Hydrogenated Fullerenes (Fulleranes) in Space

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Abstract
Since the first laboratory synthesis of C\textsubscript{60} in 1985, fullerene-related species have been proposed to interpret various astronomical features. After more than 25 years’ efforts, several circumstellar and interstellar features have been convincingly assigned to C\textsubscript{60}, C\textsubscript{70}, and C\textsubscript{+60}. These successes resulted from the recent advancements in observational, experimental, as well as computational techniques, and re-stimulated interest in searching for fullerene derivatives in space. As one of the most important fullerene derivatives, hydrogenated fullerene (fullerane) is likely to exist in circumstellar and interstellar conditions. This review gives an overview of the chemical properties and spectral signals of fulleranes focusing on those relevant to astronomy. We summarize previous proposals of fulleranes as the carrier of astronomical features at UV, optical, infrared, and radio wavelengths, and discuss the arguments favoring or disfavoring the presence of fulleranes in astronomical environments. Although no unambiguous detection of fulleranes in space has yet been reported, there are plausible evidences for supporting the formation of certain fullerane isomers.

Keywords
Circumstellar matter; ISM: molecules; Infrared: spectral observation; molecular processes

1 Introduction
The unidentified infrared emission (UIE) bands have been detected in circumstellar envelopes and the interstellar medium (ISM). Although most of the UIE bands are attributed to vibrational modes of sp\textsuperscript{2} and sp\textsuperscript{3} C–H and C–C bonds, their exact carrier has long been an enigma. Since their synthesis in laboratory\textsuperscript{[1985]}, fulleranes have been believed to exist in significant amounts in space. The carbon cage structure is highly stable against intense radiation, making fulleranes and their derivatives an attractive material candidate being partly responsible for the UIE phenomenon. As the dominant source of cosmic dust, stars leaving the asymptotic giant branch (AGB) stand as the key source of searching for astronomical fullerenes. Early efforts on searching for circumstellar fullerenes, however, were unsuccessful (see the references in\textsuperscript{Zhang & Kwok 2013}).

A breakthrough in the last ten years is that four UIE bands at 7.0, 8.5, 17.4, and 18.9 $\mu$m were properly assigned to C\textsubscript{60} (Cami et al.\textsuperscript{2010}; Sellgren et al.\textsuperscript{2010}; García-Hernández et al.\textsuperscript{2010}), the most stable member of fullerene family. These C\textsubscript{60} infrared bands were subsequently detected in various astronomical environments (see\textsuperscript{Zhang & Kwok 2013} for a review). Weaker C\textsubscript{70} bands were also detected in a few planetary nebulae (PNe) exhibiting C\textsubscript{60} features (Cami et al.\textsuperscript{2010}; García-Hernández et al.\textsuperscript{2011a}). The discovery of C\textsubscript{60} in a proto-PN suggests that this big molecule can be rapidly formed within a short timescale of $\sim$ 10\textsuperscript{3} yr (Zhang & Kwok\textsuperscript{2011}). If fullerenes are able to survive the formation of solar system, they could be detected in the pre-solar grains. However, searches for fullerenes in meteorites have yielded conflicting results (e.g. Becker et al.\textsuperscript{1995}; Heymann\textsuperscript{1997}). As fullerene molecules can be created under the laser conditions of...
studying fullerenes, one should be cautious of false positive signals (Hammond & Zare 2008). Another important finding in recent years is that the hypothesis of \( \text{C}_{60} \) as the carrier of a few infrared diffuse interstellar bands (DIBs), originally proposed by Foing & Ehrenfreund (1994), was validated by the experimental spectra (Campbell et al. 2013, 2016). Therefore, it is becoming clear that fullerenes can survive in harsh conditions and be widespread in space.

Although \( \text{C}_{60} \), \( \text{C}_{70} \), and \( \text{C}_{60}^{+} \) are the only fullerene members that have been convincingly detected so far in astronomical environments, the presence of other fullerene molecules have been extensively investigated. For instance, the possibility of buckyonions (multi-shell fullerenes) as the carrier of the interstellar extinction bump at 217.5 nm have been discussed by Iglesias-Groth (2004) and Li et al. (2008). The small fullerene \( \text{C}_{24} \) was proposed to be responsible for the UIB band at 11.2 \( \mu \)m (Bernstein et al. 2017). Through a comparison between the theoretical and observational spectra, Candian et al. (2019) argued that \( \text{C}_{44} \), \( \text{C}_{50} \), and \( \text{C}_{56} \) might be present in several \( \text{C}_{60} \) sources. Selected elements can be trapped within the carbon cage of fullerenes, providing a potential interpretation for the anomalous element enrichment in stardust (Dunk et al. 2013). These authors found that the encapsulation of a metal within \( \text{C}_{60} \) would cause some vibrational modes to become IR-active and produce features coincident with the UIB bands.

With a high electron affinities, fullerenes are chemically active. García-Hernández et al. (2013) show that fullerenes can react with small polycyclic aromatic hydrocarbons (PAHs), such as anthracene, to form Diels-Alder cycloaddition products, which exhibits spectral features similar to the UIB bands. The efficient formation of \( \text{C}_{60} \)/PAH adducts was confirmed by the gas phase experiments (Dunk et al. 2013). The high stability and rich diversity of fullerene molecules make them ideal carrier candidates of DIBs. Omont (2016) made a thorough discussion of the likely contributions to DIBs from various fullerene derivatives including metallofullerenes, heterofullerenes, hydrogenated fullerenes (fulleranes), fullerene-PAH compounds, and \( \text{H}_{2} \odot \text{C}_{60} \).

It is essentially unclear what forms of fullerene are abundant in various astronomical environments. As \( \text{C}_{60} \) has a high reaction rate with atomic hydrogen, the most abundant element in the universe, along with the facts that \( \text{C}_{60} \)-containing PNes are not H-deficient (García-Hernández et al. 2010), it is logical to put its hydrogenated/protonated analogues (i.e. fulleranes) on the top of the list. If existing, fulleranes may play a vital role on interstellar and circumstellar chemistry. The purpose of this paper is to review past efforts made to investigate fulleranes in space.

### 2 Chemistry of fulleranes

When mixing with hydrogen atoms in solvents, \( \text{C}_{60} \) can be quickly hydrogenated into \( \text{C}_{60}\text{H}_{36} \) (see e.g. Cataldo & Iglesias-Groth 2009, Iglesias-Groth et al. 2012). Various chemical methods have been developed to synthesize \( \text{C}_{60}\text{H}_{m} \) (see Briggs & Miller 2010, for a review). \( \text{C}_{60}\text{H}_{18} \) is the only species that can be produced by various methods at a high yield. Higher fulleranes (\( \text{C}_{60}\text{H}_{m} \) with \( m > 36 \)) are chemically unstable, and can be synthesized only under very severe conditions. Further hydrogenation can completely destruct \( \text{C}_{60} \) cages due to severe angle and torsional strains, and the fragments of fulleranes can result in the formation of large PAHs. Gas-phase experiments suggested that \( \text{C}_{60}^{+} \) and \( \text{C}_{60}^{2+} \) can react with hydrogen atoms to form \( \text{C}_{60}\text{H}_{m}^{+} \) and \( \text{C}_{60}\text{H}_{m}^{2+} \) with \( m = 1–3 \) and these fullerene ions are unreactive with molecular hydrogen (Petrie et al. 1992). Larger fullerene ions, like \( \text{C}_{70}^{2+} \), are less reactive than \( \text{C}_{60}^{2+} \) (Petrie & Bohme 2000).

It is established that the fullerene obeying the isolated-pentagon rule (IPR) are more stable than adjacent-pentagon fullerenes. \( \text{C}_{60} \) stands out within the fullerene family as the smallest IPR fullerene. Petrie & Bohme (1994) found that hydrogenation can greatly reduce the chemical instability induced by adjacent-pentagon structures. Higher energy is required to dissociate an adjacent-pentagon C-H bond than an isolated-pentagon C-H bond. Therefore, hydrogen atoms tend to possess or migrate to adjacent-pentagon sites, and non-IPR fulleranes are more prone to be hydrogenated, favoring the production of smaller fulleranes with non-IPR structures in interstellar and circumstellar environments, such as \( \text{C}_{20}\text{H}_{30} \).

The heating treatment of \( \text{C}_{60}\text{H}_{36} \) can cause dehydrogenation and easily release \( \text{H}_{2} \) molecules (Cataldo & Iglesias-Groth 2009, Iglesias-Groth et al. 2012). In laboratory conditions, hydrogenation and dehydrogenation of \( \text{C}_{60} \) and \( \text{C}_{60}\text{H}_{36} \) are efficient, and the \( \text{C}_{60} \) cage is highly resistant to these chemical reactions. This leads to a hypothesis that fullerenes or fullerene-like materials may provide a surface to catalyze the formation of molecular hydrogen in astronomical environments (see Cataldo & Iglesias-Groth 2010, for a review). Because direct gas-phase reactions are inefficient in the ISM, it has been recognized that catalytic reactions on surfaces of dust grains should be responsible for the abundant interstellar \( \text{H}_{2} \). Experiments show that colliding with dust grains, a hydrogen atom can be readily bound to the grain surfaces through physisorption. However, as the physisorption bond is very weak, chemisorption dominates the regions with a dust temperature higher than 20K. Theoretical calculations suggest that
the addition of pentagonal rings in graphene sheets (fullerene-like structure) can substantially reduce the activation barrier against the chemisorption of a hydrogen atom (Ivanovskaya et al. 2010). Once a hydrogen atom is chemisorbed, another hydrogen can be attached to the adjacent carbon atom without barrier, and then a third hydrogen hit atop the second one to form H2 through the Eley-Rideal mechanism. Therefore, fullerenes might play an important role on the H2 formation in warm gas.

Through an investigation of the ion/molecule chemistry of fullerene derivatives in astronomical environments, Petrie & Bohme (2000) showed that C60 can form C60+ through charge transfer electron detachment from He2+ and cosmic-ray impact. C60+ ions could be efficiently hydrogenated into C60H2+ in interstellar conditions. Hydrogenation tends to retard the addition reactions of fullerene ions with polar and small unsaturated molecules. Therefore, in H-rich environments, the association of fullerene ions and interstellar molecules might be insignificant.

It is difficult to estimate the abundance ratio of C60 and its hydrides for the reasons outlined by Omont (2016). C60H and C60H+ can be efficiently dissociated by absorbing a hard UV photon. The models of dark clouds suggest that C60 can be efficiently protonated so that the fractional abundance of C60H+ is relatively larger than C60+ (Millar 1992). However, based on the formation and dissociation rates, Omont (2016) estimated that the abundance ratios of C60H/C60 and C60H+/C60 in the ISM should be roughly 0.1–0.2 with a large uncertainty. Given their stronger H bonding, the fullerenes even with number of H atoms and higher hydrogenated fullerenes are more resistant to photolysis. The photo-dissociation rates of these fullerenes, however, are largely unknown, precluding the accurate determination of the fullerene abundance. To establish the environments in which fullerenes may be present, it is instructive to compare the interstellar and circumstellar conditions with the dehydrogenation-model predictions of large PAHs (Montillaud et al. 2013). Castellanos et al. (2014) found that C60 emission in reflection nebulae arises from the regions where the dust temperature ranges from 20–40K and large PAHs (like C54H18 and C66H20) are fully dehydrogenated. If C60Hm has a similar hydrogenation rate as large PAHs, fullerenes should not be abundantly present in these regions, but should instead survive in the dense and UV-shielded environments (such as those of PPNe) where PAHs are normal or super-hydrogenated (see Figure 13 of Castellanos et al. 2014).

3 Fullerenes as the carriers of interstellar and circumstellar spectral features

3.1 Fullerenes versus UIE bands

Based on a force-field model of fully hydrogenated C60, Webster (1991) suggested that slightly and heavily hydrogenated fullerenes may be responsible for the 3.3µm and 3.4µm UIE bands, respectively. It is well established that the two features arise from the sp2 aromatic and sp3 aliphatic C-H stretching motions (see a review by Kwok 2016). One may envision that with increasing hydrogen coverage on fullerene cages, the sp2 carbons should be gradually converted into sp3 carbons, and thus lead to a shift of the C-H stretching bond from 3.3µm to 3.4µm. The calculated spectrum of C60H60 also exhibits a number of peaks between 6–10µm associated with the rocking of C-H units, which might account for the 6–9µm plateau and the 7.7µm UIE band (Webster 1993). A recent theoretical study showed that the inclusion of non-planar structural defects in aromatic core molecular structures may account for the UIE bands, especially those lying in the 6–9µm range (Galué & Leines 2017). Fullerene fragments have a similar molecular structure, and thus are a promising UIE carrier.

An experimental study shows that when exposed to atomic hydrogen, C60 can produce a number of mid-infrared features resembling the UIE bands (Stoldt et al. 2001). Specifically, a band at 7.63µm grows with increasing hydrogen exposure, but its wavelength does not shift, which is compatible with the conjecture of fullerenes as the carrier of the 7.7µm feature (Webster 1993). Moreover, Cataldo (2003) found that the absorption spectrum of C60H36 can match several UIE bands detected in proto-PNe. The experimental spectra also reveal a C-H stretching band peaking at 3.33–3.45µm that is reasonably consistent with astronomical observations of the 3.4µm feature (Stoldt et al. 2001). However, the position of the C-H stretching band does not shift to 3.3µm even for slightly hydrogenated C60, in contrast to the proposal of Webster (1991). Therefore, the 3.3µm aromatic feature is unlikely to be carried by fullerenes. Strictly speaking, fullerenes cannot be regarded as pure aromatic molecules. The pentagon related curvature induces a slight admixture of sp3 character.

Webster (1995) proposed that C60Hm might be responsible for the so-called 21µm feature, a rare UIE band only observed in a few carbon-rich proto-PNe. The 21µm feature was first discovered with IRAS in four proto-PNe (Kwok et al. 1989), and now has been detected in 27 objects (Mishra et al. 2016). The ISO
observations showed that this feature actually peaks at 20.1 μm, and its profile is remarkably consistent among different sources (Volk et al. 1999). However, recent Spitzer/IRS spectra suggested a central wavelength of 20.47 ± 0.10 μm (Sloan et al. 2011). Intriguingly, a strong feature peaking at 21 μm was recently revealed in two supernova remnants although its observational properties differ from those of the 21 μm feature in proto-PNe (Rho et al. 2018). It is noticeable that the experimental and computational spectra of fulleranes exhibit prominent features in the 18–22 μm spectral range (Iglesias-Groth et al. 2012; Zhang et al. 2017). Theoretical calculations show that with increasing hydrogen coverage, the central wavelength monotonically shifts from 18 μm to 22 μm (Webster 1995; Zhang et al. 2021). A weighted combination of the theoretical spectra of various fullerene isomers can, in principle, reproduce the observed 21 μm feature. If the 21 μm feature could be attributed to C_60H_m, Zhang et al. (2020) found that the degree of hydrogenation must be intermediate (m =10–20). The main issue of the fullerene hypothesis is to interpret the unvaried shape of the 21 μm feature. Probably, only stable fulleranes having ‘magic numbers’ of hydrogen atoms favored by symmetry considerations can survive in the short evolutionary timescale, as suggested by Webster (1995). The hypothesis of PAH molecules as the carrier of other UIE bands faces the same problem (Kwok & Zhang 2013), but even more seriously, since the other UIE bands, unlike the 21 μm feature, have been detected in more diverse astronomical environments.

3.2 Fulleranes versus extended red emission

Extended red emission (ERE) is a broad featureless emission band spanning the wavelength range from about 5000–9000 Å (see a review by Witt & Vlah 2004). Since the first discovery in Red Rectangle nebula (Cohen et al. 1975), ERE has been detected in a variety of extended objects, including reflection nebulae, PNe, H II regions, and the high-latitude diffuse ISM. It has a full-width-half-maximum of 600–1200 Å with a long emission tail. The peak wavelength varies from 6000–8500 Å in different regions. Although the carrier of ERE remains unidentified, a general consensus is that ERE arises from carbonaceous materials, including hydrogenated amorphous carbon, quenched carbonaceous composite, nanodiamonds, etc., through a photoluminescence process (see Lai et al. 2017, and references therein). The most recently proposed ERE carrier is graphene oxide nanoparticles (Sarre 2019). Based on a measurement of ERE in the diffuse ISM, Gordon et al. (1998) estimated a strict lower limit of the ERE photon conversion efficiency of 10% ± 3%.

Webster (1993a) noted the ERE spectrum of reflection nebulae resembles the laboratory spectrum of C_60 photoluminescence, and thus suggested that C_60, C_60H_m, as well as their ions might be the carrier of ERE. However, this proposal was ruled out by Witt & Vlah (2004) because C_60 and C_60^+ were not discovered in space at that time and the quantum efficiency of C_60 is orders of magnitude lower than that required to produce ERE. Now the situation has changed with definite detection of C_60 and C_60^+ in circumstellar and interstellar environments. Perhaps it is possible that the photoluminescence efficiency could be increased through hydrogenating C_60 to certain C_60H_m isomers. It would be attractive to examine the photoluminescence spectra of fulleranes in laboratory, which are very scarce.

3.3 Fulleranes versus anomalous microwave emission

Anomalous microwave emission (AME) is a continuum emission excess above synchrotron, free-free, cosmic microwave background, and thermal dust in the frequency range of 10–60 GHz (Kogut et al. 1996; Leitch et al. 1997). It peaks at about 30 GHz and has been detected in H II regions, molecular and dust clouds, supernova remnants, external galaxies (see Dickinson et al. 2018 for a recent review), and recently in proto-planetary disks (Greaves et al. 2018), suggesting that AME holds vital clues for understanding the material cycle between ISM, stars, and planets. However, the exact mechanism responsible for AME is not yet known. A widely accepted hypothesis is that AME arises from electric dipole radiation from rapidly-rotating nanoparticles (Draine & Lazarian 1998), but the nature of these particles was not specified. PAHs can be ruled out as the AME carrier because PAHs presumably emit strong electric dipole radiation from rapidly-rotating nanoparticles (Draine & Lazarian 1998). However, the exact mechanism responsible for AME is not yet known.

The C–H bonds on the surface of fulleranes can induce a net dipole moment, and thus produce electric dipole radiation. Iglesias-Groth (2005) calculated the rotation spectra of a variety of fulleranes and found that the emission peaks in the 1–65 GHz range and shifts toward lower frequencies with increasing molecular size and increasing hydrogenation degree. Therefore, a mixture of fulleranes with appropriate size distribution and hydrogenation degree is able to reproduce the AME. Through a case study of a dark cloud, Iglesias-Groth (2006) found that to explain the AME observations the fulleranes should contain 60–80 carbon atoms and have a hydrogenation degree of C : H ≈ 3 : 1. The proto-planetary disks with AME detection also host hydrogenated nanodiamonds (Greaves et al. 2018). Fulleranes and nanodiamonds have a similar hybridization
structure, and might share a similar formation processes. To elucidate the origin of AME, it is important to investigate the correlation between the infrared bands and the AME strengths, which would be interesting projects for future James Webb Space Telescope (JWST) observations.

3.4 Fulleranes versus the 217.5 nm extinction bump

The extinction curve of the Galaxy is characterized by a conspicuous and ubiquitous bump centered at 217.5 nm. In recent years, there has been increasing interests in investigating the 217.5 nm extinction bump in high-redshift objects (e.g. Heintz et al. 2019). Although the bump was discovered more than 50 years ago (Stecher 1963), its nature is still not properly understood. A generally accepted view is that it stems from the π−π* transition of carbonaceous materials. Despite exhibiting strong UV absorption, C60 can be ruled out as the carrier of the 217.5 nm bump in that some sub-features produced by C60 are not seen in the extinction curve (Krätschmer et al. 1990). Webster (1993a, 1997) found that the spectra of C60H2 and C60H4 exhibit stronger UV absorption and weaker sub-features compared to that of C60, and thus proposed that some fullerane family might be responsible for the 217.5 nm bump. The experimental spectra of C60H36 and its deuterated analogous show that the UV absorption cross-sections of fulleranes are significantly higher than that of C60, and can match the 217.5 nm bump in wavelength, width, and shape (Cataldo & Iglesias-Groth 2009). It was shown that with dehydrogenation of fulleranes the absorption maximum will shift from 217.5 nm to longer wavelengths and the absorption coefficient will gradually decrease. Therefore, moderately hydrogenated C60, if present in the ISM, may substantially contribute to the 217.5 nm bump. The same mixture of fulleranes has been taken to interpret the AME (Iglesias-Groth 2006).

3.5 Fulleranes versus DIBs

DIBs refer to a class of absorption features detected in our Galaxy and other galaxies at optical and near infrared wavelengths (see Geballe 2016 for a recent review). Since the first detection by Heger (1922), the origin of DIBs has been a century old puzzle. A variety of species have been proposed as the carrier of DIBs, including fulleranes (Webster 1992a) and C60 (Foing & Ehrenfreund 1994). The successful assignment of a few DIBs to C60+ (Campbell et al. 2013, 2016) has rekindled the interests of investigating fullerene derivatives as the DIB carrier (Omont 2016). With a great physical stability and a high chemical activity, fulleranes and their analogues (see e.g. Iglesias-Groth 2007) could reproduce the observed pattern of DIBs. The number of hydrogen atoms may vary depending on different interstellar environments, and thus produce different DIBs. Although there is no complete coincidence between fullerane features and DIBs, the spectra of C60H2 and C60H4 exhibit a strong peak near 4350 Å, which is comparable to a broad extinction feature centered near 4300–4400 Å (Webster 1997). The main challenge in this area is the vast number of fullerane isomers with only a few having laboratory spectra. The DIB strengths are not correlated with those of the 217.5 nm bump (Xiang et al. 2011). If attributing both to fulleranes, the fulleranes producing DIBs and the 217.5 nm bump should be in different phase and/or have different hydrogenation degrees.

4 Searching for fulleranes in astronomical environments

So far, all attempts of searching for astronomical fulleranes have not yielded unambiguous results. Becker et al. (1992) and Becker, & Bunch (1997) reported a positive detection of fulleranes in a sample of the Allende meteorite, which however was questioned by Heymann (1997) who did not discover extractable C60H2 in Allende. It remains unclear why different research groups found different results. A possible explanation is that fulleranes are heterogeneously distributed throughout the Allende meteorite in a trace level. Webster (1992b) suggested that the C-H 3.4 μm feature could shift toward longer wavelengths due to the effect of the vacancy of the neighboring C-H bonds. As each C-H bond of fulleranes has three neighboring carbon atoms, there are four possible configurations, namely 0, 1, 2, and 3 neighboring carbon bonded with hydrogen. It follows that four peaks are expected to appear at the wavelength range from 3.4–3.6 μm, and their relative strengths can reflect the degree of hydrogenation. Indeed, these peaks can be seen in the experimental spectra of C60H18 and C60H36 with an integrated molar absorptivity comparable to those of C60 mid-infrared bands (Iglesias-Groth et al. 2012). Therefore, if these fulleranes have a similar abundance as C60, they should be detectable through the C-H stretching features.

Six C60-containing sources have ISO/SWS spectra. Using signal-to-noise ratios as weights, we stacked the 3–4 μm spectra of the six sources, as shown in Figure 1. A few weak features are visible in the 3.4–3.6 μm, although we cannot uniquely attribute them to C60Hm (Zhang & Kwok 2013) marginally detected.
four peaks at 3.40, 3.48, 3.51, and 3.58 μm in the spectrum of a C_{60} proto-PN. If the four peaks originate from C_{60}H_m, their relative intensities indicate a moderate hydrogenation with m = 20–40. This is consistent with the experimental results that C_{60}H_{36} are produced at high yield and can be further heated to form C_{60}H_{18} (see e.g. Cataldo & Iglesias-Groth 2009, Iglesias-Groth et al. 2012).

However, the C_{60}-containing PNe do not exhibit prominent C-H stretching bands at 3.4-3.6 μm, in contrast to the expectation that fulleranes should coexist with C_{60} in hydrogen-rich environments. Díaz-Luis et al. (2016) carried out a deep spectroscopic study of two Galactic PNe exhibiting strong C_{60} features, but failed to detect any feature in the 3.4-3.6 μm spectral range. Since hydrogenation of C_{60} has been proven to be reversible (Cataldo & Iglesias-Groth 2009, Iglesias-Groth et al. 2012), these observations suggest that the C-H aliphatic bonds can be quickly destroyed by shocks and/or UV radiation during the PN stage. Therefore, if existing, fulleranes in PNe presumably have a relatively low hydrogenation degree (see also Díaz-Luis et al. 2018), and thus are not able to produce intense bands at 3.4 μm.

Theoretical computations show that the C-H stretching mode is greatly suppressed in cations or slightly hydrogenated fulleranes (Pauzat et al. 1995, Zhang et al. 2017). In such cases, the feature around 3.4 μm is not an ideal proxy to search for fulleranes. Based on quantum chemistry methods and a thermal excitation model, Zhang et al. (2017) calculated the mid-infrared spectra of a number of C_{60}H_m isomers with m = 2–36. For each C_{60}H_m, with a given m value, the coadded spectra of five isomers are presented in Figure 2. It appears that two features approximately peaking at 8.5 μm and 15 μm grow with hydrogenation. The emission bands around 8.5 μm have been commonly discovered in astronomical objects, and cannot be uniquely attributed to fulleranes as they can be carried by other aromatic hydrocarbon materials. Arising from the coupling of carbon skeleton modes and C-H bending motion, the 15 μm feature might be able to trace the existence of fulleranes. However, a thorough search of this feature in C_{60}-containing objects did not yield any solid detection although two of them seem to marginally reveal a peak at 15 μm (Zhang et al. 2017). Figure 3 presents the stacked spectrum of all C_{60}-containing objects. Although an extremely faint peak can be seen at 15 μm, we cannot firmly conclude that it is a real feature, rather than noise. This seems to disfavor the coexistence of fulleranes (at least those with high H content) and fulleranes. However, one cannot completely rule out the possibility that fulleranes exist in condensed phase so that the 15 μm band is strongly suppressed. Indeed, the laboratory spectrum of C_{60}H_{18} does not reveal the band at 15 μm as strong as that at 8.5 μm (Iglesias-Groth et al. 2012).

Strikingly, a weak band at 15.8 μm was found to be associated with the 21 μm feature (Hrivnak et al. 2008, Zhang & Kwok 2011, Sloan et al. 2014), which is compatible with the hypothesis of fulleranes as the carrier of the two features; no 21 μm sources have been detected in C_{60} though. If the 21 μm feature is carried by moderately hydrogenated C_{60}, this might suggest that most of the C_{60} molecules have been hydrogenated in the favorable environments of proto-PNe.

With a high proton affinity, C_{60} is readily protonated into C_{60}H^+ in the PN stage. Palotás et al. (2019) presented the experimental infrared spectrum of C_{60}H^+, which exhibits strong bands in the spectral range of 6.4–8.7 μm, mainly corresponding to C-C stretching vibrations. The authors found a close correspondence between the experimental spectrum of C_{60}H^+ and the observed spectra of C_{60} PNe in the 6–9 μm range. The C-H stretching band at 3.4 μm is not seen in the experimental spectrum, which is consistent with the non-detection of this feature in C_{60} PNe.

There are other considerations favoring the existence of C_{60}H_m. C_{60} was detected in PNe through four mid-infrared bands, but their relative intensity ratios disagree with the model predictions of fluorescent or thermal emission (Bernard-Salas et al. 2012, Zhang & Kwok 2013, Brieva et al. 2016). With slight hydrogenation, the C_{60} cage is distorted and emits the four mid-infrared bands with different intrinsic strengths, thus providing a natural solution for the discrepancy between the observed and predicted intensity ratios (Zhang et al. 2017). Indeed, Duley & Williams...
Fig. 2 The theoretical spectra of $C_{60}H_m$ computed from a thermal excitation model, where the temperature is assumed to be 300 K. The $m$ values are marked on the up-left corner. A feature around $15 \mu m$ appears, as marked by the vertical dashed lines.

It was shown that in literature, fulleranes have been proposed to explain almost all the unidentified features in astronomical spectra, including the extinction bump at 217.5 nm, DIBs, ERE, UIE, and AME. Early studies of astronomical fulleranes did not gain adequate attention because they were largely based on some plausibility.
Fig. 3 The stacked Spitzer/IRS spectrum of all C_{60} sources in the 10–19 μm range

sible conjectures. Recently, the evident discoveries of fullerenes in various astronomical environments boost the interests of searching for fulleranes. It is instructive to review these early attempts that can provide important guideline and foster future research in this area. With remarkable advancements in observational, computational, and experimental techniques, we are now in a position to revisit the fullerane hypothesis. The identification of fulleranes in space has been severely impeded by the vast number of fullerane isomers and the absence of laboratory spectra. It is worthwhile to construct a database of theoretical and laboratory spectra of various fullerane isomers. Although previous search efforts are not conclusive, we cannot rule out the existence of fulleranes in astronomical environments. With high infrared sensitivity and high angular resolution, the upcoming JWST will provide a unique capability to investigate astronomical fulleranes.

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