The Diffuse Interstellar Bands
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Can Fullerene Analogues be the Carriers of the Diffuse Interstellar Bands?

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Abstract. Fullerenes and their derivatives are amongst the most stable carbonaceous species known and have therefore been proposed as ideal candidates to carry some of the diffuse interstellar bands (DIBs). Evidence for these species in space first came from a few DIBs that have been tentatively identified with electronic transitions of C_{60}^{+}; in recent years, infrared observations have furthermore revealed fullerenes in a variety of circumstellar and interstellar environments. With the presence of the fullerene family in space established, we review what is known about cosmic fullerenes and their derivatives and what role they could play as potential DIB carriers.

Keywords. ISM: atoms, ISM: molecules, ISM: lines and bands

1. Introduction

Fullerenes are a class of large carbonaceous molecules in the shape of a hollow spherical or ellipsoidal cage that is constructed from hexagonal and pentagonal rings. The best-known member is the "buckminsterfullerene" C_{60} whose structure is often likened to an old-style black and white European football (and is hence also known as a "bucky-ball"). Fullerenes were discovered in a series of laboratory experiments that simulate the conditions under which carbon nucleates in carbon star environments (Kroto *et al.* 1985); the experiments were set up to investigate whether these conditions would result in the formation of carbon chain molecules, and wether these chains could be DIB carriers. Kroto *et al.* (1985) immediately recognized that fullerenes are amongst the most stable species known (see also Kroto 1987) and thus ideally suited to survive the harsh conditions in the interstellar medium (ISM). Consequently, they proposed that fullerenes could be widespread and abundant in space, and could themselves be the carrier of the DIBs. In recent years, observational evidence has confirmed that fullerenes exist in circumstellar and interstellar environments. It is thus worthwhile to review the possible role of fullerenic materials as DIB carriers.

2. Early searches for C_{60} in the optical/near-UV

C_{60} has a set of weak Herzberg-Teller induced electronically forbidden transitions in the 4000–7000Å wavelength range, and a series of nine allowed $^1T_{1u}$–^1A_g transitions between 2000–4000Å (see e.g. Leach 1992; Sassara *et al.* 2001). These latter transitions in the near-UV are much stronger than the optical transitions. Astronomical searches have included both wavelength ranges, but with no success (Somerville & Bellis 1989; Snow & Seab 1989; Ehrenfreund & Foing 1997; Herbig 2000). However, C_{60} would most likely be ionized in the ISM, and two DIBs were found (at 9577Å and 9632Å) very near the predicted wavelengths for some of the electronic transitions of C_{60}^{+} (Foing & Ehrenfreund

1994, 1997). More recently, additional near-IR DIBs have been detected in the Orion Nebula that could be coincident with C_{60}^+ (Misawa *et al.* 2009). Final confirmation of this assignment must come from a comparison to a cold gas-phase spectrum of C_{60}^+.

3. IR Detections of Fullerenes in Space

C_{60} also has four infrared (IR) active vibrational modes at 7.0, 8.5, 17.4 and 18.9 μm. Early searches for these bands with the Short Wavelength Spectrometer (SWS; de Graauw *et al.* 1996) on board the Infrared Space Observatory (ISO; Kessler *et al.* 1996) did not result in any detections (Clayton *et al.* 1995; Moutou *et al.* 1999). More recently, the Infrared Spectrograph (IRS; Houck *et al.* 2004) on board the Spitzer Space Telescope (Werner *et al.* 2004) has offered IR spectroscopic views of a large number of astronomical objects at much smaller spatial scales and better sensitivity than ever before, and this turned out to be a crucial factor that finally resulted in success.

We analyzed Spitzer-IRS observations of the young, low-excitation carbon-rich planetary nebula (PN) Tc 1. Often, the mid-IR spectra of such objects are dominated by the strong emission bands due to polycyclic aromatic hydrocarbons (PAHs). In the unnusual IR spectrum of Tc 1 however, these are absent, and instead the spectrum exhibits all four C_{60} emission bands, with clear additional peaks at the wavelengths of the vibrational modes of C_{70} (Cami *et al.* 2010). The characteristic C_{60} bands (especially the 17.4 and 18.9μm bands) have since been found in many more objects, including several evolved stars (in our Milky Way galaxy as well as in the Magellanic Clouds; see e.g. García-Hernández *et al.* 2010, 2011a,b; Gielen *et al.* 2011; Zhang & Kwok 2011; Otsuka *et al.* 2013b) but also interstellar environments (Sellgren *et al.* 2010; Rubin *et al.* 2011; Peeters *et al.* 2012; Boersma *et al.* 2012) and young stellar objects (YSOs, Roberts *et al.* 2012). The spectrum of the Reflection Nebula (RN) NGC 7023 turns out to be particularly rich. Sellgren *et al.* (2007) suggested C_{60} as a possible carrier for the band at 18.9μm in this source; they later also detected the 7.0μm band (Sellgren *et al.* 2010). Furthermore, near the central star, Berné *et al.* (2013) found several weak bands that are coincident with the vibrational modes of C_{60}^+.

If fullerene analogues are to play an important role in the DIB problem, they should be abundant and widespread in the ISM. The detections in various environments described above may suggest that this is indeed the case; however, it is important to realize that fullerene detections are really quite rare, and represent only a small fraction of objects. For instance, of all the galactic PNe that were observed with Spitzer-IRS, only about 3% of them exhibit the 17.4 and 18.9μm bands (Otsuka *et al.* 2013a). It is not clear whether this is representative for the overall distribution of fullerenes in the ISM.

4. The Formation and Evolution of Cosmic Fullerenes

Various laboratory experiments have detailed some of the conditions under which fullerenes can form. In the original experimental setup by Kroto *et al.* (1985), graphite was vaporized in a hydrogen-poor environment, producing bare carbon clusters of various sizes. Fullerenes grow from the collisions between these clusters, and survive as the most stable species. Similar results are obtained when starting from a hydrocarbon precursor gas, and also in environments containing hydrogen, but only at high temperatures ($T \gtrsim 3500$ K; Jäger *et al.* 2009). At lower temperatures, hydrogen inhibits the formation of fullerenes, and PAHs are formed instead (de Vries *et al.* 1993; Wang *et al.* 1995; Jäger *et al.* 2009). In these experiments, it appears that bottom-up processes first make small fullerene cages; closed network growth then produces the larger fullerenes (Dunk *et al.* 2012). Similar processes are responsible for the formation of small amounts of fullerenes when HAC grains are being photo-processed (Scott *et al.* 1997).

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Fullerenes can also form very differently following a top-down route. When a flat graphene sheet loses an edge carbon atom, a pentagonal ring forms that triggers the curving of the graphene into a closed fullerene structure (Chuvilin *et al.* 2010). Based on these results, Berné & Tielens (2012) suggested that cosmic fullerenes could also form from large PAHs through (radiation-induced) dehydrogenation and carbon loss. Molecular dynamics simulations furthermore show that larger fullerenic cages shrink on short timescales to the island of stability represented by C_{60} (Irle *et al.* 2006). Micelotta *et al.* (2012) argued that in space, carbon loss and aromatization of abundant small (∼few hundred carbon atoms) non-planar arophatic nano-particles could result in the formation of large cages that subsequently would shrink to smaller sizes.

Some clues to the formation and further evolution of cosmic fullerenes can be derived from the astronomical observations, and in particular by considering only the carbon-rich evolved stars between the tip of the AGB and the mature PNe phase. While fullerenes clearly form in the circumstellar outflows of such objects, they are only detected in a small fraction of observed sources (∼3%; Otsuka *et al.* 2013a). Thus, the conditions that are required for the formation and/or excitation of fullerenes must either be very specific so that they are only rarely met, or alternatively occur only for a short period of time. The latter is much more plausible. Indeed, cosmic fullerenes are clearly associated with a well-defined evolutionary stage early in the transition from the AGB to PNe since all fullerene-rich sources are young, low-excitation PNe while no fullerenes have been found in mature PNe. Furthermore, no obvious physical or chemical characteristics have been reported that distinguish the fullerene-rich from the fullerene-poor objects.

The prevalence of fullerenes in young, low-excitation sources has two important implications. First, it seems unlikely that the formation of fullerenes in these environments is driven by photo-processing of PAHs or HACs. If such were the case, one would expect to see fullerenes primarily in the more mature objects where PAHs and HACs are abundant, and where the hotter central stars make photo-processing more efficient. Second, as PNe mature, their fullerene spectral signature disappears, indicating that the fullerenes must be further chemically processed. Indeed, destruction of these stable species is unlikely given that PAHs (that are presumably less stable) are abundant in many mature PNe.

Another key observation is the location of the fullerenes in Tc 1. In that source, the fullerene emission peaks in a ring segment roughly 8,000 AU away from the central star , while the mid-IR continuum and the emission of other dust features originate from much closer to the central star (Bernard-Salas *et al.* 2012). If photo-processing can be ruled out, this then suggests that shocks, related to a developing ionization front, are a key ingredient in creating the conditions for fullerene formation. Such shocks could possibly fragment larger carbonaceous dust grains into smaller aromatic clusters and provide sufficient densities and energies for the closed network growth mechanism to grow them into fullerenes. If this is indeed related to a developing ionization front, it may explain the preferential occurence of fullerenes in young PNe.

5. The Fullerene Family and the DIBs

We now turn our attention to the role of fullerenes and fullerene compounds in the context of the DIB problem. It should be clear that neutral, pure C_{60} cannot be a carrier of the currently known DIBs. Indeed, the electronic spectrum of C_{60} is well known, and no interstellar bands have been found near the expected wavelengths of these features. The case for C_{60}^+ as a DIB carrier has been made (Foing & Ehrenfreund 1994, 1997; Ehrenfreund & Foing 1997, §2), and awaits confirmation. The detection of the IR C_{60}^+

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bands in NGC 7023 offers more support for C_{60}^{+}, but it is puzzling then that the 9577 and 9632Å DIBs are not seen toward its central star HD 200775 (Berné *et al.*, this volume).

Given that the fullerenes are further chemically processed in PNe, there may be many more members of the “extended” fullerene family that could play a role as DIB carriers: higher (or lower) fullerenes and their substituted variants (e.g. including ^{13}C), but also chemically related species such as hydrogenated fullerenes, metal-complexed fullerenes, bucky-onions or even more exotic species such as carbon nanotubes are interesting candidates. To get a sense of how viable fullerene-related species are as DIB carriers, consider a generic molecule M, made up of N_C carbon atoms, as a putative carrier for a DIB occurring at wavelength λ, and let us denote with $\chi_{\rm M}$ the fraction of elemental carbon that is locked up in M. With a carbon abundance of 1.4×10^{-4} (relative to H), we can expect to measure an equivalent width per unit reddening of

$$\frac{W_\lambda}{E(B-V)} = 3 \times 10^{-3} \left(\frac{\chi_M}{10^{-4}}\right) \left(\frac{60}{N_C}\right) \left(\frac{\lambda}{5000\ \text{Å}}\right)^2 \left(\frac{f}{10^{-2}}\right) \tag{5.1}$$

where f is the oscillator strength of the transition in question and the result is expressed in Å mag^{-1}. Note that 10^{-4} is the quoted *peak* abundance of C_{60} found in NGC 7023 (Berné & Tielens 2012) and that $f \sim 10^{-2}$ for the narrow C_{60} electronic bands near 4000Å. From these estimates, it is clear that fullerenes could at best be responsible for some of the weak DIBs, and we find the familiar result that the DIB carriers need to be very abundant (much more abundant than quoted interstellar C_{60} values) and/or be a species with unusually strong transitions. Therefore, it is not likely that the strong DIBs (including the 4428Å DIB) are due to larger fullerenes and/or buckyonions as was suggested by García-Hernández & Díaz-Luis (2013); this would require an extremely large fraction of the cosmic carbon to be locked up in these species. Note that García-Hernández & Díaz-Luis (2013) reported unusually strong DIBs in the spectra of the fullerene-rich objects Tc 1 and DY Cen; however, the measured DIB strengths in these sources are perfectly normal when comparing to e.g. HD 183143 (Hobbs *et al.* 2009).

A much more appealing class of fullerene-related DIB carrier candidates are then the fullerene analogues considered by Kroto & Jura (1992). In particular, these authors argue that protonated fullerenes could be the most abundant fullerene analogue in the ISM, and furthermore also consider endohedral and exohedral metal-complexed fullerenes and their ions. Experimental work suggests that these metallofullerenes form as easily as regular fullerenes in the presence of seed metals; thus, one could argue that in space, metallofullerenes could well be more abundant than their pure counterparts. Such metallofullerenes have various types of electronic transitions, and their large dipole moments will generally lead to unusually large oscillator strengths. Of special interest for the DIB problem may be charge transfer bands. These transitions involve a large charge displacement, thus boosting the band strength up by up to two orders of magnitude and avoiding abundance problems. While metallofullerenes would be an excellent class of species to consider, charge transfer bands could also be considered as a relevant process for other possible DIB carriers. Protonated cations (of fullerenes, but possibly also other species) should also be considered as carrier in particular for e.g. the 5780 DIB given the tight correlation of the 5780 DIB with neutral hydrogen (Herbig 1995; Friedman *et al.* 2011).

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