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Fullerenes in Circumstellar and Interstellar Environments

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Abstract. We recently identified several emission bands in the Spitzer-IRS spectrum of the unusual planetary nebula Tc 1 with the infrared active vibrational modes of the neutral fullerene species C_{60} and C_{70}. Since then, the fullerene bands have been detected in a variety of sources representing circumstellar and interstellar environments. Abundance estimates suggest that C_{60} represents ∼0.1%–1.5% of the available carbon in those sources. The observed relative band intensities in various sources are not fully compatible with single-photon heating and fluorescent cooling, and are better reproduced by a thermal distribution at least in some sources. The observational data suggests that fullerenes form in the circumstellar environments of evolved stars, and survive in the interstellar medium. Precisely how they form is still a matter of debate.

Keywords. astrochemistry, circumstellar matter, ISM:molecules, infrared:ISM

1. Introduction

Fullerenes are large molecules made of carbon hexagons and pentagons that are organized in the shape of a hollow sphere or ellipsoid. The best-known member of the class is the archetypal so-called "buckminsterfullerene" C_{60} whose structure is the same as a soccer ball (see Fig. 1). Fullerenes were discovered in a series of laboratory experiments that simulated the circumstellar environment of carbon stars and that were aimed at understanding the formation of long carbon chains in such outflows (Kroto *et al.* 1985). Their unique properties has made them the topic of much research in very diverse fields on Earth – from superconductivity over nanotechnology to targeted drug delivery.

As soon as they were discovered on earth, it was suggested that fullerenes could also form in carbon star outflows and be injected into the interstellar medium (ISM). Since they are amongst the most stable carbon species known, they would then be ideally suited to survive the harsh conditions in the ISM.

Dedicated searches for the electronic bands of neutral C_{60} in the ISM and in circumstellar shells were negative (Snow & Seab 1989; Somerville & Bellis 1989; Herbig 2000). Foing & Ehrenfreund (1994) on the other hand reported the detection of two diffuse interstellar bands (DIBs) whose wavelengths are consistent with transitions of the C_{60}^+ cation as measured in solid matrices (Fulara *et al.* 1993); more recently, several more DIBs have been found that could be due to the same cation (Misawa *et al.* 2009). However, since the technique of matrix isolation spectroscopy introduces unpredictable shifts in the frequencies of the absorption bands, this promising case awaits confirmation from a comparison to a cold gas phase spectrum which is not yet available.

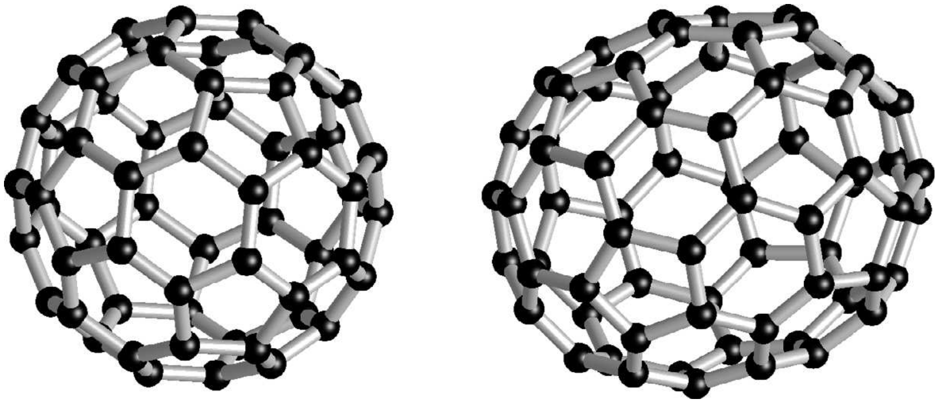

Figure 1. A representation of the molecular structure of C_{60} (left) and C_{70} (right).

Fullerenes can also be detected through their vibrational modes at infrared (IR) wavelengths (see Sect. 2), and several efforts have focused on these spectral signatures (Moutou *et al.* 1999; Clayton *et al.* 1995). Again, no conclusive evidence was found for the presence of C_{60} in space. More recently, Sellgren *et al.* (2007) analyzed the 15–20 μm spectrum of the reflection nebula NGC 7023 obtained with the Infrared Spectrograph (IRS, Houck *et al.* 2004) on board the Spitzer Space Telescope (Werner *et al.* 2004). They suggested that C_{60} could be one of the possible carriers for the spectral features in this source at 17.4 and 18.9 μm.

Cami *et al.* (2010) presented the unusual Spitzer-IRS spectrum of the planetary nebula (PN) Tc 1, and identified several emission features with the vibrational modes of the fullerene species C_{60} and C_{70}. Since then, fullerenes have been confirmed in many more sources of different nature, indicating that these species may be quite widespread in the Universe. A lively discussion has ensued especially over their excitation properties and formation mechanism.

Here, we briefly review some of the relevant properties of C_{60} and C_{70} in Sect. 2. We present the case for fullerenes in Tc 1 in detail, and summarize the other detections in Sect. 3. Some aspects of the excitation mechanism are discussed in Sect. 4, and the formation of fullerenes in space in Sect. 5.

2. Spectroscopic properties of C_{60} and C_{70}

A representation of a C_{60} molecule is shown in Fig. 1. The 60 carbon atoms are arranged in the shape of a truncated icosahedron (I_h symmetry): a hollow sphere that is made of 20 hexagons and 12 pentagons. C_{60} has 174 vibrational modes, but owing to its symmetry, many modes are degenerate and only 4 distinct modes are IR active: the $T_{1u}(1)$ mode at 18.9 μm; the $T_{1u}(2)$ mode at 17.4 μm; the $T_{1u}(3)$ mode at 8.5 μm and the $T_{1u}(4)$ mode at 7.0 μm. Laboratory experiments have measured the frequencies of these transitions in the pure, solid state (Krätschmer *et al.* 1990; von Czarnowski & Meiwes-Broer 1995) as well as in the gas-phase (Frum *et al.* 1991; Nemes *et al.* 1994). In those experiments, the measured bands are fairly broad and symmetric, and thus well characterized by a central wavelength and a width. The differences between the measured frequencies primarily reflect the effect of temperature: a higher temperature shifts the bands to lower frequencies and causes broadening (Nemes *et al.* 1994).

The intrinsic strength of the C_{60} bands is less well known, and the literature offers quite different values for the absorption coefficients (even relative to one another), obtained either from laboratory experiments or theoretical calculations. Cami *et al.* (2010) used data from Martin *et al.* (1993); Fabian (1996); Sogoshi *et al.* (2000); for the analysis of NGC 7023 by Sellgren *et al.* (2010), strengths from Choi *et al.* (2000) were used. Also Iglesias-Groth *et al.* (2011) presented molar absorptivities derived from laboratory experiments.

Whereas the model for the C_{60} geometry has traditionally been a soccer ball, the C_{70} molecule is a prolate top more like a rugby ball. The lower symmetry (D_{5h}) results in more IR active modes: of the 204 fundamental vibrational modes, 31 are IR active, and laboratory studies as well as theoretical DFT calculations are available (von Czarnowski & Meiwes-Broer 1995; Stratmann *et al.* 1998; Schettino *et al.* 2002). Most of the C_{70} IR active bands are weak, and furthermore blend with the C_{60} bands; but several isolated bands of medium strength are at 14.8, 21.8, 12.6 and 15.6 μm.

3. Fullerenes in astrophysical environments

3.1. *The planetary nebula Tc 1*

Cami *et al.* (2010) reported the identification of the IR C_{60} bands in the unusual Spitzer-IRS spectrum of the planetary nebula (PN) Tc 1. The high quality of the spectrum and the lack of contaminating features make this source the clearest case for the presence of fullerenes in space.

Fig. 2 shows the continuum-subtracted Spitzer-IRS observations of the planetary nebula Tc 1. Apart from the strong (typically forbidden) emission lines that are characteristic for PNe, the spectrum is very unusual, and exhibits clear emission bands at the wavelengths of all four fundamental modes of C_{60}†. Weaker and narrower features are present at the wavelengths of the strongest (unblended) C_{70} bands. In addition to the fullerene bands, a broad underlying plateau is evident between 6–9 μm, as is a broad emission feature at 11.5 μm that is generally attributed to SiC (Speck *et al.* 2009). There is not much else left in the spectrum though, and thus little contamination confuses the analysis of the fullerene spectral features.

As mentioned in Sect. 2, the experimentally obtained central wavelengths and band widths for the C_{60} bands depend on the temperature, and thus a comparison with laboratory data requires some estimate of a typical temperature for the fullerenes in Tc 1. Surprisingly, the observed band strengths for both C_{60} and C_{70} are consistent with a thermal population distribution over the vibrational levels (see Sect. 4). For C_{60}, we can thus derive an excitation temperature of 332 K; for C_{70} the derived temperature is 179 K. All other measurable quantities are consistent with such a temperature. Indeed, the central wavelengths of all C_{60} emission bands in the spectrum of Tc 1 correspond especially well to experimental values measured at ~300 K (rather than values measured at e.g. 1000 K). Further support comes from the band widths: laboratory spectra show temperature-dependent widths (FWHM) from about 8 cm^{-1} at 300 K to 13 cm^{-1} at 1000 K (Nemes *et al.* 1994) for both the 17.4 and 18.9 μm C_{60} bands. For Tc 1, the measured band widths are 9.9 and 12.6 cm^{-1} for the bands at 18.9 and 17.4 μm respectively, but since both bands suffer from contamination by the C_{70} bands, their true band widths are necessarily smaller, and thus only compatible with the lower temperature regime. The C_{60} bands at 7.0 and 8.5 μm are not resolved and thus offer no such information. Also the

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† Note however that a significant fraction of the strong emission at 7.0 μm is due to an [ArII] line.

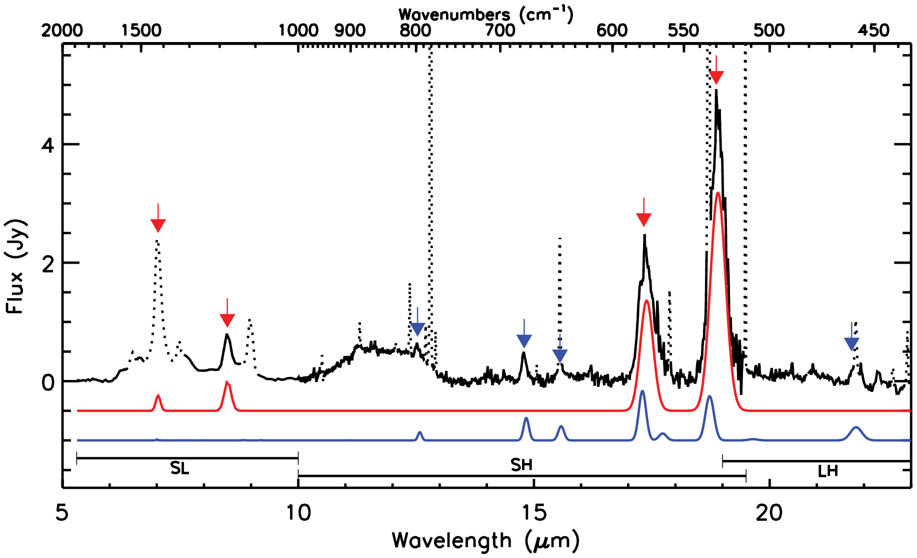

Figure 2. A composite IR spectrum of the planetary nebula Tc 1 as observed by Spitzer-IRS is shown on top. The spectrum is the combination of observations with the Short-Low module (SL, $\lambda/\Delta\lambda \sim 60-120$) and Short- and Long-High (SH and LH, $\lambda/\Delta\lambda \sim 600$) modules. A featureless dust continuum was subtracted from the spectrum. Known strong emission lines are masked and shown here as dotted lines. The curve below it is a thermal emission model for C_{60}; the bottom curve a similar model for C_{70}. Figure taken from Cami *et al.* (2010).

central wavelengths of the four isolated C_{70} features compare better to the frequencies measured at low temperatures.

Summarizing, we can conclude that the spectrum of Tc 1 shows the clear spectral fingerprint of the fullerene species C_{60} and C_{70}, and that all measurable quantities (wavelengths, widths and band ratios) are consistent with laboratory experiments at temperatures of a few hundred K.

3.2. *Other Evolved Objects*

With the clean fullerene spectrum of Tc 1 as a template, the presence of C_{60} has been confirmed in the circumstellar environments of a variety of evolved objects. García-Hernández *et al.* (2010) found the C_{60} bands in several other carbon-rich PNe. In most cases, the spectra are contaminated by PAH features, thus complicating the analysis; a notable exception is the PN SMP SMC 16 in the Small Magellanic Cloud that looks quite similar to Tc 1. No conclusive confirmation of the weaker C_{70} features has been reported in these objects though. At first, these detections suggested fullerenes form in the PN phase. However, they are already present in at least one proto-PN object (Zhang & Kwok 2011), and the C_{60} bands are also seen in the Spitzer-IRS spectra of a few post-AGB stars (Gielen *et al.* 2011).

In the search for fullerenes in space, special attention was given to the R Coronae Borealis (RCB) stars, a class of hydrogen-poor and helium-rich supergiants. Under typical conditions in circumstellar environments, the presence of hydrogen inhibits the formation of fullerenes (see Sect. 5), and thus the hydrogen-poor nature of the circumstellar environments of RCB stars was considered ideal to form C_{60}. The first search for C_{60} in such environments did not turn up any evidence for fullerenes (Clayton *et al.* 1995).

More recently, C_{60} has been detected in two RCB stars that were studied with the Spitzer Space Telescope (García-Hernández *et al.* 2011). Surprisingly, those two objects represent the most H-rich objects in a larger sample of RCB stars. In another study, an additional detection was made in one more RCB star (Clayton *et al.* 2011).

3.3. *Interstellar environments*

The spectral features of C_{60} have also been detected in interstellar environments – in the two reflection nebulae NGC 7023 and NGC 2023 (Sellgren *et al.* 2010), and also in the Orion Bar (Rubin *et al.* 2011). These sources are spatially resolved, and Sellgren *et al.* (2010) showed that in NGC 7023, the peak emission of PAHs originates from a different location as the peak emission from C_{60} (see Fig. 5). This has some implications for the formation and excitation of fullerenes (see Sect. 4 and 5).

3.4. *Abundances*

With the presence of fullerenes in space firmly established, an important question to address is what fraction of the cosmic carbon they represent, and different methods have been applied to estimate the fullerene abundances. In the evolved stars, of the order of 0.06–1.5% of the available carbon is estimated to be in the form of C_{60} (Cami *et al.* 2010; García-Hernández *et al.* 2010; Zhang & Kwok 2011). For NGC 7023 on the other hand, Sellgren *et al.* (2010) find that 0.1–0.6% of the interstellar carbon is in C_{60}. This latter is compatible with earlier estimates of 0.3–0.9% of the cosmic carbon that was estimated to be in the form of C_{60}^{+} (Foing & Ehrenfreund 1994).

It is interesting to see that the abundance estimates in the evolved objects are comparable to the interstellar fullerene abundances. If only a fraction of the carbon-rich evolved stars would produce fullerenes, one would expect the interstellar abundances to be much lower than the circumstellar abundances in individual objects. If the derived abundances are realistic, this then implies that the formation of fullerenes must be fairly common. In any case, the derived abundances represent a significant fraction of the cosmic carbon for a single molecular species.

The presence of C_{60} in diverse evolved objects suggests that fullerenes form in circumstellar outflows whenever conditions are right, and the detection of fullerenes in interstellar environments is then a testimony to the stability of these species that allows them to survive the harsh conditions in the ISM. In very general terms, the available observational data on the fullerenes thus confirm the early suggestion by Kroto *et al.* (1985): fullerenes form in carbon-rich circumstellar environments, and survive and thrive in the interstellar medium.

4. Excitation mechanism

Having identified several emission bands with a specific molecular carrier offers the prospect of using these spectral features as a diagnostic tool to extract quantitative information about the physical conditions that reign in the environment in which they reside. Precisely what information can be obtained depends somewhat on the molecules excitation mechanism at play.

Large, free molecules such as fullerenes and PAHs are generally thought to be excited by the absorption of a single photon (typically in the UV range). Rapid internal conversion then leaves the molecule in the electronic ground state, but in highly excited vibrational states; and as the molecule relaxes, it emits IR photons. For all relevant

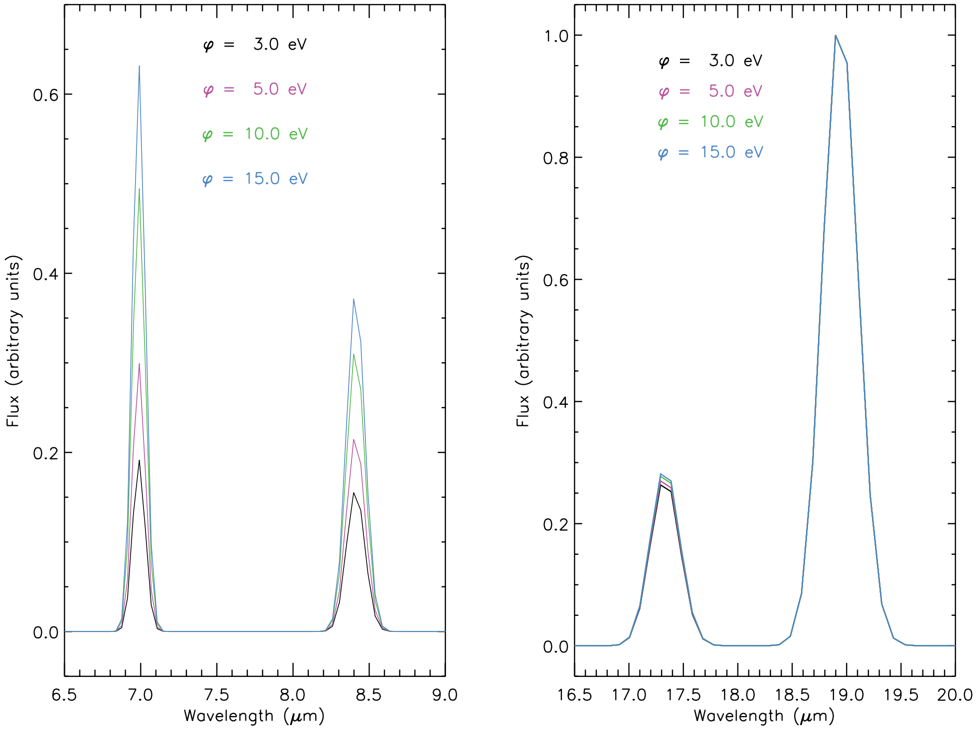

Figure 3. A few illustrative examples of how the C_{60} fluorescent emission spectrum changes for average photon energies of 3 eV, 5 eV, 10 eV and 15 eV (the lowest photon energies corresponding to the weakest emission). All spectra are normalized to the peak intensity of the 18.9 μm band. Widths were taken to be 10 cm^{-1} for the 17.4 and 18.9 μm bands and 20 cm^{-1} for the bands at 7.0 and 8.5 μm – consistent with the widths measured in the spectrum of Tc 1.

processes pertaining to the excitation & cooling mechanism, fullerenes have indeed very similar properties to PAHs (see e.g. Tielens 2005). Sellgren *et al.* (2010) analyzed the C_{60} in NGC 7023 using such an excitation model.

The resulting emission spectrum of this fluorescent cooling process can be calculated in various ways (e.g. **?**Joblin *et al.* 2002). The only free parameter in these calculations is the average photon energy that is absorbed by the molecules – which is a function of the ambient radiation field and the absorption cross section of the molecule in question. Fig. 3 shows a few examples of how the resulting IR spectra change following absorption of photons with different energies. Note how there is little change in the ratio between the 17.4 μm band and the 18.9 μm band for the energies considered here. For typical PNe conditions ($\varphi \gtrsim 7$ eV) however, the bands at 7.0 and 8.5 μm should be fairly strong, and the band ratios $I_{7.0}/I_{18.9}$ and $I_{8.5}/I_{18.9}$ could in principle be used as a sensitive measure of the average photon energy.

However, the numerical values for the band ratios depend on the intrinsic band strengths used in the calculations; as mentioned in Sect. 2, these are not well known, and different values are available in the literature. Using the intensities as given by Choi *et al.* (2000) (as was done for the analysis of the C_{60} bands in the reflection nebula NGC 7023 presented by Sellgren *et al.* (2010)), the $I_{17.4}/I_{18.9}$ band ratio should be roughly constant at about 0.28 for photon energies relevant to PNe environments. The measured band ratio in Tc 1 however is 0.59; when accounting for the contamination by C_{70} the

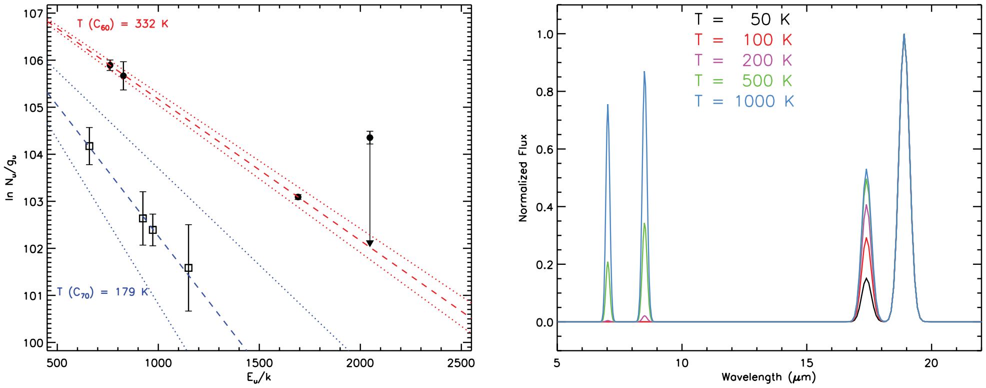

Figure 4. *(left)* Excitation diagram for the C_{60} and C_{70} bands in the Spitzer-IRS spectrum of Tc 1 (Fig. from Cami *et al.* 2010). *(right)* Illustrative examples of the spectral variations in the C_{60} bands. The bands at 7.0 and 8.5 μm are virtually absent for excitation temperatures below ~200 K, whereas the 17.4/18.9 μm band ratio shows large variations for temperatures up to ~500 K.

ratio is somewhat lower, but can never be brought in agreement with the expected ratio for fluorescent emission when adopting these intrinsic strengths. The 8.5/18.9 μm band ratio on the other hand is too low to be consistent with the same fluorescent cooling model.

One could argue that the adopted intensities for the bands are not correct, but also the other observations of the C_{60} bands pose difficulties in the framework of fluorescence. For all detected sources, the band ratios (including $I_{17.4}/I_{18.9}$) show significant variations from source to source (see e.g. García-Hernández *et al.* 2010). This is also evident from the different excitation temperatures (~200–700 K) that are derived assuming a thermal distribution over the vibrational bands. In many cases, the bands are contaminated by PAH features, but it is not clear if that alone can explain all the observed spectral variations. If true, these variations (and especially the $I_{17.4}/I_{18.9}$ band ratio) are not compatible with fluorescent cooling, irrespective of the intrinsic strength values used.

The fairly clean fullerene spectrum of Tc 1 offers the possibility of directly calculating the population distribution over the excited vibrational states from the total emitted power in the bands; and this can be done for both C_{60} and C_{70}. Surprisingly, the population distribution is fully consistent with a thermal distribution (see Fig. 4) over the vibrational states corresponding to an excitation temperature of 332 K for C_{60}, and 179 K for C_{70}.

Thermal models show quite different spectral variations as a function of temperature (Fig. 4) compared to the fluorescent cooling models and can more easily accommodate some of the observed changes in the $I_{17.4}/I_{18.9}$ band ratios. The cases where the 7.0 and 8.5 μm band are missing would then correspond to excitation temperatures $\lesssim 200\ K$, whereas an unacceptably low photon energy would be required in the fluorescence model.

It is not easy to understand how free C_{60} molecules in circumstellar or interstellar environments could produce an emission spectrum that is consistent with thermal excitation rather than with stochastic heating and fluorescent cooling. Since gas densities are typically orders of magnitude lower than the critical density, it is unlikely that gas collisions could keep the fullerenes thermalized. It was thus proposed that the fullerene molecules are not free, but in direct contact with the surface of dust grains, or in the solid state themselves Cami *et al.* (2010). In such a case, the fullerenes would be in equilibrium with the dust grains, which themselves are in equilibrium with the ambient radiation field. However, the derived excitation temperatures are hard to understand in this scenario. Further observations and analyses will be required to settle the excitation mechanism conclusively.

5. The formation of astrophysical fullerenes

From the fairly large number of evolved objects in which the C_{60} bands have been detected, it seems clear that these species do indeed form in the circumstellar environments of evolved stars. Precisely how this happens is far less clear though, and there has been some discussion about the precise pathways to fullerene formation†.

In this context, it is worthwhile to consider what we know from laboratory experiments. In the original experiments by Kroto *et al.* (1985), fullerenes self-assemble from much smaller carbon fragments by collisions. At very low gas densities, a broad distribution of cluster sizes is observed; but as the gas density is increased, collisions become more numerous, and only the most stable species (C_{60}) survives. If in carbon-rich circumstellar environments, collisional processes (occurring under the similar conditions) are driving the chemistry, fullerenes could form in the same way. The efficiency of the fullerene formation process is then a function of the density. However, an important condition in this formation process is the absence of hydrogen. It has long been realized that the presence of H will inhibit the formation of fullerenes (see e.g. Kroto & McKay 1988). Indeed, laboratory experiments show that the mere presence of hydrogen (as little as 0.4%) in such conditions already greatly reduces fullerene formation. At a hydrogen fraction of 10%, no fullerenes are formed anymore, and the experiments result in large amounts of PAHs instead (de Vries *et al.* 1993; Wang *et al.* 1995).

Based on the Spitzer-IRS spectrum of Tc 1 alone, it would seem that its circumstellar environment is fairly analogous to this laboratory setup. Indeed, the available material is clearly carbon-rich, while at the same time, the fullerene-rich IR spectrum does not show much evidence for the presence of PAHs nor any other H-containing species. It is thus conceivable that the region where the fullerenes are located is hydrogen-poor. However, it is clear that H is present at large in the nebula (see e.g. Milanova & Kholtygin 2009; Williams *et al.* 2008), and even in the photosphere of the central star (Mendez *et al.* 1988). Thus, if the formation of fullerenes in Tc 1 involves collisional growth of carbon clusters under similar conditions as in the laboratory experiments, there must have been H-poor regions in the nebula to allow the fullerenes to form.

García-Hernández *et al.* (2010) argue against a formation scenario in which a H-poor environment is required. They note that in their PNe data, the Spitzer-IRS spectra show the simultaneous presence of the C_{60} features and PAHs. From this, they conclude that both species co-exist, and that the fullerenes form at the same time and place as PAHs, in a H-rich environment. They propose photo-processing of solid Hydrogenated Amorphous Carbon (HAC) as the most plausible fullerene formation route in PNe environments. Support for that assertion is found in experimental results that show how such processing produces PAHs and fullerenes at the same time (Scott *et al.* 1997). Moreover, all C_{60} PNe furthermore show the so-called 30 μm feature that is generally attributed to MgS (see e.g. Hony *et al.* 2002), but that also has been linked to HACs (Grishko *et al.* 2001). They then interpret the PAH-poor and fullerene-dominated sources Tc 1 and SMP SMC 16

† Bettens & Herbst (1995) additionally discuss a possible formation route for fullerenes under interstellar conditions.

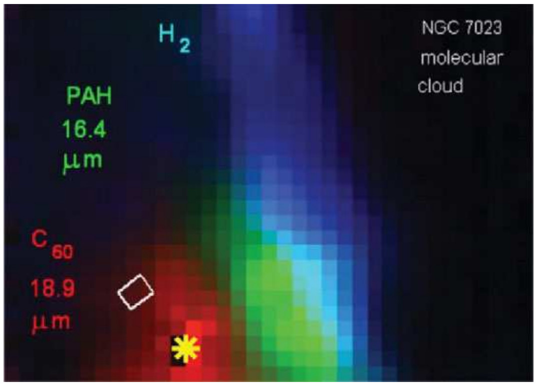

Figure 5. The spatial distribution of molecular hydrogen, PAHs and C_{60} in the reflection nebula NGC 7023 (Fig. from Sellgren *et al.* 2010)

as environments where the more hardy C_{60} molecules have survived whereas the PAHs have been destroyed.

It is clear that – in the context of astrophysical fullerenes – this scenario presents several difficulties as well. First, if HAC photo-processing is the general mechanism to produce PAHs and fullerenes in PNe, and if the 30 μm feature is indeed related to HACs, one would expect all PNe that exhibit the 30 μm feature to also exhibit PAH and fullerene bands. Second, it seems unlikely that UV photo-processing is a viable mechanism to explain the formation of C_{60} in evolved stars with much lower UV irradiation than is the case in the PNe – such as the proto-PN IRAS 01005+7910 (Zhang & Kwok 2011) but especially the two post-AGB stars presented by Gielen *et al.* (2011) with effective temperatures of the order of only 6,000 K. Finally, if Tc 1 and SMP SMC 16 represent environments where the fullerenes have survived and PAHs have not, it is hard to explain the numerous PNe that show clear PAH features but no C_{60} bands.

It is important to realize that the mixture of carbonaceous species that results from HAC photo-processing in the laboratory experiments is quite different from what is observed in the C_{60} PNe. The mass spectra reported by Scott *et al.* (1997) do indeed show the presence of fullerenes, but fullerenes certainly do not dominate the mass distribution. In all experiments, the photo-processing products include many more (dehydrogenated) PAHs, and low-mass molecules (and molecular fragments) containing H. Thus, to explain objects such as Tc 1 and SMP SMC 16 where abundant C_{60} is seen but no PAHs nor small species are present, significant *additional* processing of these sputtered species would be required to destroy the smaller molecules and the PAHs. UV radiation could conceivably dissociate some of the smaller molecules, but it is not clear how PAHs could be destroyed by radiation in the low-excitation environments represented by the C_{60} PNe. If, on the other hand, collisions are involved, the carbon clusters are processed under similar conditions as described above – and either result in fullerenes dominating the distribution (in the absence of H), or in the formation of PAHs.

Finally, it should be noted that the simultaneous presence of the C_{60} bands and the PAH features in the spectra of some PNe does not necessarily imply that they are co-located – merely that they are both located in the Spitzer beam. In fact, there is clear observational evidence in another object that PAHs and fullerenes are *not* co-located. In Fig. 5, we have reproduced the spatial distribution of molecular hydrogen, PAHs and fullerenes in the reflection nebula NGC 7023 (Sellgren *et al.* 2010, their Fig. 3). The C_{60} emission peaks on the central star, whereas the PAHs are clearly located further away from the star. Thus, although the spectra of the entire nebula show both PAH and fullerene features, both components show clearly different spatial distributions – no PAH emission is found where the C_{60} peaks. Such a distribution could well be the case for (some of) the PNe as well.

The two processes discussed above are not the only ways to form circumstellar fullerenes. An important third route involves high-temperature processes, and allows the formation of fullerenes in H-rich environments. Laboratory experiments carried out by Jäger *et al.* (2009) demonstrate that the temperature in the condensation zone determines the formation pathways of carbonaceous particles with a clear distinction between the resulting condensation products. At temperatures higher than 3500 K, the resulting particles are fullerene compounds and fullerene-like carbon grains (even in the presence of hydrogen); at temperatures lower than 1700 K, soot is formed with a large mixture of PAHs as by-products. This high-temperature mechanism may be relevant to explain the fullerenes in the RCBs (García-Hernández *et al.* 2011; Clayton *et al.* 2011), but a value of 3500 K is certainly not a typical temperature in the circumstellar environment of carbon stars. It remains to be seen whether such a formation route is also important for PNe.

Finally, a promising route in the astronomical settings presented here, is that fullerenes form following the destruction of PAHs. Micelotta *et al.* (2010a,b) studied the effects of shocks on interstellar PAHs, and found that the PAH structure is at least significantly altered (if not destroyed) for shocks with velocities between 75–150 km s^{-1} and in the hot post-shock gas. PAHs first lose their peripheral H-atoms, and then the resulting carbon clusters could assemble into fullerenes on fairly short timescales. This would certainly also be a viable route in PNe. Assembling fullerenes from PAH destruction could also explain the different spatial distribution of PAHs and fullerenes in NGC 7023 (see Fig. 5).

6. Conclusions & outlook

The fullerene species C_{60} and C_{70} have been identified in a variety of astronomical objects. It seems clear that fullerenes form in the circumstellar environments of evolved stars, and that they survive and thrive in the interstellar medium as well. It is less clear precisely how they form, and what their excitation mechanism is, and those topics remain a matter of debate and further research. The derived abundances indicate that $\sim$0.5% of the cosmic carbon could be in the form of C_{60}, and thus fullerenes represent a significant component of interstellar matter.

Fullerenes and fullerene compounds have often been suggested as possible carriers for some of the diffuse interstellar bands (DIBs). Neutral C_{60} is probably not a DIB carrier, but C_{60}^+ has been suggested as a carrier for some DIBs (Foing & Ehrenfreund 1994, 1997; Misawa *et al.* 2009).

Fullerene compounds offer many more possibilities. Fullerenes are readily protonated (see e.g. the review on C_{60} cation chemistry by Bohme 2009, and references therein), and it is thus quite possible that fulleranes (hydrogenated fullerenes) might be present in the ISM or in circumstellar environments as well. It has been suggested that fulleranes could play a role in the formation of H_2 (Cataldo & Iglesias-Groth 2009) and in interstellar extinction. C_{60}^+ was found to be generally quite unreactive at room temperature; nonetheless, many derivatization reactions have been studied in laboratory experiments, including reactions with species that have been detected in the ISM (again, see Bohme 2009) and could thus also be relevant for interstellar chemistry. Fullerenes are also unique in their ability to lock up atoms and small molecules inside their carbon cage. Such endohedral species have also been proposed as DIB carrier candidates, but have only been poorly studied in detail spectroscopically. Given the clear presence of fullerenes in space, we encourage further laboratory work and theoretical calculations on these species.

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Discussion

GUÉLIN: You were able to resolve spatially the PAH source from the C_{60} source. Do you see any shift in position between the lines attributed to fullerenes?

CAMI: The spatial distribution shown is for the reflection nebula NGC 7023 as presented by Sellgren *et al.* (2010). In that source, most C_{60} bands show contamination by neighbouring PAH features which certainly complicates matters; no shift in wavelength has been reported in that source.

STERNBERG: Does the preferential formation of PAHs versus C_{60} in the hydrogen-rich environments depend on whether the hydrogen is ionized or not?

CAMI: The laboratory experiments I referred to used an atmosphere of Ar and H_2; I am not aware of experiments with protons.

RAWLINGS: Would you care to comment on the expected degree of hydrogenation of the fullerenes in space?

CAMI: C_{60} is quite easily protonated, so I would certainly expect to see hydrogenated fullerenes in space.