environments have been recently confirmed by the Spitzer Space Telescope via the detection of the mid-infrared C₆₀ and C₇₀ fullerene features in the spectrum of the young Planetary Nebula (PN) Tc 1 [4].

It has been demonstrated that fullerenes are efficiently formed in H-rich circumstellar environments only [5, 6], challenging our previous understanding of the fullerenes formation in space. In particular, the simultaneous detection of C₆₀ fullerenes and PAHs in several PNe with normal hydrogen abundances has been reported [5, 7, 8, 9]. García-Hernández et al. [5] propose that both fullerenes and PAHs in H-rich circumstellar ejecta may form from the photochemical processing of hydrogenated amorphous carbon (HAC) in agreement with the experimental results of Scott et al. [10].

Duley & Williams [11] predict the production of fullerenes via thermal heating of HAC and this process may explain the detection of fullerenes in H-rich circumstellar environments (e.g.,
Interestingly, they predict also the formation of hydrogenated fullerenes (fulleranes). On the other hand, Iglesias-Groth et al. [12] found that the 3.44 and 3.55 μm bands of several fulleranes display molar extinction coefficients which are similar to those of the 17.4 and 18.8 μm bands of the isolated C_{60} molecule [13]. Thus, it could be expected to find fulleranes with line intensities similar to the ones already measured with Spitzer at 17.4 and 18.8 μm in fullerene-containing PNe.

2. Mid-infrared VLT/ISAAC spectroscopy of PNe with fullerenes
We acquired 3-4 μm infrared (IR) spectra of the fullerene PNe Tc 1 (S/N ~26 at the continuum), and M 1-20 (S/N ~11 at the continuum).

The M 1-20 spectrum includes the atomic hydrogen lines Pf at 3.07 μm, a blend of the UIE feature at 3.31 with Pf at 3.32 μm, Pf at 3.75 μm, and Br at 4.05 μm. It also includes the tentatively identified H I (6-17), H I (6-15), and He I (4-5) lines at 3.76, 3.91, and 4.04 μm, respectively. In Figure 1, we display the M 1-20 spectrum (left panel) in the 2.9-4.1 μm range.

The Tc 1 spectrum includes the atomic hydrogen lines Pf, Pf, the tentatively identified H I (6-17) and H I (6-15) lines, and Br. It also includes the tentative He I (4-5) line at 4.04 μm. In Figure 1, we display the Tc 1 2.9-4.1 μm spectrum (right panel).

![Figure 1. VLT/ISAAC spectra of M 1-20 (left panel) and Tc 1 (right panel).](image)

3. The 3.3 μm UIE feature
We clearly detect the 3.3 μm UIE feature in M 1-20, while this feature is completely lacking in Tc 1. This is consistent with the Spitzer spectra; M 1-20 displays UIE features (PAH-like) at 6.2, 7.7, 8.6, and 11.3 μm, but these are absent in Tc 1 (e.g., [5]).

A wide variety of molecules have been proposed as possible carriers of the 3.3 and 11.3 μm UIE bands. Nowadays, the most accepted idea is that they originate from the C-H vibration modes of aromatic compounds or PAHs. However, still it is not clear if these bands are only due to aromatic compounds or to mixed aromatic/aliphatic structures characteristic of amorphous organic solids.

4. Non detection of the fullerane features
The IR laboratory spectra (R~500) of several fullerenes such as C_{60}H_{18}, C_{60}H_{38} or C_{70}H_{38} [12] show that the strongest features in the mid-IR (2-20 μm) are those at ~3.44, 3.51 and 3.54 μm, being the best IR bands for searching these molecules in the circumstellar environments of
fullerene-rich PNe. However, none of these three emission features is detected in our VLT/ISAAC spectra of Tc 1 and M 1-20.

We could estimate approximate upper limits to the fluxes of the hydrogenated fullerene features (see Table 1). In order to obtain 2σ upper limits to the expected emission line fluxes of the fullerene features at ~3.5 μm, we measure the rms in our flux calibrated VLT/ISAAC spectra; rms values of ~4.28 × 10^{-19} erg cm^{-2} s^{-1} Å^{-1} and ~6.65 × 10^{-18} erg cm^{-2} s^{-1} Å^{-1} for Tc 1 and M 1-20 are obtained, respectively. Then we multiply these values by the widths (FWHMs in the range 0.02-0.10 μm) of the fullerene bands measured in the infrared laboratory spectra. Finally, we divided these fluxes by the area (~0.6'' arcsec²) for both PNe of the emission in the 3-4 μm range covered by our ISAAC observations.

On the other hand, by using the molar absorptivity values for the fullerenes and fulleranes reported by Iglesias-Groth et al. [13, 12], we may estimate the predicted fluxes for the fullerene features in Tc 1 and M 1-20 (see Table 1). By taking the molar absorptivity ratio (e.g., ε_{C_{60}}/ε_{fulleranes}) of the fullerene and fullerane bands and the observed fluxes of the C_{60} and C_{70} infrared bands less contaminated by other species [8] we estimate the expected flux of the fullerene features at ~3.5 μm.

Table 1 shows some examples of the estimated 2σ upper limits (in units of 10^{-16} erg cm^{-2} s^{-1} Å^{-1}/arcsec²) and the predicted fluxes for the fullerane bands. The expected fluxes for all fullerane bands of C_{60}H_{18}, C_{60}H_{36}, and C_{70}H_{38} (by using the observed Spitzer fluxes of the C_{60} 8.5 and 17.4 μm and C_{70} 14.9 μm bands) are in the range of ~1.7-30 × 10^{-14} and ~1.4-5.6 × 10^{-13} erg cm^{-2} s^{-1} /arcsec² in Tc 1 and M 1-20, respectively.

By comparing the values of the predicted fluxes with our 2σ upper limits (Table 1), we find that the expected fluxes are a factor of ~20-1000 and ~10-100 higher than the 2σ upper limits for Tc 1 and M 1-20, respectively. From these estimations we thus conclude that if fullerenes are present in Tc 1 and M 1-20, then they seem to be by far less abundant than C_{60} and C_{70}.

As we mentioned above, thermal heating via chemical reactions internal to HAC dust may explain the detection of fullerenes in the H-rich circumstellar environments of PNe, and would potentially form fullerenes [11]. In addition, Duley & Hu [14] suggest an evolutionary sequence for the conversion of HAC to fullerenes, in which initial HAC de-hydrogenation is followed by

| Fullerane          | λc (μm) | FLUX (Tc 1) (10^{-14} erg cm^{-2} s^{-1} /arcsec²) | Predicted fluxes (Tc 1) (10^{-14} erg cm^{-2} s^{-1} /arcsec²) | Predicted fluxes (M 1-20) (10^{-13} erg cm^{-2} s^{-1} /arcsec²) |
|-------------------|-------|-----------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| C_{60}H_{18}      | 3.42  | 2.93                                          | 2.65                                            | 2.65                                            |
|                   | 3.46  | 2.93                                          | 2.65                                            | 2.65                                            |
|                   | 3.51  | 2.93                                          | 2.65                                            | 2.65                                            |
| C_{60}H_{36}      | 3.42  | 2.93                                          | 2.65                                            | 2.65                                            |
|                   | 3.45  | 2.93                                          | 2.65                                            | 2.65                                            |
|                   | 3.51  | 2.93                                          | 2.65                                            | 2.65                                            |
| C_{70}H_{38}      | 3.44  | 2.93                                          | 2.65                                            | 2.65                                            |
|                   | 3.54  | 2.93                                          | 2.65                                            | 2.65                                            |
|                   | 3.54  | 2.93                                          | 2.65                                            | 2.65                                            |
PFs formation and subsequent conversion of PFs to closed cage structures such as C_{60}. Under the Duley & Hu [14] scenario, Tc 1 would represent the last stage in the HAC de-hydrogenation process (i.e., only fullerenes are present), while the proto-PN IRAS 01005+7910 would represent an intermediate stage where the PFs are being converted to fullerenes. Remarkably, fulleranes may be also by-products of this conversion from HAC to fullerenes [14].

Interestingly, Zhang & Kwok [15] have (tentatively) detected fulleranes in the proto-PN IRAS 01005+7910; three strong C-H stretching bands at 3.48, 3.51, and 3.58 µm are apparently present in its ISO spectrum with fluxes comparable to the one of the 3.3 µm feature.

Our non-detection of fulleranes in more evolved PNe (such as Tc 1 and M 1-20 with T_{eff} > 30,000 K) together with their detection in less evolved sources (like IRAS 01005+7910 with T_{eff} < 21,500 K) thus suggest that fulleranes may be formed in the short transition phase between AGB stars and PNe but they are quickly destroyed; e.g., photochemically processed by the rapidly changing UV radiation from the central star.

Acknowledgments
We acknowledge Kameswara Rao for his help during the data analysis. J.J.D.L., D.A.G.H., and A.M. acknowledge support provided by the Spanish Ministry of Economy and Competitiveness (MINECO) under grants AYA–2014–58082–P and RyC–2013–14182 (DAGH). This work is based on observations obtained with ESO/VLT under the programme 290.D-5093(A).

References
[1] Cataldo F and Iglesias-Groth S 2009 Mon. Not. R. Astron. Soc. 400 291
[2] García-Hernández D A and Díaz-Luis J J 2013 Astron. Astrophys. 550 L6
[3] Díaz-Luis J J, García-Hernández D A, Rao N K, Manchado A and Cataldo F 2015 Astron. Astrophys. 573 A97
[4] Cami J, Bernard-Salas J, Peeters E and Malek S E 2010 Sci. 329 1180
[5] García-Hernández D A, Manchado A, García-Lario P, Stanghellini L, Villaver E, Shaw R A, Szczepan R and Perea-Calderón J V 2010 Astrophys. J. Lett. 724 L39
[6] García-Hernández D A, Rao N K and Lambert D L 2011 Astrophys. J. 729 126
[7] García-Hernández D A, Iglesias-Groth S, Acosta-Pulido J A, Manchado A, García-Lario P, Stanghellini L, Villaver E, Shaw R A and Cataldo F 2011a Astrophys. J. Lett. 737 L30
[8] García-Hernández D A, Villaver E, García-Lario P, Acosta-Pulido J A, Manchado A, Stanghellini L, Shaw R A and Cataldo F 2012 Astrophys. J. 760 107
[9] Otuka M, Kemper F, Cami J, Peeters E and Bernard-Salas J 2014 Mon. Not. R. Astron. Soc. 437 2577
[10] Scott A, Duley W W and Pinho G P 1997 Astrophys. J. Lett. 489 L193
[11] Duley W W and Williams D A 2011 Astrophys. J. Lett. 737 L44
[12] Iglesias-Groth S, García-Hernández D A, Cataldo F and Manchado A 2012 Mon. Not. R. Astron. Soc. 423 2868
[13] Iglesias-Groth S, Cataldo F and Manchado A 2011 Mon. Not. R. Astron. Soc. 413 213
[14] Duley W W and Hu A 2012 Astrophys. J. Lett. 745 L11
[15] Zhang Y and Kwok S 2013 Earth, Planets and Space 65 1069