On the detections of C_{60} and derivatives in circumstellar environments

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C_{60} (buckminsterfullerene) was recently discovered in a variety of circumstellar environments by the *Spitzer Space Telescope*, suggesting that the envelopes around evolved stars are active sites for the synthesis of fullerenes. However, the physical state, excitation mechanism, and formation route of circumstellar C_{60} are not completely understood so far. These open issues are discussed in this paper. For that purpose we investigate the observed wavelengths and strengths of C_{60} bands and compare them with the experimental values. We also statistically study the environments and emission properties of the C_{60} sources. We would like to stress that improved flux measurements and more accurate Einstein coefficients are required to draw solid conclusions. Furthermore, we present possible detections of hydrogenated C_{60} and C_{60}^+, and discuss their implications on fullerene chemistry in circumstellar environments.
Key words: Infrared, ISM, AGB and post-AGB, circumstellar matter, molecules.

1. Introduction

The I_h-symmetrical buckminsterfullerene C_{60}, arranged as 12 pentagons and 20 hexagons, is the smallest closed carbon cage molecule (fullerene) satisfying the isolated pentagon rule (IPR; followed by higher fullerenes C_{70}, C_{74}, C_{76}, C_{78}, C_{80}, and so on), and thus is remarkably stable. Although its existence has been early predicted (Osawa, 1970; Bochvar and Galpern, 1973), C_{60} was first discovered in laboratory experiments simulating the circumstellar chemistry (Kroto *et al.*, 1985). Krätschmer *et al.* (1990b) developed a method to efficiently produce C_{60} in the laboratory, making it possible to study in detail its electronic and vibrational properties. Because of its high stability and symmetry, C_{60} can be taken as a benchmark to study other fullerenes. C_{60} and its derivatives have long been suspected to be present in the universe. The search for this compound in nature started soon after its synthesis in the laboratory, and its detections in geological materials and meteorites have been reported by several groups (e.g. Buseck *et al.*, 1992; Becker and Bada, 1994; Becker *et al.*, 1994; Heymann *et al.*, 1996)[1].

The detection of C_{60} in deep space has proven a long lasting challenging task (Snow and Seab, 1989; Clayton *et al.*, 1995; Kwok *et al.*, 1999; Moutou *et al.*, 1999; Herbig, 2000; Sassara *et al.*, 2001). C_{60} has three broad peaks at 216, 264, and 339 nm in its electronic spectrum, and four infrared (IR) vibrational modes at 7.0, 8.5, 17.4, and 18.9 μm. Hydrogen-poor and carbon-rich circumstellar envelopes, such as R Coronae Borealis (RCB) stars (Goeres and Sedlmayr, 1992), are analogous to the laboratory conditions for the synthesis of fullerenes and thus were suggested to be ideal sites to search for C_{60}; however, this was not supported by observations (García-Hernández *et al.*, 2011b). So far, there is no successful report on the detection of electronic transitions of C_{60}. The Infrared Spectrograph (IRS; Houck *et al.*, 2004) on the *Spitzer Space Telescope* (*Spitzer*; Werner *et al.*, 2004) now provides an unprecedented opportunity to detect the IR vibrational transitions. The first convincing detection was recently made by Cami *et al.* (2010), who detected C_{60} and C_{70} in the *Spitzer*/IRS spectrum of the young planetary nebula (PN) Tc 1. Soon after, C_{60} was detected in a variety of evolved stars, including PNs in the Milky Way and the Magellanic Clouds, a protoplanetary nebula (PPN), post asymptotic giant branch (AGB) stars, modestly hydrogen-deficient RCB stars, and a peculiar binary object (García-Hernández *et al.*, 2010, 2011a, b; Clayton *et al.*, 2011; Gielen *et al.*, 2011; Zhang and Kwok, 2011; Evans *et al.*, 2012; Roberts *et al.*, 2012). Fullerenes may also be widely present in the interstellar medium (ISM). C_{60}^+ has been proposed as the possible carrier of diffuse interstellar bands (Léger *et al.*, 1988), and its electronic spectra in Ar and Ne matrices indeed show a reasonable match to two near-IR diffuse bands (Foing and Ehrenfreund, 1994). Photoabsorption by fullerenes and multi-layered fullerenes (buckyonions) has been suggested as the origin of the 217 nm extinction feature (de Heer and Ugarte, 1993; Iglesias-Groth, 2004; Li *et al.*, 2008). Recently, the C_{60} IR bands have been detected in reflection nebulae (RNs) and the Orion nebula (Sellgren *et al.*, 2010; Rubin *et al.*, 2011). Furthermore, Roberts *et al.* (2012) detected C_{60} in pre-main-sequence objects including young stellar objects and a Herbig Ae/Be star. These detections suggest that C_{60} can be formed in a short time scale between AGB and PN stages, and can survive (or be resynthesized under favorable conditions) in the ISM.

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[1]However, some contrary results have been reported by different research groups (e.g. de Vries *et al.*, 1993; Ebbesen *et al.*, 1995; Heymann, 1997).

However, based on a laboratory spectroscopic investigation, Duley and Hu (2012) presented that the 7.0, 8.5, 17.4, and 18.9 μm features in the spectra dominated by aromatic infrared bands (AIBs) actually arise from proto-fullerenes that are precursors of C_{60}, and thus the C_{60} molecules were detected only in sources that do not show AIBs. García-Hernández et al. (2012b) did not detect C_{60} electronic transitions in the optical spectrum of a RCB star that exhibit AIBs and the (supposed) C_{60} IR features, and suggested that this supported the conclusion of Duley and Hu (2012). However, it is surprising that C_{60} electronic transitions are not detected in the high-quality optical spectrum of the strongest C_{60} source without AIB emission, Tc 1 (García-Hernández and Díaz-Luis, 2013).

The formation route of C_{60} is a subject of debate. Investigating this problem may provide significant insights into the circumstellar chemistry. The experiments of Kroto et al. (1985) suggest that small carbon clusters can self-assemble into C_{60} in a hydrogen-poor environment (bottom-up), and otherwise the formation of polycyclic aromatic hydrocarbons (PAHs) is favored. This scenario is supported by the fact that no AIBs are detected in the PN Tc 1 (Cami et al., 2010). Nevertheless, Jäger et al. (2009) found that fullerenes can be formed by gas-phase condensation reactions in the presence of hydrogen at very high temperature (>3500 K). Another formation mechanism of C_{60} is through shock- or UV-induced decomposition of hydrogenated amorphous carbon (HAC) grains (top-down), through which PAHs can be simultaneously formed (García-Hernández et al., 2010; Bernard-Salas et al., 2012; Micelotta et al., 2012). The supporting evidence comes from the facts that most of the C_{60} sources also exhibit AIBs, and C_{60} is not detected in extremely hydrogen-poor RCB stars (García-Hernández et al., 2011b). A similar mechanism was proposed by Berné and Tielens (2012), in which C_{60} is formed through UV-induced dehydrogenation and isomerization of graphenes. This model can explain the observation of the RN NGC 7023 by Sellgren et al. (2010) that the C_{60}/AIB flux ratios decrease with increasing distance from the central star. Moreover, Boersma et al. (2012) found that C_{60} can coexist with the carriers of AIBs in the shielded regions of Orion.

A related question is what drives the excitation of C_{60} IR emission. Thermal excitation of solid fullerenes (Cami et al., 2010; García-Hernández et al., 2011a) and UV-excitation of gas-phase C_{60} molecules (Sellgren et al., 2010) have been discussed. The first systematical comparison of the two mechanisms was made by Bernard-Salas et al. (2012) who found that the IR spectra of three PNs with strong C_{60} features favor fluorescence as the excitation mechanism. However, Roberts et al. (2012) and García-Hernández et al. (2012a) argued that thermal excitation can better explain the observed C_{60} flux ratios.

Mapping the spatial distributions of C_{60} and AIBs is essential to understand the formation routes of fullerenes in astrophysics. However, this is very difficult for circumstellar envelopes given their compactness and the weakness of C_{60} emission. Another approach to investigate this problem is to probe hydrides of fullerenes (fulleranes). The presence of fulleranes in space has been predicted (e.g. Web-

ster, 1992, 1993; Petrie and Bohme, 2000; Cataldo and Iglesias-Groth, 2009). When hydrogen atoms are attached to carbon atoms of C_{60}, the conversion of delocalized π- into σ-character orbitals decreases the bond angle strain. Therefore, when exposed to atomic hydrogen, C_{60} can be quickly hydrogenated into $C_{60}H_m$ ($m = 2, 4, ..., 60$). On the other hand, heavily hydrogenated C_{60} is highly unstable because of large strain resulting from hydrogen-hydrogen repulsion. It follows that moderately hydrogenated C_{60} is likely to exist in circumstellar environments. Indeed, in laboratory conditions, it is easy to produce $C_{60}H_{36}$ that can further form $C_{60}H_{18}$ through thermal annealing (e.g. Iglesias-Groth et al., 2012) but the production of fulleranes with a larger or lower degree of hydrogenation is much more difficult. Roberts et al. (2012) noticed that two C_{60} sources also exhibit the very rare C-H emission from hydrogen-coated nanodiamonds, a species that can be formed together with fullerenes, so it is reasonable to believe that C-H emission from $C_{60}H_m$ is also detectable in some C_{60} sources.

In this paper, we study the properties of all the reported C_{60} sources and compare the observations with existing experimental and theoretical results. In Section 2, we investigate the wavelengths and widths of the C_{60} IR bands, aiming at understanding the physical state of circumstellar C_{60}. In Sections 3 and 4, we respectively discuss the excitation and formation problems of fullerenes based on the measured band strengths. In Section 5, we present a search for fulleranes in the carbon-rich PPN IRAS 01005+7910 utilizing the spectrum obtained by the *Infrared Space Observatory* (*ISO*; Kessler et al., 1996), and briefly discuss C_{60}^{+} and C_{60}^{-} in the PN Tc 1. The conclusions are given in Section 6.

2. Wavelengths of the IR-active Bands

C_{60} has 174 normal vibrational modes that are distributed among 46 frequencies owning to its icosahedral symmetry. Of these modes, only 4 IR-active vibrational bands of F_{1u} symmetry and 10 Raman-active bands of A_g and H_g symmetries have been observed in laboratory experiments. Throughout this paper we only focus on the four IR C_{60} bands that are of astrophysical interest. Because of intermolecular interactions, the wavelengths of IR bands from solid C_{60} clusters might differ from those from gas-phase molecules and depend on the environment temperatures. Therefore, the comparison between the observed and experimental wavelengths of the C_{60} IR bands enables us to investigate the physical state of circumstellar fullerenes.

Krätschmer et al. (1990a) and Frum et al. (1991) have made the laboratory measurements of the solid- and gas-phase spectra of C_{60}, respectively. By comparing their results and the observed spectra, Evans et al. (2012) concluded that C_{60} in the peculiar binary XX Oph is in the solid phase. Temperature-dependent studies of C_{60} IR spectra have been presented by Chase et al. (1992), Nemes et al. (1994), and Iglesias-Groth et al. (2011) showing that the peak wavelengths shift to higher values with increasing temperature. In Fig. 1, we compare these experimental wavelengths and the spectra of three C_{60} sources, Tc 1, NGC 7023, and IRAS 01005+7910. There is no evidence showing that the peak wavelengths of C_{60} features shift between different sources[2], suggesting that fullerenes in all
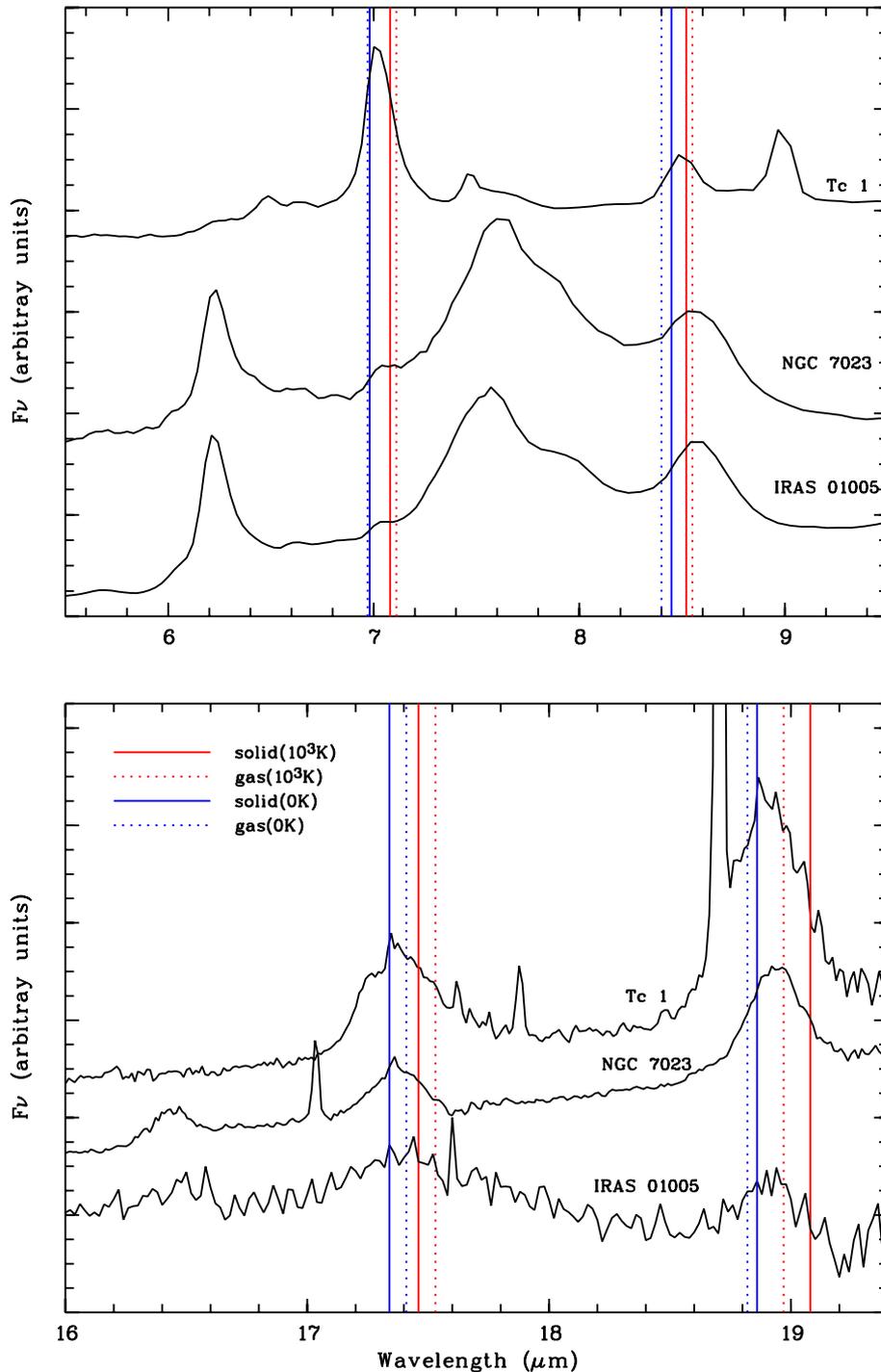
Fig. 1. The comparison of the experimental wavelengths of the four IR bands of solid- and gas-phase C_{60}. The solid black curves are the observed spectra of IRAS 01005+7910, NGC 7023, and Tc 1 (courtesy of Kris Sellgren, Jan Cami, and Jeronimo Bernard-Salas). Note that the 7.0, 8.5, and 17.4 μm features are blended with AIBs in the spectra of NGC 7023 and IRAS 01005+7910.

the circumstellar envelopes are probably in a similar physical state. An inspection of Fig. 1 indicates that the peak wavelengths of the 17.4 μm feature seem to suggest that circumstellar C_{60} is in the solid phase at a low temperature (<500 K) rather than in the gas phase. The conclusion, however, is arguable in that the spectra of NGC 7023 and IRAS 01005+7910 exhibit the 16.4 μm features, and thus the 17.4 μm feature is probably blended with an AIB (Sellgren *et al.*, 2010; Berné and Tielens, 2012). The observed peak-wavelengths of the other three C_{60} features lie well in-

side the experimental wavelength ranges of both solid- and gas-phase C_{60}. Therefore, we cannot completely rule out a gas-phase origin although a solid-phase origin is favored.

Experimentally, the 17.4 and 18.9 μm features in the

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[2]Note that the 8.5 μm feature in the spectra of NGC 7023 and IRAS 01005+7910 is essentially invisible because of severe blending with the AIB at 8.6 μm, and the 7.0 μm feature in Tc 1 is contaminated with a [Ar II] line at 7.0 μm. This statement also applies to most of the C_{60} sources, and thus additional complexity can be introduced into the discussion of band strength ratios in the next section.
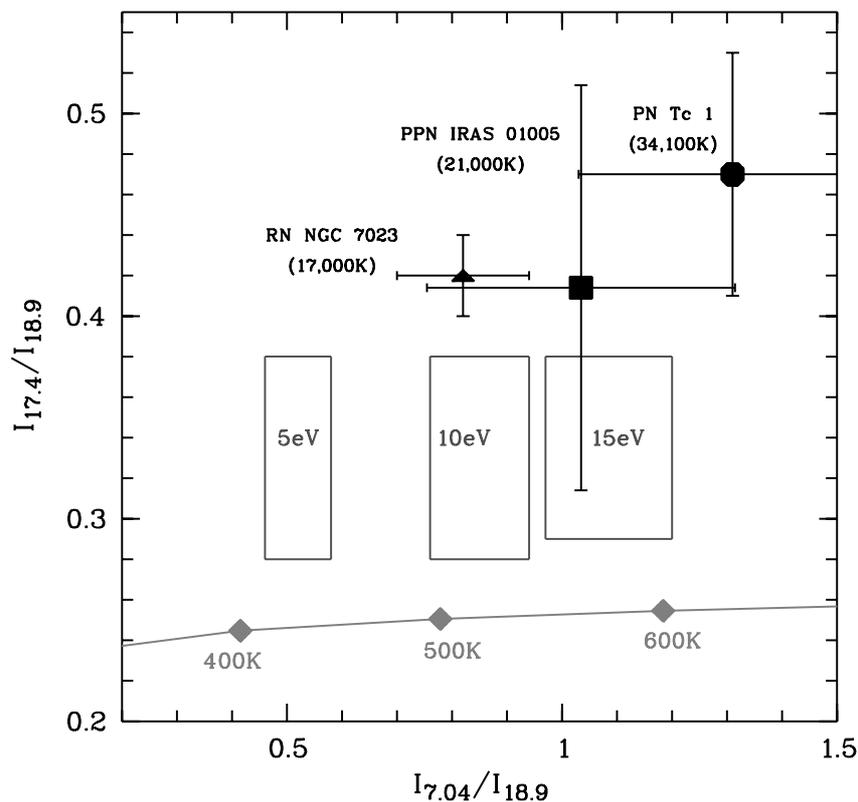
Fig. 2. The 17.4 μm / 18.9 μm versus 7.0 μm / 18.9 μm band ratios for NGC 7023, IRAS 01005+7910, and Tc 1. The effective temperatures of their excitation sources are given in brackets. The closed boxes represent the predictions of UV-excitation model by Sellgren *et al.* (2010). The average photon-energy is given within each box. The curve marked with lozenges represents the predictions of thermal model. The A-values for both models are taken from the same literature (Choi *et al.*, 2000).

gas-phase IR spectrum have a full-width at half maximum (FWHM) of about 0.4 μm at 1065 K (Frum *et al.*, 1991). Chase *et al.* (1992) found that the band widths of C_{60} shift little in the solution and in the solid state, suggesting that C_{60} in the solid state is virtually a gas-phase-like, freely rotating molecule. The band widths are partially due to vibration-rotation coupling, scaling roughly with the square root of the temperature. Therefore, one can, in principle, estimate the temperature by comparing the observed band widths with the experimental values. A comparison between the experimental results of Frum *et al.* (1991) and Chase *et al.* (1992) suggests that the band widths of solid-phase C_{60} are 2–3 times narrower than those of gas-phase at the same temperature. The FWHMs of the observed 17.4 and 18.9 μm features are 0.26–0.36 μm, implying a gas temperature of 400–900 K. The implicated temperature might be higher if C_{60} is in the solid phase. While interesting, these results should be viewed with some caution because they might be related to the experimental conditions, which are quite different from those of circumstellar envelopes. The 17.4 and 18.9 μm features might be blended with weak C_{70} emission (see, e.g., figure 1 of Cami *et al.*, 2010), slightly affecting their FWHMs. Moreover, if the C_{60} bands arise from regions with large temperature fluctuations, the situation will be complicated in that the shifts of peak wavelengths can make an additional contribution to the band broadening.

3. On the Excitation of C_{60} Vibrational Spectra

It is essential to understand the excitation mechanism of fullerene emission as it enables us to accurately determine the abundance of C_{60} and establish how useful the C_{60} bands are to probe circumstellar environments. Two possible scenarios have been discussed in previous paper, but results remain conflicting. Cami *et al.* (2010) found that a thermal model can interpret the C_{60} emission in Tc 1. In that case, C_{60} is attached to dust grains which are in equilibrium with the UV radiation field, and one can calculate the thermal temperature from the Boltzmann excitation diagram of C_{60} band ratios. García-Hernández *et al.* (2011a) derived thermal temperatures of 200–500 K for a sample of C_{60}-detected PNs. On the other hand, Sellgren *et al.* (2010) assumed that C_{60} is isolated free molecules in the gas phase and has a similar excitation mechanism with PAHs as discussed by Allamandola *et al.* (1989). In this scenario, C_{60} is excited to high electronic states by absorbing UV starlight, and then the electronic energy is quickly redistributed via internal conversion, followed by IR emission through cascading down the vibrational ladder to the ground vibrational state. Since the probabilities of UV-photon absorption and IR-photon emission respectively depend on the absorption cross-sections and Einstein A-values of the corresponding energy levels, a Monte Carlo technique[3] can be used to simulate this process. Therefore, if the UV-excitation model is valid, the C_{60} IR bands can be used to probe the circumstellar radiation field. The model of Sellgren *et al.* (2010) can reasonably explain the C_{60} intensity ratios ob-

Table 1. C_{60} band strengths normalized to that of the 18.9 μm feature.

Ref.	7.0 μm	8.5 μm	17.4 μm	18.9 μm
Experiments				
Chase *et al.* (1992)	0.34	0.28	0.34	1.0
Fu *et al.* (1992)	0.36	0.29	0.39	1.0
Martin *et al.* (1993)	0.38	0.45	0.48	1.0
Winkler *et al.* (1994)	0.36	0.16	0.28	1.0
Onoe and Takeuchi (1996)	0.24	0.22	0.30	1.0
Hara *et al.* (1997)	0.38	0.20	0.27	1.0
Choi *et al.* (2000)	0.46	0.31	0.26	1.0
Iglesias-Groth (2004)	0.27	0.26	0.43	1.0
Theoretical calculations				
Bertsch *et al.* (1995)	2.7	0.17	0.47	1.0
Esfarjani *et al.* (1998)	1.7	0.18	0.08	1.0
Stanton and Newton (1988)	4.4	1.9	0.33	1.0
Adams *et al.* (1994)	0.31	1.4	0.65	1.0
Bertsch *et al.* (1995)	0.41	0.59	0.65	1.0
Giannozzi and Baroni (1994)	0.57	0.36	0.63	1.0

served in NGC 7023, but predicts too large $I_{7.0}/I_{18.9}$ ratios in NGC 2023. A recent study of three PNs by Bernard-Salas *et al.* (2012) does not favor the thermal model because (1) the excitation classes of these PNs are very different while the C_{60} flux ratios are fairly similar, and (2) C_{60} is located in a region far from the central star and would be difficult to be heated to the deduced thermal temperatures. However, a different conclusion was subsequently drawn by García-Hernández *et al.* (2012a) who subtracted the contribution of C_{70} to the observed 7.0 μm flux and found that the UV-excitation model cannot explain the C_{60} flux ratios for a larger sample of PNs. Bernard-Salas *et al.* (2012) did not take into account the contribution of C_{70} because the band strengths cannot be accurately estimated without appropriate excitation model.

To investigate this problem, in Fig. 2 we compare the 17.4 μm / 18.9 μm and 7.0 μm / 18.9 μm band ratios for three well C_{60}-detected sources at different evolutionary stages. The predictions of UV-excitation (Sellgren *et al.*, 2010) and thermal models are also plotted in Fig. 2, where the A-values are derived from Choi *et al.* (2000) for both models. The thermal model is constructed using the same way as described by Bernard-Salas *et al.* (2012). Similar to the thermal model for >500 K, the UV-excitation model predicts a nearly invariable 17.4 μm / 18.9 μm band ratio (also see Bernard-Salas *et al.*, 2012). An inspection of Fig. 2 shows that the observations are situated at positions closer to the predictions of the UV-excitation model. In the scenario of UV-excitation, the 7.0 μm / 18.9 μm band ratios increase with increasing UV radiation. This is consistent with the observational facts that among the three sources the central star of the PN Tc 1 has the highest effective temperature, and it is followed by the PPN IRAS 01005+7910 and the RN NGC 7023. Nevertheless, the observed 17.4 μm / 18.9 μm band ratios appear larger than the model predictions. This is partially due to the contamination of an

AIB to the 17.4 μm feature (except for Tc 1 which does not show AIBs). Another possible cause is that the $A_{17.4}$ value of Choi *et al.* (2000) has been underestimated. This is also shown in figures 5 and 6 of Bernard-Salas *et al.* (2012).

In Fig. 3, we compare the A-values obtained from the band strengths given in previous literatures, as listed in Table 1. The theoretical band strengths are remarkably inconsistent with the experimental values. The theoretical calculations, based on semi-empirical or first-principle models, differ significantly in the resultant band strengths, especially for the 7.0 μm / 18.9 μm band ratios. The experimental band strengths are more concentrated in Fig. 3 than the theoretical values, yielding an average strength ratio of $(0.35 \pm 0.07) : (0.27 \pm 0.09) : (0.34 \pm 0.08) : 1.0$ for the 7.0, 8.5, 17.4, and 18.9 μm bands. We can see that, indeed, the $A_{17.4}$ value of Choi *et al.* (2000) is a factor of 1.3 lower than the average value. Through the comparison, we estimate that the A-values have a 20–30% error. It should be noted that all the experiments were performed in condensed phases and the results might be perturbed by intermolecular effects. Experiments of gas-phase C_{60} will be invaluable to improve the A-values in the future. In addition, the UV-excitation model also relies on the photoabsorption cross section of C_{60} which contains some uncertainties (Yasumatsu *et al.*, 1996; Iglesias-Groth *et al.*, 2002; Yagi *et al.*, 2009).

The thermal-model predictions using A-values obtained by different groups are compared in Fig. 4 along with the observed band ratios of all the C_{60} sources. It is clear that with higher $A_{17.4}$ value the prediction of thermal models can better match the observed 17.4 μm / 18.9 μm flux ratios. Gielen *et al.* (2011) did not detect the C_{60} 7.0 μm band in two post-AGB stars. This is understandable in terms of both models since their central stars have relatively low effective temperatures. However, the observed band ratios for most of the C_{60} sources exhibit a wide variation, and some of them significantly deviate from both model predications. We suspect that the flux measurements of C_{60} IR bands, which are subject to the subtraction of continuum emission and the decomposition from other features, prob-

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[3]The Monte Carlo model of Sellgren *et al.* (2010) applies to single-photon excitation. If the UV radiation field is sufficiently intense, it is more appropriate to use the statistical equilibrium method (A. Li, private communication).
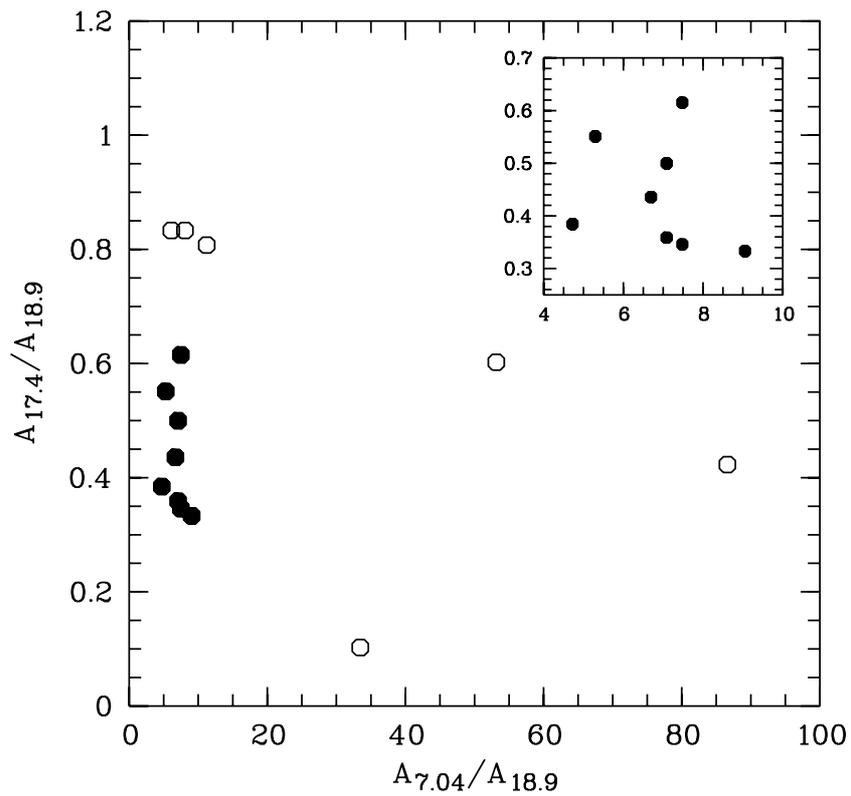
Fig. 3.   The comparison of Einstein coefficients (A-values) taken from previous literatures. The open and filled circles represent the theoretical and experimental values, respectively. The insert at the low-left corner is a zoom-in view of the experimental values.
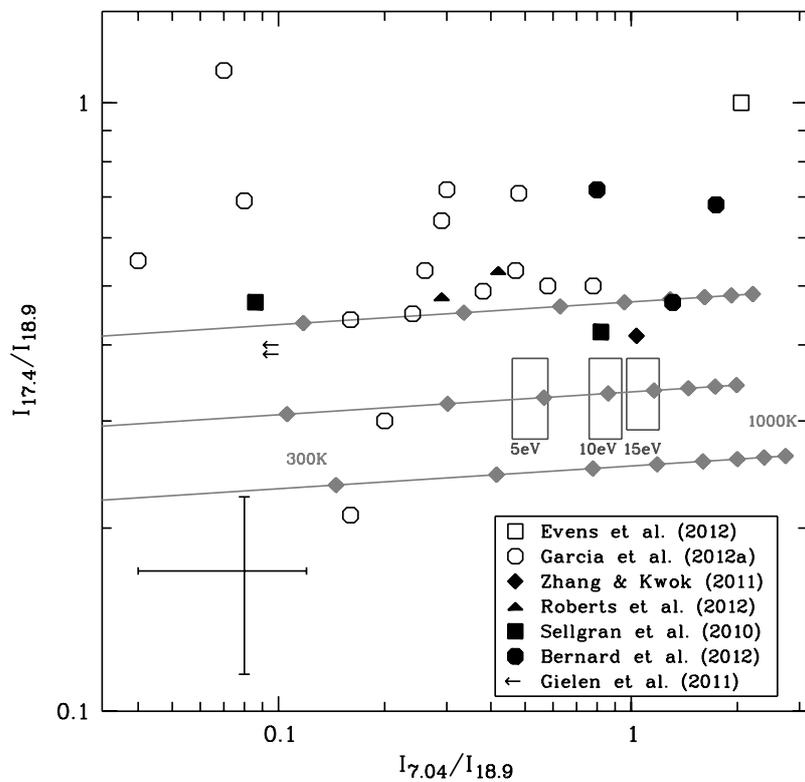

Fig. 4.   Same as Fig. 2, but for all the reported C$_{60}$ sources. The typical error bar is indicated in the lower left-hand corner. The solid curves denote the predicted values by thermal models with temperatures from 300 to 1000 K at an interval of 100 K, for which the A-values (from up to down) are taken from Martin *et al.* (1993), Chase *et al.* (1992), and Choi *et al.* (2000), respectively.
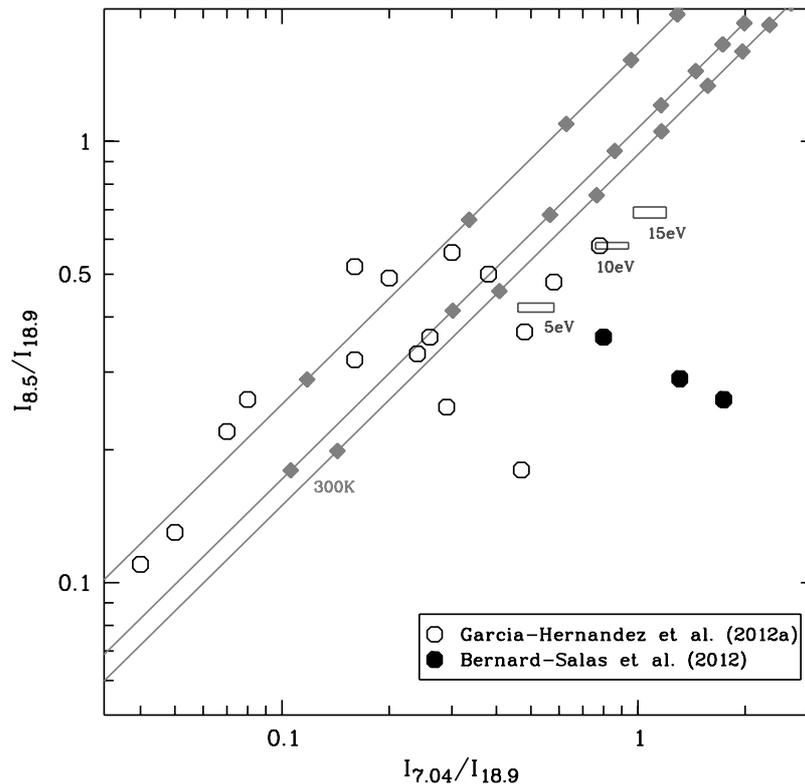
Fig. 5. The 8.5 μm / 18.9 μm versus 7.0 μm / 18.9 μm band ratios. The symbols are the same as in Fig. 4. Note that the 7.0μm band strengths of García-Hernández *et al.* (2012a) were estimated from thermal models, and thus cannot be used to argue against the fluorescence model (see the text).

ably have rather large uncertainties. For example, even for the strongest fullerene emission PN Tc 1, Bernard-Salas *et al.* (2012) and García-Hernández *et al.* (2012a) gave quite different flux ratios.

The C_{60} 8.5 μm band can be detected only in objects that do not exhibit strong AIBs. In Fig. 5, we compare the 8.5 μm / 18.9 μm and 7.0 μm / 18.9 μm band ratios. Compared with those by Bernard-Salas *et al.* (2012), the band ratios obtained by García-Hernández *et al.* (2012a) systematically shift toward the left side of the figure. This is attributed to the different estimates for the contamination of C_{70} emission. Assuming a Boltzmann population ratio, García-Hernández *et al.* (2012a) estimated the strengths of the C_{60} 7.0 μm band from the 8.5, 17.4, and 18.9 μm bands. Thus, it is only natural that the data points of García-Hernández *et al.* (2012a) are more close to the predictions of thermal models, which cannot be used to argue against the conclusion of Bernard-Salas *et al.* (2012). The main problem of the thermal model is that a high fullerene temperature (mostly > 300 K) is required, and hardly agrees with those implicated by dust thermal emission. On the other hand, Fig. 5 demonstrates that the UV-excitation model predicts an unacceptably low average photon energy (mostly <5 eV). This is the main argument of García-Hernández *et al.* (2012a) against the UV-excitation model. However, the UV-excitation model of Sellgren *et al.* (2010) applies only for free-flying C_{60} molecules. If the circumstellar fullerenes are in a cluster state, more intense radiation field will be expected to excite the C_{60} IR bands, and the model of Sellgren *et al.* (2010) only gives the lower limits of the average photon energy. If this was the case, the scattering band ratios in

Figs. 4 and 5 would partially reflect the variation of cluster sizes in these sources.

Some alternative mechanisms, such as the release of chemical energy (Duley and Williams, 2011) and atom impacts (Papoular, 2012), have been introduced to explain the excitation of AIBs. It remains unknown whether these mechanisms play a role on the excitation of C_{60} IR bands.

4. On the Origin of C_{60}

The synthesis of fullerenes in nature has been a subject of intense discussion for many years. It is unclear whether they form through assembly of small carbon-bearing molecules (bottom-up) or fragmentations of large compounds (top-down). The discovery of fullerenes in rocks (Buseck *et al.*, 1992) suggests that fullerenes can be generated through a solid-state process. Many interesting scenarios, such as cataclysmic impact, extensive wildfires, chondritic impactor, vaporization of carbon by lightning strike, and pyrolysis of organic matter, have been proposed to explain the formation of fullerenes in geological environments (see Buseck, 2002, and references therein). To investigate C_{60} formation in circumstellar environments, it is instructive to compare the observations with experimental knowledge. In laboratory, the most effective two ways to produce fullerenes are through vaporization of graphite followed by growth of carbon clusters and through combustion of hydrocarbons. The other experimental routes, such as pyrolysis of hydrocarbons and chemical synthesis, are unlikely to happen under circumstellar environments. The method of graphite evaporation (bottom-up) requires a carbon-rich environment, otherwise the fullerene formation

is strongly suppressed. However, C_{60} has been detected in O-rich binary post-AGB stars (Gielen *et al.*, 2011), contrary to what is required by the bottom-up route[4].

In Table 2 we compare the effective temperatures of the central stars and the other emission features of C_{60} objects. They all have effective temperatures of <35,000 K, suggesting that fullerenes cannot form or survive in strong UV-radiation fields. This situation is similar to that of the unidentified 21 μm feature that has been discovered in a small number of PPNs (Kwok *et al.*, 1989). Most of the sources exhibit AIBs arising from C-H modes, consistent with the experimental results of hydrocarbon combustion. Not all of them show the 30 μm feature and the 15–20 μm plateau. It is intriguing that the plateau emission at 6–10 μm and 10–14 μm is revealed in all the sources, indicating that their carriers are likely to be related to fullerene formation. Kwok and Zhang (2011) presented that AIBs and plateau emission can be uniformly attributed to stretching and bending modes of mixed aromatic-aliphatic organic nanoparticles (MAONs), and during stellar evolution, aliphatic chains can be processed into aromatic rings. García-Hernández *et al.* (2010) and Micelotta *et al.* (2012) proposed that fullerenes can be formed from HAC grains and "arophatic" clusters, both of which have a structure similar to that of MAONs. Thus, we infer that circumstellar fullerenes are produced by MAONs following the scheme suggested by Micelotta *et al.* (2012). In this scenario, proto-fullerenes, as proposed by Duley and Hu (2012), are first formed through dehydrogenation of MAONs accompanied by introduction of pentagons following the IPR and a pathway of minimizing the number of dangling bonds, and later on are processed into vibrational-excited closed cages by reducing the number of dangling bonds to zero. The fullerenic cages can be transformed into the most stable isomers by means of a series of Stone-Wales rearrangements. Finally, the fullerenic cages are shrink to smaller cages like C_{60} by releasing excess energy. The dehydrogenation may be induced by either UV photons or shocks, but the latter seems to be favored at least for a few C_{60} sources whose central stars have relatively low effective temperatures (<7000 K; Table 2). The percentage of carbon in circumstellar C_{60} is estimated to be less than 0.3% (Zhang and Kwok, 2011; García-Hernández *et al.*, 2012a). Since the carriers of AIBs presumably lock up 6% of the cosmic carbon (Cerrigone *et al.*, 2009), we infer that only small amounts of MAONs can be transformed into C_{60} even under the most favorable conditions.

Because MAONs have a 3D structure, the formation process of fullerenic cages can take place in a layered structure. This provides a possible route for the formation of buckyonions, which have been suggested as the carrier of the 217 nm interstellar absorption feature.

The C_{70}/C_{60} abundance ratio has important implications in understanding the formation route of fullerenes. The C_{70}/C_{60} ratio of PNs ranges from 0.02 to 0.21 (García-Hernández *et al.*, 2012a), comparable to the values of geological fullerenes (0.08 in the Allende meteorite, Becker

Table 2. C_{60} and other features.

ID.	Ref.	Assign.	$T_{\rm eff}$ (K)	Bands			Plateaus	
				AIBs	30 μm	6–10 μm	10–14 μm	15–20 μm
Tc 1	Cami *et al.* (2010)	PN	34,100	No	Yes	Yes	Yes	No
IRAS 01005	Zhang and Kwok (2011)	PPN	21,000	Yes	Yes	Yes	Yes	Yes
XX Oph	Evans *et al.* (2012)	Peculiar nebula	20,000:	Yes	No	Yes	Yes	Yes
IRAS 06338	Gielen *et al.* (2011)	Post-AGB	6,250	Yes	No	Yes	Yes	Yes
V854 Cen	García-Hernández *et al.* (2011b)	RCB star	6,750	Yes	No	Yes	Yes	Yes
HD 97300	Roberts *et al.* (2012)	Herbig Ae/Be star	10,500	Yes	No	Yes	Yes	No
SSTGC 372630	Roberts *et al.* (2012)	Massive YSO	7,000:	Yes	No	Yes	Yes	No
NGC 7023	Sellgren *et al.* (2010)	RN	17,000	Yes	No	Yes	Yes	Yes

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[4]The detection of C_{60} in O-rich sources is rare. It is unclear whether C_{60} in these sources was produced through a different mechanism with those in C-rich objects.

et al., 1994; 0.21–0.36 in terrestrial clays, Heymann *et al.*, 1996). In laboratory, the C_{70}/C_{60} ratio is highly variable. The hydrocarbon combustion process yields a C_{70}/C_{60} ratio ranging from 0.26 to 0.57 (Howard *et al.*, 1991), which tends to increase with increasing pressure. This ratio is much larger than that obtained through graphite evaporation methods (0.02–0.18, e.g. Ajie *et al.*, 1990). One cannot simply argue that the low C_{70}/C_{60} ratio in PNs seems not to favor the top-down scenario, because the circumstellar envelopes have a significantly lower pressure than laboratories and the fullerene formation in combustion experiments is not completely understood. Moreover, this range of C_{70}/C_{60} ratio is very uncertain since C_{70} has been measured only in a very few sources. The abundance of generated higher fullerenes beyond C_{70} is relatively low, which cannot be theoretically explained. In addition, we cannot rule out the possibility that the C_{70}/C_{60} ratio can be modified by chemical processes in circumstellar envelopes. Circumstellar envelopes around evolved stars, therefore, provide an unique laboratory to investigate fullerene formation and processes under low pressure environments.

5. Derivatives of C_{60}

5.1 A possible detection of fullerane in IRAS 01005+7910

The pioneer work of Webster (1992) suggested that the wavelength of the aliphatic C-H stretching vibration may shifts toward longer wavelengths from $3.4\,\mu$m due to the absence of hydrogen atoms on neighboring carbon atoms. Each carbon atom of $C_{60}H_m$ has three neighboring carbon atoms, results in three possibilities of the absence of hydrogen atoms. Therefore, $C_{60}H_m$ is expected to exhibit three peaks in the wavelength range longer than $3.4\,\mu$m. The experimental spectra of $C_{60}H_{18}$ (Iglesias-Groth *et al.*, 2012) do exhibit three peaks in the wavelength range from 3.4–$3.6\,\mu$m. Iglesias-Groth *et al.* (2012) proposed that because the C-H stretching band of $C_{60}H_m$ is intense and can be easily distinguished from other features, it can serve as an indicator to search for these molecules in astrophysical environments. This band, however, is out of the wavelength range accessible to *Spitzer*/IRS.

Previously, we have detected C_{60} and AIBs in IRAS 01005+7910 (Zhang and Kwok, 2011). If C_{60} and hydrogen are located in the same region, fulleranes are very likely to be present in this object. As a PPN, IRAS 01005+7910 does not emit atomic lines, and thus provides a good platform to search for fulleranes. The *ISO* spectrum of IRAS 01005+7910 has been described by Hrivnak *et al.* (2000). Figure 6 displays the continuum-subtracted *ISO* spectrum of IRAS 01005+7910 in the C-H stretching region. The sp^2 C-H stretch at $3.3\,\mu$m has been detected by Hrivnak *et al.* (2000). The weak peak at $3.42\,\mu$m might be due to the asymmetric stretch of -CH_2- groups or just an artifact. The three peaks, presumably ascribed to fulleranes by Webster (1992), are clearly visible at 3.48, 3.51, and $3.58\,\mu$m, and have fluxes comparable to the $3.3\,\mu$m feature. Through a multi-Gaussian fitting, we estimate the fluxes of the four features, corresponding to 0, 1, 2, and 3 non-H-bonded neighboring carbon atoms (referred as R_0, R_1, R_2, and R_3 hereafter), to be 1.64×10^{-15}, 2.69×10^{-15}, 1.78×10^{-15},

and 1.61×10^{-15} W m^{-2}, respectively. Note that the R_3 feature might be blended with an unknown feature (Fig. 6).

Assuming that the C_{60} emission and the C-H stretching emission of $C_{60}H_m$ origin from UV-excitation, the fractions of carbon locked up in fullerenes and fulleranes ($f_C^{C_{60}}$ and $f_C^{C_{60}H_m}$) can be estimated using the method described by Berné and Tielens (2012). Based on the fluxes of C_{60} bands given by Zhang and Kwok (2011), we find $f_C^{C_{60}}/f_C^{C_{60}H_m} \approx 1$, suggesting that about 50 percent of fullerenes have been hydrogenated.

Under the assumption that all the features have the same oscillator strength, the relative strengths of R_0, R_1, R_2, and R_3 are equal to the relative probabilities of the four cases (0, 1, 2, 3 non-H-bonded neighboring carbon atoms), and thus the relative strengths of the four $C_{60}H_m$ features can reflect the degree of hydrogenation (the m value). With increasing number of C atoms bonded with H, the strength of R_3 decreases compared to R_0. Figure 7 depicts the calculated relative strengths as functions of m values. The observed strengths indicate that the m value is very likely to lie within the range from 25–40. This is consistent with the experimental results in which $C_{60}H_{36}$ is the dominant product of hydrogenation reaction of C_{60}. Furthermore, experiments show that $C_{60}H_{36}$ can be transferred to $C_{60}H_{18}$ through thermal annealing. We find that the relative strength of R_3 is slightly higher than that expected for $C_{60}H_{36}$ (Fig. 7), suggesting that $C_{60}H_{18}$ might be also present. On the other hand, the calculations were purely from a mathematical consideration and did not take into account the chemical structure. Therefore, the fraction of R_3 relative to R_0 might be underestimated due to ignoring the hydrogen-hydrogen repulsion.

IRAS 01005+7910 does not exhibit the $21\,\mu$m feature. Many candidate carriers of this feature have been proposed in previous studies (see Zhang *et al.*, 2009, and references therein), among which Justtanont *et al.* (1996) and García-Lario *et al.* (1999) have attributed it to the mixture of fullerenes with various degree of hydrogenation. The absence of the $21\,\mu$m feature in IRAS 01005+7910 and the non-detection of C_{60} in $21\,\mu$m-detected PPNs do not support this identification.

During the post-AGB phase, the UV radiation field gradually increases with the evolution of the central star, and molecular H_2 is more likely to be photodissociated into atomic H. Moreover, shocks created by fast stellar winds tend to dissociate H_2 through collisions. This enhances the possibility of hydrogenation of C_{60}. If C_{60} is highly hydrogenated, the bond-breaking may occur due to large angle strain, and thus destruct this compound. Besides, intense UV light can directly destroy fullerenes. This can account for the fact that fullerenes were never observed in evolved PNs.

5.2 C_{60}^+ and C_{60}^- in Tc 1

C_{60} has an ionization potential of 7.6 eV, and thus is possibly present as the cation C_{60}^+ in circumstellar environments. Ionized C_{60} may contribute to the diffuse interstellar bands and initiate intriguing chemical reactions (e.g. Foing and Ehrenfreund, 1994; Moutou *et al.*, 1999; Petrie and Bohme, 2000; Leidlmair *et al.*, 2011). C_{60}^- is generally thought to be scarce in circumstellar environments
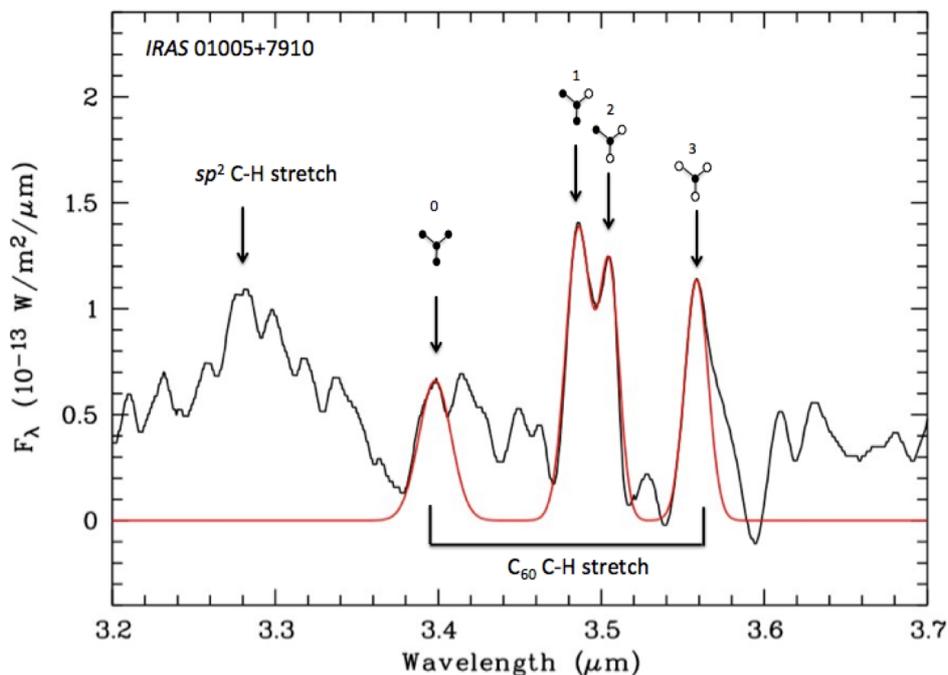
Fig. 6. The *ISO* spectrum of IRAS 01005+7910 in the C-H stretching region. The peaks for 0, 1, 2, and 3 non-H-bonded neighboring carbon atoms are marked. The red line is a multi-Gaussian fitting.
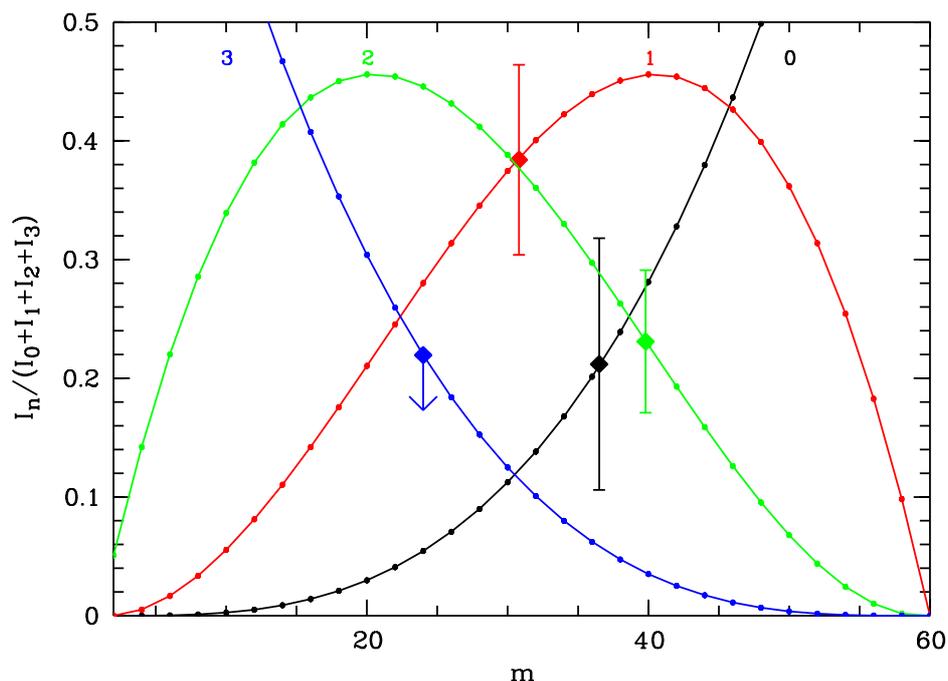

Fig. 7. The calculated probabilities of the four cases (0—black, 1—red, 2—green, and 3—blue non-H-bonded neighboring carbon atoms) for a hydrogen bonded carbon atom of C$_{60}$H$_m$ vs. the m values. The observed fractional strengths of the four corresponding features are overplotted with lozenges.

in that electron attachment to C$_{60}$ is prohibited due to its high activation barrier (0.26 eV). However, there are alternative routes generating C$_{60}^-$ (Petrie and Bohme, 2000). Recently, Berné *et al.* (2013) detected C$_{60}^+$ IR emission bands in NGC 7023. C$_{60}^-$ have never been detected in space so far.

Based on an experiment in 5 K neon matrices, Fulara *et al.* (1993) obtained the IR spectrum of C$_{60}^+$ and C$_{60}^-$, which reveals the vibrational features at 7.11 and 7.51 μm from C$_{60}^+$, and those at 7.22 and 8.32 μm from C$_{60}^-$. Figure 8

shows the spectrum of Tc 1, where the wavelengths of C$_{60}^+$ and C$_{60}^-$ bands are indicated. It is clear that there is no detectable C$_{60}^-$ emission, and thus the content of circumstellar C$_{60}^-$ is safely negligible. However, the presence of C$_{60}^+$ cannot be ruled out. Although the strong forbidden line and C$_{60}$ band hamper the detection of the 7.11 μm band, there is a blended feature on the red side of the H I (Pfα) line at 7.46 μm, which may be partially contributed by the C$_{60}^+$ 7.51 μm band. After subtracting the continuum and
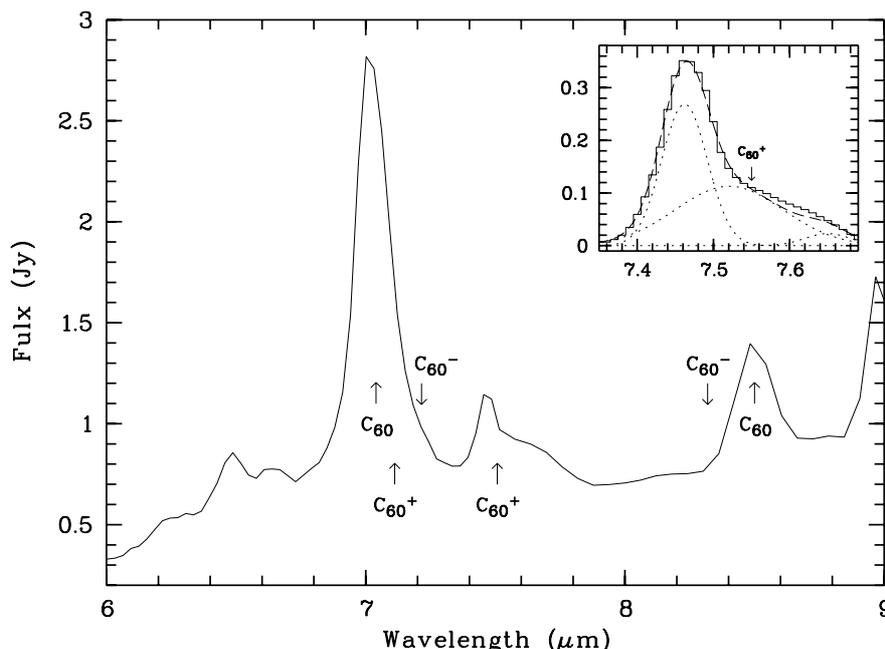
Fig. 8. The *Spitzer* spectrum of Tc 1 at 6–9 μm. The experimental wavelengths of C$_{60}$, C$_{60}^+$, and C$_{60}^-$ are marked. Note that there is a strong [Ar II] forbidden line at 7.0 μm. The decomposition of the C$_{60}^+$ 7.51 μm feature is shown in the insert where the solid and dashed curves respectively represent the observed and fitted spectra, and the dotted curves denote the individual components.

6–10 μm plateau emission, we decompose this feature, as shown in the insert of Fig. 8. A broaden 7.51 μm band with a FWHM of 0.1 μm and two narrow atomic lines that are interpreted as H I and [Ne VI] lines can reasonably fit the observations. According to the fitting, the flux of the C$_{60}^+$ 7.51 μm band is estimated to be about 1.0×10^{-15} W m^{-2}.

The abundance of C$_{60}^+$ can be determined using the formulae given by Moutou *et al.* (1999). For the calculations (see equation 4 of Moutou *et al.*, 1999), the C/H abundance ratio was taken from Pottasch *et al.* (2011), and the 7.11 μm / 7.51 μm cross-section ratio was assumed to be 2.2. Based on a blackbody fitting of the *Spitzer* spectrum of Tc 1, we estimate that the total IR emission from dust is $(1.5–3.0) \times 10^{-12}$ W m^{-2}. As a result, we obtained that about 0.12%–0.23% carbon is locked up in C$_{60}^+$ in Tc 1 if the detection is real. This is comparable to the upper limit of 0.26% in NGC 7023 (Moutou *et al.*, 1999), and the value of 0.3%–0.9% in the ISM that was estimated by Foing and Ehrenfreund (1994) from two near-IR diffuse bands.

However, as noted recently by Berné *et al.* (2013), a new spectroscopic measurement performed by Kern *et al.* (2012) suggests that the 7.51 μm band might be due to C$_{60}^-$ rather than C$_{60}^+$. Thus the above discussion is only tentative.

6. Conclusions

C$_{60}$ and higher fullerenes have been detected in circumstellar and geological environments. This strengthens the idea that a variety of carbon-based compounds, including fullerenes, can be efficiently produced by stars, be ejected into the ISM, reach the early Solar System, and be partially brought to Earth by comets and asteroids (Kwok, 2011). The study of C$_{60}$ and its derivatives in circumstellar envelopes can help to understand the chemical evolution of galaxies. However, it is unclear how circumstellar

C$_{60}$ is formed and excited. In this paper, we investigate the relations between the emission properties of C$_{60}$-detected sources, as well as between the observations and existing experimental results. Through a comparison of wavelengths and fluxes of C$_{60}$ bands, we conclude that the UV-excitation of C$_{60}$ in cluster state may account for the observations, although other excitation schemes, such as the release of chemical energy, remain possible. We would like to emphasize that the Einstein A-values and flux measurements are too uncertain to allow definite conclusions. We also propose that C$_{60}$ is one of the products of the dehydrogenation of MAONs through a scenario presented by Micelotta *et al.* (2012). The fullerene formation thus reflects a transformation from sp^3 to sp^2 hybridization in MAONs. We have tentatively detected hydrogenated C$_{60}$ in IRAS 01005+7910 and C$_{60}^+$ in Tc 1. The presence of C$_{60}$ derivatives has the implications that fullerenes have been UV photochemically processed during the post-AGB evolution and the C$_{70}$/C$_{60}$ ratio can be significantly modified. A combination of further experiments and observations are required to obtain complete picture of fullerene formation and processes in circumstellar environments.

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