Infrared spectroscopy of fullerene C$_{60}$/anthracene adducts

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Accepted 2013 xx xx. Received 2012 xx xx; in original form 2012 xx xx

ABSTRACT

Recent Spitzer Space Telescope observations of several astrophysical environments such as Planetary Nebulae, Reflection Nebulae, and R Coronae Borealis stars show the simultaneous presence of mid-infrared features attributed to neutral fullerene molecules (i.e., C$_{60}$) and polycyclic aromatic hydrocarbons (PAHs). If C$_{60}$ fullerenes and PAHs coexist in fullerene-rich space environments, then C$_{60}$ may easily form adducts with a number of different PAH molecules; at least with catacondensed PAHs. Here we present the laboratory infrared spectra ($\sim$2–25 $\mu$m) of C$_{60}$ fullerene and anthracene Dies-Alder mono- and bis-adducts as produced by sonochemical synthesis. We find that C$_{60}$/anthracene Dies-Alder adducts display spectral features strikingly similar to those from C$_{60}$ (and C$_{70}$) fullerenes and other unidentified infrared emission features. Thus, fullerene-adducts - if formed under astrophysical conditions and stable/abundant enough - may contribute to the infrared emission features observed in fullerene-containing circumstellar/interstellar environments.

Key words: astrochemistry; circumstellar matter; ISM: molecules; methods: laboratory; techniques: spectroscopic

1 INTRODUCTION

Fullerene molecules (e.g., C$_{60}$ and C$_{70}$) were first synthesized at laboratory in an effort to unveil the formation mechanism of long-chain carbon molecules in interstellar and circumstellar media (Kroto et al. 1985). The possible existence of fullerenes in astrophysical environments has been a controversial issue until recently when these complex organic molecules were identified in a young Planetary Nebula (Tc 1; Cani et al. 2010). Based on the lack of the classical aromatic infrared bands (AIBs) (e.g., at 3.3, 6.2, 7.7, 8.6, and 11.3 $\mu$m) usually attributed to polycyclic aromatic hydrocarbons (PAHs; e.g., Leger & Puget 1984), Cani et al. (2010) proposed that fullerenes flourish in the H-deficient and C-rich inner regions of Tc 1. This interpretation was in agreement with the original laboratory studies on the formation of fullerenes (Kroto et al. 1985; de Vries et al. 1993) that show that fullerene formation at laboratory are efficiently produced in the absence of hydrogen. However, García-Hernández et al. (2010) reported the simultaneous detection of C$_{60}$ fullerenes and PAHs in several Planetary Nebulae (PNe) with normal H abundances. In addition, the unexpected detection of C$_{60}$ fullerenes together with PAHs only in the two least H-deficient R Coronae Borealis stars DY Cen and V854 Cen (García-Hernández et al. 2011a,b) confirmed the surprising results obtained in PNe. This challenged our understanding of the fullerenes formation in space, showing that, contrary to general expectation, fullerenes are efficiently formed in H-rich circumstellar environments only. Indeed, the C$_{60}$ fullerene has since then been detected also in a variety of environments such as the interstellar medium (Sellgren et al. 2010), a post-asymptotic giant branch (post-AGB) star and post-AGB circumbinary discs (Zhang & Kwok 2011; Gielen et al. 2011), the Orion nebula (Rubin et al. 2011), a Herbig Ae/Be star and young stellar objects (YSOs; Roberts et al. 2012).

The detection of fullerenes around evolved stars such as our Sun indicates that these complex molecules are much more common and abundant in circumstellar/interstellar environments than was originally believed. It reinforces the idea that fullerenes and molecular-related species are ubiquitous in the interstellar medium, playing an important role in many aspects of circumstellar/interstellar Chemistry. In addition, fullerenes and PAHs may be mixed in the circumstellar envelopes of (proto-) PNe (e.g., García-Hernández et al. 2010, 2011c, 2012a; Zhang & Kwok 2011), raising the exciting possibility of forming adducts of fullerenes with PAHs.

C$_{60}$ fullerene is an electron deficient polyolefin, which is able to give adducts with a number of different molecules (e.g., Yurovskaya & Trushkov 2002; Hirsch & Brettreich...
In particular, C_{60} fullerene can react with catacondensed PAHs (e.g., acenes such as anthracene, pentacene) to form fullerene/PAH adducts via Diels-Alder cycloaddition reactions (Briggs & Miller 2006). It is to be noted here that the Diels-Alder reaction between fullerenes and pericondensed or very large PAHs has not been explored experimentally and the possible formation of such more complex fullerene/PAH adducts is still an open issue. The formation of a Diels-Alder adduct of C_{60} with anthracene is the simplest fullerene/PAH adduct and was one of the first [4+2] addition reactions discovered where the former molecule is acting as a dienophile and the latter as a diene (e.g., Komatsu et al. 1993a,b). C_{60} fullerene can react with anthracene and form the C_{60}/anthracene mono-adduct and the bis-adduct. Figure 1 displays an addition reaction scheme of the C_{60} fullerene with anthracene. C_{60} and anthracene react under different reaction condition to form the C_{60}/anthracene mono-adduct (adduct #5 in Fig.1) and, in case of anthracene excess also the trans–1 bis–adduct (adduct #6 in Fig. 1). Different yields of the C_{60}/anthracene mono- and bis-adducts can be obtained at laboratory depending on the method employed in the production process (see e.g., Cataldo et al. 2013 for a review). The efficiency of the cycloaddition of anthracenes and other acenes to C_{60} can be improved by performing the reaction under the conditions of high speed vibration grinding of solid reagents, known as mechanochemical synthesis (e.g., Komatsu et al. 1999; Wang et al. 2005). Inspired by this mechanochemical synthesis we have recently been stimulated to explore the sonochemical synthesis of these C_{60}/anthracene adducts (Cataldo et al. 2013).

The interest in the C_{60}/anthracene and other fullerene/PAHs adducts regards the access to new fullerene-related molecules, which may be present in the circumstellar and interstellar environments where C_{60} fullerenes have already been found (see above). For example, the possible presence of other complex fullerene-based molecules (e.g., fullerenes bigger than C_{60} or multishell fullerenes) in fullerene-containing space environments is strengthened by a recent study of the diffuse interstellar bands (DIBs) in PNe with fullerenes (García-Hernández & Díaz-Luis 2013). In addition, C_{60} fullerenes seem to be mixed with PAHs and the present debate involves not only how and where fullerenes was formed but also if C_{60} may interact with PAHs forming adducts. In this paper we show that C_{60} is not inert toward PAHs and under certain circumstances (e.g., where the two reagents co-exist) they can react forming new products where fullerene cage is functionalized by PAHs moieties attached on it by covalent bonds. We report the laboratory infrared spectra (\(~2–25 \mu\text{m}\)) of C_{60}/anthracene Diels-Alder mono- and bis-adducts - the simpler example of a family of fullerene/PAHs adducts - as produced by sonochemical synthesis. These laboratory spectra are compared with the Spitzer Space Telescope spectra of fullerene PNe in an attempt to identify some still unidentified mid-IR features displayed by some of these sources.

\section{2 \textsc{sonochemical synthesis of C_{60}/anthracene adducts}}

C_{60} fullerene was 99\% pure grade and was obtained from MTR Ltd (USA). Anthracene and all the solvents used were obtained from Sigma-Aldrich (Germany and USA). The Fourier-Transform infrared (FT-IR) spectra (at a spectral resolution of \(\sim 600\)) were recorded on a IR300 spectrometer from Thermo-Fischer in transmittance mode with samples embedded in KBr. The infrared band shift and band broadening effects by passing from KBr matrix to solid Ar matrix and to the gas phase spectra are relatively small (see e.g., Iglesias-Groth et al. 2011 for the case of the C_{60} and C_{70} fullerenes). Consequently, also for the C_{60}/anthracene adducts we do not expect important differences from our spectra measured in KBr in the lab and those which could derive from the adduct in different environmental conditions than those used in the lab.

The ultrasonic bath used for the synthesis was a Branson 1510. The reaction between C_{60} and anthracene (at 1:1 and 1:2 initial molar ratio) has been successfully conducted by us under sonication in a ultrasonic bath using a benzene solution (see Cataldo et al. 2013 for more details). In short, C_{60} and anthracene were dissolved in a conical flask at room temperature and the flask was suspended in the ultrasonic bath filled with water. The sonication was run for 5 h and the grey reaction product was recovered by distillation of benzene under reduced pressure in a water bath kept at 338 K. Our detailed thermogravimetric analysis (TGA) and differential thermal analysis (DTA) (Cataldo et al. 2013) show that the grey C_{60}/anthracene reaction mixture is composed by 33\% of the mono-adduct and by 66\% of the trans-1 bis-adduct that are shown in the addition reaction scheme of Figure 1 (see Section 3.1). The synthesis of the C_{60}/anthracene adducts is made starting from pure...
C$_{60}$ and pure anthracene and the undesired by-products in the adduct reaction were removed during the purification process (Section 3.2; see also Cataldo et al. 2013 for more details). Thus, there are no other contaminants available even as minor impurities.

From literature data it is known that the mechanochemical synthesis of C$_{60}$/anthracene adducts in the solid state can reach a $55\%$ yield in 1 h (e.g., Komatsu et al. 1999; Wang et al. 2005) with the mono-adducts and bis-adducts representing $4/5$ and $1/5$ of the mixture, respectively. However, the main product of our novel sonochemical synthesis of C$_{60}$/anthracene adducts is the trans-1 bis-adduct (Cataldo et al. 2013). In addition, such a product can be obtained almost pure after appropriate purification of the reaction mixture (see below). Thus, the sonochemical synthesis gives a direct access to pure C$_{60}$/anthracene trans-1 bis-adducts (see Sections 3.2 and 4).

The grey 1:1 and 1:2 adducts (51 mg and 52 mg, respectively) were exhaustively extracted in a Soxhlet apparatus for 6 h using n-hexane as extracting solvent. This causes the extraction of the mono-adduct from the mixture and at the end of the extraction process, the n-hexane solutions contained free unreacted C$_{60}$ and unreacted anthracene (Cataldo et al. 2013). The bis-adducts are instead insoluble in n-hexane and were recovered in 26.5 mg and 26.8 mg after drying for the 1:1 and 1:2 initial molar ratio, respectively. Thus, the yields of both adducts over the grey reaction product was $\sim 50\%$.

### 3 LABORATORY SPECTRA OF C$_{60}$/ANTHRACENE ADDUCTS

#### 3.1 Grey reaction product of C$_{60}$/anthracene adducts

The FT-IR spectra of the grey, unpurified reaction mixtures recovered (irrespective of the initial molar ratio of the reactants adopted) show a series of infrared bands, which are those of free C$_{60}$ and free anthracene (see Figure 2). In Figure 2 it is possible to distinguish the characteristic four band pattern of pure C$_{60}$ at $\sim 7.0$, $8.5$, $17.4$, and $18.9 \mu$m (or at 1426, 1180, 575, and 525 cm$^{-1}$). Furthermore, the strongest infrared bands due to free anthracene can be clearly distinguished as well (see Figure 2); for example those at 11.3, 13.8, 21.1, and 21.6 $\mu$m (or at 882, 725, 475, and 464 cm$^{-1}$).

The rest of spectral features seen in the FT-IR spectra of the C$_{60}$/anthracene reaction mixtures (composed by 33% of the mono-adduct and by 66% of the trans-1 bis-adduct) are identical to those displayed by the purified trans-1 bis-adducts and that are discussed in the next Section. However, it is worth mentioning that a few infrared bands (e.g., at 14.8 $\mu$m) in the unpurified reaction mixtures appear stronger than in the purified C$_{60}$/anthracene bis-adducts (Figure 2). This is likely due to the extra-contribution from the C$_{60}$/anthracene mono-adduct at these wavelengths.

Figure 2. FT–IR normalised spectra in KBr. From top to bottom: C$_{60}$ reference spectrum; purified C$_{60}$/anthracene (1:1 initial molar ratio); purified C$_{60}$/anthracene (1:2 initial molar ratio); grey reaction mixture of C$_{60}$/anthracene (1:1 initial molar ratio); grey reaction mixture of C$_{60}$/anthracene (1:2 initial molar ratio); anthracene reference spectrum. Note that the neutral C$_{60}$ (dotted) and Anthracene (dashed) band positions are marked.

#### 3.2 Purified C$_{60}$/anthracene bis-adducts

As we have mentioned before, the purification of the grey C$_{60}$/anthracene mixture with n-hexane causes the extraction of the mono-adduct from the mixture (together with the extraction of the not reacted C$_{60}$ and anthracene). The residue of the extraction is essentially constituted by almost pure trans-1 bis-adducts (Figure 1, adduct #6).

Surprisingly, the purified C$_{60}$/anthracene bis-adducts obtained through the sonication of the 1:1 and 1:2 initial molar ratio mixtures display an identical FT-IR spectrum (Figure 2). This strongly suggests that both C$_{60}$/anthracene bis-adducts have the same chemical structure. Clear evidences of the adduct formation derive from the C-H infrared bands displayed by the adduct and due to the cycloaliphatic nature of the C-H bonds connecting the anthracene molecule with the fullerene cage (see Figure 1). In the adduct C$_{60}$ maintains its individuality and its cage structure while anthracene being a dienophile loses the aromaticity of the central ring of the molecule forming a cycloaliphatic structure. However, the other two anthracene rings are still aromatic and display the typical aromatic bands in the infrared spec-

1 Note that these previous works on C$_{60}$/anthracene adducts permit us to clearly identify our products.
pared to only two aliphatic C-H). A theoretical calculation of the $C_{60}$/anthracene IR spectrum (although out of the scope of this paper) would be very useful to completely understand the laboratory spectra and band assignments for a structure like that of $C_{60}$/anthracene adducts.

Interestingly, the purified $C_{60}$/anthracene bis-adducts show also strong spectral features which are coincident with those of neutral $C_{60}$ (e.g., at $\sim 7.0$, $8.4$, $17.3$, and $19.0$ $\mu$m; Iglesias-Groth et al. 2011) - even the relative strengths are strikingly similar (Figure 2). The presence of the $\sim 7.0$, $8.4$, $17.3$, and $19.0$ $\mu$m $C_{60}$ bands in our $C_{60}$/anthracene bis-adducts FT-IR spectrum gives additional evidence that the fullerene cage is completely intact in the adduct while there are no more bands attributable exclusively to free anthracene as instead happened in the case of the unpurified product.

Moreover, the purified $C_{60}$/anthracene bis-adducts also show a series of new infrared absorption bands, which are not present in the spectra of pure $C_{60}$ or pure anthracene. The latter IR bands are located at $\sim 6.5$, $6.8/6.9$, $13.2$, $13.5$, $13.8$, $14.3$, $14.9$, $15.1$, $15.6$, $17.0$, $17.8$, and $21.6$ $\mu$m. Indeed, some of these new IR bands seem to be coincident with the known transitions of the neutral $C_{70}$ fullerene (e.g., at $\sim 7.0$, $13.8$, $14.9$, $15.6$, $17.3$, $17.8$, and $18.9$ $\mu$m; Iglesias-Groth et al. 2011). This is shown in Figure 3, where we display the FT-IR spectrum of the purified $C_{60}$/anthracene bis-adducts (1:2 initial molar ratio) together with the neutral $C_{70}$ reference spectrum. As we have mentioned before, our synthesis and purification process gives almost pure trans-1 bis-adducts, and therefore also $C_{70}$ is not available even as a minor impurity.

4 FORMATION OF FULLERENES AND FULLERENE/PAHS ADDUCTS

The formation route of fullerenes in evolved stars such as PNe and in the interstellar medium is still not fully understood. Several scenarios for fullerene formation have been proposed, including: i) photochemical processing of hydrogenated amorphous carbon grains (HACs; García-Hernández et al. 2010); ii) destruction of large PAHs by shocks (Cami et al. 2011); iii) photochemical processing of PAHs where PAHs are converted into graphene, and subsequently fullerenes (Berné & Tielens 2012).

The coexistence of fullerenes and PAHs - as well as of other molecular species such as HACs, PAH clusters, and small dehydrogenated carbon clusters (planar $C_{24}$ or protographene) - in the infrared spectra of PNe with fullerenes (García-Hernández et al. 2011c, 2012a) strongly supports the laboratory experiments carried out by Scott and colleagues in the nineties, which showed that the decomposition of HACs is sequential with small dehydrogenated PAH molecules being released first, followed by fullerenes and large PAH clusters (Scott et al. 1997). The most recent

\footnote{Note that the 13.8 $\mu$m band may be due to the out-of-plane bending vibration of anthracene (see above).}

\footnote{Bettens & Herbst (1996) proposed and alternative route in the interstellar medium through ion/molecule synthesis in which previously formed tricyclic rings can be converted to fullerenes by collisional processes.}
studies about fullerenes in PNe (Bernard-Salas et al. 2012; García-Hernández et al. 2012a; Micelotta et al. 2012) seem to support the HAC’s photochemical processing (e.g., by UV irradiation) originally proposed by García-Hernández et al. (2010) as the most likely fullerene formation route. In particular, Micelotta et al. (2012) present a good review on the possible fullerene formation processes in space, showing for example that the top-down fullerene formation scenario by Berné & Tielens (2012) cannot probably work in PNe and concluding that formation of fullerenes in PNe likely starts from HAC processing.

It is worth mentioning that the spatial distribution of the 16.4 \( \mu \text{m} \) emission (and other PAH-like features in the 15-20 \( \mu \text{m} \) range) is found to be different to that of the 18.9\( \mu \text{m} \) C\(_{60}\) emission in the reflection nebula NGC 7023 (Sellgren et al. 2010; Berné & Tielens 2012; Peeters et al. 2012). This fact has been used to favor the destruction of large PAHs for fullerene formation, either by shocks (Cami et al. 2011) or by UV irradiation (Berné & Tielens 2012) against the HAC’s scenario. As far as we know there is no firm identification of the carrier of the 16.4 \( \mu \text{m} \) feature (the same holds for the other features in the 15-20 \( \mu \text{m} \) range) although the latter authors attribute this feature to PAHs. For example, Duley & Hu (2012) show that HAC nano-particles also display a feature at 16.4 \( \mu \text{m} \) and they attribute this feature to proto-fullerenes. In addition, the 16.4 \( \mu \text{m} \) feature is lacking in all PNe where fullerenes have been detected so far (García-Hernández et al. 2012a). Thus, one can not extrapolate the results in NGC 7023 to PNe. Furthermore, PAHs are seen everywhere in NGC 7023 (see Figure 1 in Berne & Tielens 2012); the only difference is that fullerenes and PAHs appear to coexist in the same location close to the central star, while only PAHs are detected further away from the star (Berne & Tielens 2012; Micelotta et al. 2012). Actually, the unique information on the spatial distribution of fullerenes and other dust species in PNe is coming from Bernard-Salas et al. (2012). The latter authors presented tentative evidence (at a marginal spatial resolution of 2''/pixel) that the 8.5 \( \mu \text{m} \) emission (and attributed to C\(_{60}\)) in Tc 1 is extended and peaks at 2-3 pixels from the central star while the 11.2 \( \mu \text{m} \) emission peaks at a similar distance to the other side of the star. It should be noted here that both emissions coexist in the nebula but they peak at different places. Indeed, fullerenes could be formed in clumps and the tentative evidence by Bernard-Salas et al. (2012) may point to this. Mid-IR images at much higher spatial resolution (e.g., at sub-arcsecond level) are desirable before reaching a conclusion about the relative spatial distribution of fullerenes and PAHs in Tc 1 and other PNe.

In summary, the most accepted idea about fullerene formation (at least in PNe) is that these complex molecular species probably evolved from HAC processing and present observations of the relative spatial distribution of fullerenes and PAHs cannot conclusively demonstrate a different location for the latter species. Thus, fullerenes and PAHs may be mixed in the circumstellar envelopes of PNe, opening the possibility of forming adducts of fullerenes with PAHs. We have shown here that fullerenes can at least react with cata-condensed PAHs via the Diels-Alder cyclo-addition reaction. In principle, the smallest PAHs are expected to be destroyed quite fast in the harsh UV irradiation field present in PNe or in the ISM. A small number of such fullerene adducts may be formed in regions where fullerenes and PAHs co-exist, although it seems unlikely that they would be abundant enough to be detected in astrophysical environments. Fullerene adducts with larger and more stable PAHs (like pericondensed or very large PAHs) are expected to be more stable towards UV irradiation and hence more abundant in space. However, the possible Diels-Alder reaction between fullerences and pericondensed or very large PAHs has to be explored at laboratory.

The fullerene C\(_{60}/\text{anthracene adduct} \) reported here is just the simpler example of the variety of C\(_{60}\)/PAHs molecules that may be formed. The UV irradiation of C\(_{60}\) and anthracene mixtures - at least in the laboratory conditions - favors the formation of the C\(_{60}/\text{anthracene mono- and bis-adducts} \) (Mikami et al. 1998); although other byproducts such as the anthracene dimer are also formed. In addition, the bis-adduct (with a decomposition temperature \( T_{\text{dec}}=533 \) K) appears more stable than the mono-adduct which decomposes at \( T_{\text{dec}}=394 \) K, yielding back free C\(_{60}\) and anthracene (Cataldo et al. 2013). Taking into account that the fullerene C\(_{60}\) temperatures are higher than 400 K

\[ C_{60}/\text{anthracene adducts} \]
for most fullerene PNe (García-Hernández et al. 2012a), this would imply that C$_{60}$/anthracene-adducts - if formed and stable/abundant enough in the UV irradiated environments of PNe - are most likely in the form of trans-1 bis-adducts.

5 COMPARISON WITH PLANETARY NEBULAE SPECTRA

As in the case of the C$_{60}$ and C$_{70}$ fullerenes (Iglesias-Groth et al. 2011), we expect the strength and position (and width) of the infrared features of C$_{60}$/anthracene adducts to be temperature dependent. With this in mind, we have compared the laboratory FT-IR spectrum of the pure C$_{60}$/anthracene bis-adducts with the dust continuum subtracted Spitzer Space Telescope spectra of the fullerene PNe Tc 1 and M 1-20 (García-Hernández et al. 2010) in Figures 4 and 5, respectively. M 1-20 displays clear PAH-like features (e.g., those at 6.2, 7.7, and 11.3 $\mu$m) while Tc 1 show a fullerene-dominated spectrum with no clear signs of PAH-like features. For comparison, the laboratory spectra of neutral C$_{60}$ and C$_{70}$ molecules (Iglesias-Groth et al. 2011) are also shown in Figures 4 and 5. The laboratory spectra of C$_{60}$/anthracene bis-adducts seem to show tentative resemblance with the Spitzer spectrum of the PN M 1-20. For example, the substructure of the 13-15 $\mu$m emission complex observed in M 1-20 is somewhat similar to the C$_{60}$/anthracene features in this spectral region. In addition, M 1-20 displays a weak feature around 17 $\mu$m that is slightly blue-shifted (at 16.88 $\mu$m) and is weaker than the 17.3 $\mu$m fullerene feature, something that is also observed in the C$_{60}$/anthracene bis-adducts spectrum. The 13-15 $\mu$m emission complex and the weak 17 $\mu$m feature are, however, not observed in Tc 1 that also lacks the PAH-like features.

The still unidentified 17$\mu$m feature is observed in a variety of strong PAH emitters (e.g., reflection nebulae, H II regions, Herbig Ae/Be stars) that also show emission features at $\sim$17.4 and 18.9 $\mu$m (e.g., Boersma et al. 2010). The latter three features are usually accompanied by a much stronger and still unidentified 16.4 $\mu$m feature. Indeed, by studying the IR spectra of HAC nano-particles samples, Duley & Hu (2012) suggest that the set of four IR emission lines previously identified with C$_{60}$ in objects that also show the 16.4 $\mu$m feature and other strong PAH bands arise from proto-fullerenes rather than C$_{60}$ (see also García-Hernández

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Note that the 17$\mu$m feature in the hotter PN LMC 99 (see Fig. 6) is red-shifted (at 17.11 $\mu$m). These small displacements towards the blue and red in M 1-20 and LMC 99, respectively, are also seen in the other mid-IR features (e.g., at 17.4 and 18.9 $\mu$m), being consistent with different average temperatures for these sources.
et al. 2012b). Our IR laboratory spectra of C$_{60}$/anthracene adducts, show, however, that these four features at $\sim$7.0, 8.4, 17.3, and 18.9 $\mu$m (and other IR features coincident with C$_{70}$ transitions) may also arise from fullerene-adducts. It should be noted that the 16.4 $\mu$m feature is not present in fullerene PNe and the PAH bands are very weak (García-Hernández et al. 2012a). In addition, some fullerene PNe still displays the 17$\mu$m feature and/or a rich IR spectrum with several unidentified features (García-Hernández et al. 2011c). In Figures 6 and 7, we attempt a tentative identification of these unidentified features by comparing our IR laboratory spectra of pure C$_{60}$/anthracene bis-adducts with the Spitzer Space Telescope observations of PNe LMC 99 and LMC 02. LMC 99 is the fullerene PNe with the strongest PAH bands while LMC 02 displays an IR spectra richer than other fullerene PNe. It can be seen that LMC 99 displays the $\sim$17.0, 17.3, and 18.9 $\mu$m features together with the lack of the 16.4 $\mu$m feature (Fig. 6). Also, some C$_{60}$/anthracene adduct laboratory features (e.g., at 13.2, 13.8, 14.3, and 17.0 $\mu$m) find a counterpart in the LMC02’s spectrum (Fig. 7). However, other IR features (e.g., at 16.6, 18.0, and 18.4 $\mu$m) that are observed in LMC 02, are not present in the laboratory spectra. In any case, this comparison suggests that other fullerene-related molecules such as bigger fullerene-adducts could be potential candidate carriers for these peculiar and still unidentified IR features seen in some fullerene PNe.

Our comparison of the fullerene-adducts laboratory spectra with the PNe spectra do not permit us to unambiguously infer the presence of these fullerene-based molecules in PNe. As we have mentioned above, we expect the exact wavelength positions (also the relative intensities and widths) of the C$_{60}$/anthracene adduct spectral features to be temperature dependent (e.g., $\pm$0.1 $\mu$m in wavelength; e.g., Iglesias-Groth et al. 2011, 2012). A detailed study on the dependence of the IR bands of C$_{60}$/anthracene adducts over a wide range of temperatures is planned, which will be useful for the search and identification of fullerene-adducts in space. However, it is clear that fullerene-adducts display mid-IR features strikingly similar to the features that have been previously attributed to C$_{60}$ (and C$_{70}$). Our work show that C$_{60}$/anthracene adducts may be indistinguishable from C$_{60}$ (and C$_{70}$) on the basis of the Spitzer mid-IR ($\lambda > 5$ $\mu$m) spectra alone. A possible spectroscopic test to discriminate between fullerene-adducts and isolated C$_{60}$ (and C$_{70}$) molecules could be offered by the 3-4 $\mu$m spectral region. The laboratory spectra show that the 3-4 $\mu$m region may be the best spectral range to distinguish between fullerene-adducts and neutral C$_{60}$ (and C$_{70}$). This is shown in Figure 8 where we compare the 3-4 $\mu$m laboratory spectrum of C$_{60}$/anthracene adducts with those of isolated C$_{60}$ and anthracene. C$_{60}$/anthracene adducts display the typical aromatic C-H bands around 3.3 $\mu$m and a series of aliphatic C-H bands at 3.39, 3.43, and 3.52 $\mu$m, which are not present in the C$_{60}$ spectrum. These aliphatic C-H bands appear cleanly separated at the resolution (R$\sim$600) of our experimental set-up. In principle, the possible carrier (e.g., C$_{60}$ vs. C$_{70}$) could be identified.
C_{60}/PAHs adducts) of the mid-IR features seen in fullerene PNe by Spitzer could be elucidated through high-resolution (R>500) spectroscopic observations in the 3-4 µm range. However, the appearance in our laboratory C_{60}/anthracene adducts spectrum of C-H stretching bands that are typical for CH_{2} and CH_{3} groups (see below) is not yet completely understood. The aliphatic C-H bands in the 3.4-3.5 µm spectral region (e.g., asymmetric and symmetric stretching vibrations of aliphatic CH_{2} and CH_{3} groups) are also very typical of several carbonaceous materials (see e.g. Pendleton & Allamandola 2002). For example, Pendleton & Allamandola (2002) show that even the measured positions of the 3.4-3.5 µm bands due to aliphatic CH_{2} and CH_{3} groups in HAC are quite close to those in fullerene-adducts. Therefore, a careful analysis of the whole infrared spectra as well as a much better understanding of our C_{60}/anthracene adducts laboratory spectrum (e.g., the nature of the 3-4 µm C-H stretching bands) would be needed, in order to fully disentangle the possible carrier of these emission bands.

6 CONCLUDING REMARKS

The detection of fullerenes in evolved stars as common as our Sun has opened the exciting possibility that other forms of carbon such as hydrogenated fullerenes, fullerene-adducts, and multitshell fullerenes (buckyonions) may be widespread in the Universe. In particular, if fullerenes and PAHs evolve from the decomposition of HACs, then both species may be mixed in the circumstellar envelopes of fullere PNe, forming fullerene/PAHs adducts (at least with catacondensed PAHs). Our IR laboratory spectra of C_{60}/anthracene adducts show that C_{60} (and C_{70}) and other unidentified infrared emission features could also arise from fullerene-adducts.

Interestingly, Bernard-Salas et al. (2012) could not explain their observations of C_{60} fullerenes (spatial distribution, relative strenght of the features) in several PNe and they suggest that other emitting species (e.g., fullerene clusters or nanocrystals) may be present. In this paper, we present some evidence that fullerene-based molecules such as fullerene/PAH adducts could be present in PNe and may contribute to the mid-IR features attributed to C_{60}. This could be a more natural explanation because fullerenes and PAHs may coexist in PNe. The possible presence of other fullerene-based molecules (e.g., fullerenes bigger than C_{60} and buckyonions) in fullerene PNe is also suggested by the special characteristics of the DIBs seen towards Te 1 and M 1-20 (García-Hernández & Díaz-Luis 2013).

We speculate that fullerene/PAHs adducts - if formed under astrophysical conditions and abundant enough - could contribute to the infrared emission features seen in fullerecontaining environments. The C_{60}/anthracene adduct presented in this paper is just a first example of a family of C_{60}/PAHs molecules, which could be present in various space environments. In this context, fullerene adductcs with larger catacondensed PAHs (e.g., C_{60}/pentacene) or even adducts with pericondensed or very large PAHs could represent potential candidate carriers of the still unidentified infrared features seen in fullerene PNe but a definitive answer requires further laboratory and observational efforts.

ACKNOWLEDGMENTS

The present research work has been supported by grant AYA2007–64748 Expte. NG–14–10 of the Spanish Ministerio de Ciencia e Innovacion. D.A.G.H. and A.M. also acknowledge support provided by the Spanish Ministry of Economy and Competitiveness under grant AYA–2011–27754.

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