Are fulleranes responsible for the 21 micron feature?

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ABSTRACT

Recent detections of C_{60}, C_{70}, and C_{60}^{+} in space induced extensive studies of fullerene derivatives in circumstellar environments. As the promising fullerene sources, protoplanetary nebulae (PPNe) show a number of unidentified bands in their infrared spectra, among which a small sample exhibits an enigmatic feature at $\sim 21 \, \mu m$. Hydrogenation of fullerenes can produce fulleranes emitting new infrared bands. In this paper, we investigate the possibility of fulleranes (C_{60}H_{m}) as the carrier of the 21 $\mu m$ feature in terms of theoretical vibrational spectra of fulleranes. The evidences favoring and disfavoring the fullerane hypothesis are presented. We made an initial guess for the hydrogen coverage of C_{60}H_{m} that may contribute to the 21 $\mu m$ feature.

Subject headings: infrared: stars — stars: AGB and post-AGB — stars: circumstellar matter

1. Introduction

The ‘21 $\mu m$’ feature refers to an infrared emission band peaking at 20.1 $\mu m$ that was first discovered by Kwok et al. (1989) in four circumstellar envelopes of evolved stars. This feature is rare compared to other circumstellar dust features. Thus far, it has been detected toward only 27 evolved stars, including 18 in the Galaxy and 9 in the Large and Small Magallenic Clouds (Mishra et al. 2016). The 21 $\mu m$ sources have some properties in common. Their optical-infrared spectra reveal two blackbody components, corresponding to radiation from the stellar photosphere and the dust shell. This is an evidence that stellar outflows have terminated and the envelope has been detached from the central star. Therefore, they
represent a short evolutionary stage between the asymptotic giant branch (AGB) and the planetary nebula (PN), usually denoted as protoplanetary nebula (PPN). All the 21 µm sources are carbon rich, exhibiting absorption features from C₂, C₃, and CN [Bakker et al. 1995] as well as the aromatic C-H bands at 3.3 and 11.3 µm [Hrivnak et al. 2008]. Moreover, a broad emission band around 30 µm always appears along with the 21 µm feature [Hrivnak et al. 2008]. The identification of the 30 µm feature is another unsolved problem (see Jiang et al. 2010 for a review). It is worth noting that the spectra of two supernova remnants show a strong dust feature exactly peaking at 21 µm [Rho et al. 2018]. Although its peak wavelength slightly differs from the 21 µm feature, it would be interesting to investigate whether their carriers belong to a similar molecular family.

Identification of the 21 µm feature is vital for understanding circumstellar chemistry and matter cycle in galaxies. Although a number of candidate materials have been proposed as its carrier (see Jiang et al. 2010 and the references therein), no consensus emerges. Some of them can be rejected. Zhang et al. (2009) found that S-, Si-, and Ti-containing compounds are unlikely responsible for the 21 µm feature as a cause of low abundances of these elements. The strength of the 21 µm feature suggests that its carrier is composed of rich elements. Fe oxides can be ruled out because they would emit too broad 21 µm feature or some subfeatures that were never detected (Zhang et al. 2009; Li et al. 2013). A carrier candidate that has not been adequately examined by these authors is hydrogenated fullerenes (fulleranes).

Since the discovery of C₆₀ [Kroto et al. 1985], fullerenes or their derivatives have been long conjectured to be ubiquitous throughout interstellar and circumstellar space. This was subsequently confirmed by the detection of C₆₀ and C₇₀ in PNe [Cami et al. 2010; García-Hernández et al. 2010] and the convincing assignment of a few diffuse interstellar bands as C₆₀⁺ [Campbell et al. 2015]. C₆₀ can be rapidly formed in PPN stage [Zhang & Kwok 2011]. García-Hernández et al. (2010) suggested that the environments of forming fullerenes could be hydrogen-rich. Fulleranes have high proton affinities. When mixed with atomic hydrogen, C₆₀ can be efficiently hydrogenated into fulleranes in laboratory [Cataldo & Iglesias-Groth 2009; Iglesias-Groth et al. 2012]. Given the high stability of fullerene structure as well as the high abundance of cosmic carbon and hydrogen, it is attractive to investigate the vibrational spectra of fulleranes and search for their existence in circumstellar envelopes.

Based on a simple force-field model, Webster (1995) found that fulleranes can radiate a broad band in the wavelength range from 19–23 µm, and raised the possibility of fulleranes as the carrier of the 21 µm feature. In laboratory environments, only specific fulleranes can be synthesized, making it hard to verify this hypothesis. Recently, more accurate calculations of vibrational spectra can be performed with the development of computational chemistry methods and computing facilities, allowing us to re-examine whether fulleranes can account
for the 21 $\mu$m feature. This motivates the current paper.

2. Computations

In order to test the proposal of C$_{60}$H$_m$ as the carrier of the 21$\mu$m feature, we calculated the vibrational spectra of selected C$_{60}$H$_m$ with even number of hydrogen atoms (see Zhang et al. [2017] for the details). It is computationally impossible to derive the spectra of all C$_{60}$H$_m$ because of the enormous isomer number. In laboratory conditions, C$_{60}$ can be readily hydrogenated into C$_{60}$H$_{36}$ and then form C$_{60}$H$_{18}$ through thermal annealing (e.g. Iglesias-Groth et al. [2012]). With increasing hydrogen coverage, the carbon hybridization goes from sp$^2$ to sp$^3$. This reduces the stability of the carbon cage. Moreover, fulleranes are exposed to ultraviolet (UV) photons which are abundantly present in PPNe, and thus undergo dehydrogenation. As a result, C$_{60}$H$_m$ with large $m$ number is unlikely exist in PPNe. A total of 55 isomers belonging to 11 C$_{60}$m species ($m = 2, 4, ..., 20, 36$) were selected for the computations. These isomers should represent those with lowest energy and thus being the most stable ones for a given $m$ number. For computational convenience, we did not consider fulleranes with odd number of hydrogen atoms and their ionized counterparts although they are possibly present in astronomical objects. A theoretical investigation of those species will be the subject of a follow-up paper.

We performed density functional theory (DFT) calculations using the B3LYP and BH&HLYP hybrid functionals in combination with polarization consistent basis set PC1. The vibrational frequencies were obtained using a double-scaling-facter scheme (Laury [2012]). This method can well reproduce the experimental spectrum of C$_{60}$ (Zhang et al. [2017]). Assuming that C$_{60}$H$_m$ infrared spectra are thermally excited in circumstellar environments, we derived the fluxes through scaling the computed intrinsic strengths by a Boltzmann factor with a temperature of 300 K. A Drude profile with a fixed width of 0.3$\mu$m was convolved to broaden the features, for the purpose of comparing the computed spectra with the observed ones. Finally, the spectrum of each C$_{60}$H$_m$ was obtained by co-adding its isomer spectra.

3. Results and discussion

The theoretical spectra of C$_{60}$H$_m$ in the 5–30$\mu$m range are presented in Figure 1. Although the vibrational modes are spread out over a wide wavelength range, strong emission features mainly concentrate between 5–10, 13–17, and 18–23$\mu$m. The 3–4$\mu$m wavelength range, where the C-H stretching modes can produce strong features, has been extensively
discussed in a previous paper (Zhang et al. 2017), and thus is not included in this figure. For comparison, this figure also shows the observational spectrum of a PPN IRAS 04296+3429, which was taken from the Spitzer archive (Zhang et al. 2010). As shown in Figure 1 a strong 21 \( \mu m \) emission band exists in the spectrum of IRAS 04296+3429, which is well confined in the wavelength range of 18–23 \( \mu m \). It is clear that a weighted combination of different C\(_{60}\)H\(_m\) spectra provides a potential to reproduce the 21 \( \mu m \) feature. The features grouping in the wavelength of 5–10 \( \mu m \) are also detected in the observational spectrum, providing a further support for C\(_{60}\)H\(_m\) as the carrier of the 21 \( \mu m \) feature. However, no strong feature in the 13–17 \( \mu m \) range is detected in the observational spectrum, but which instead exhibits features in 10–13 \( \mu m \) range. The 10–13 \( \mu m \) features are not seen in the theoretical spectra of C\(_{60}\)H\(_m\), and usually are attributed to silicon carbides in the literature.

Any single C\(_{60}\)H\(_m\) spectrum is unable to reproduce the observed 21 \( \mu m \) feature. Fulleranes, if being responsible for the 21 \( \mu m \) feature in PPNe, should be a mixture of various isomers with different hydrogenation degrees. It is natural to expect that their spectral pattern may vary from source to source. However, astronomical observations have shown that the 21 \( \mu m \) features have a remarkably consistent profile (Volk et al. 1999). The same problem exists for the mixtures of polycyclic aromatic hydrocarbon molecules as the carrier of unidentified infrared emission bands, and has been extensively discussed (see Kwok & Zhang 2013, for the details). In order to explain the observations, we conjecture that only certain fullerane family can be formed and survive in the exclusive PPN environment. If the UV radiation is absent, hydrogen is mainly in the molecular state, and thus hydrogenation of C\(_{60}\) is unlikely to occur; if it is too strong, it may substantially dehydrogenate fulleranes, or even break the carbon cage. The rigorous environments required for the existence of fulleranes are compatible with the rareness of the 21 \( \mu m \) feature in astronomical objects.

Figure 1 indicates that C\(_{60}\)H\(_{36}\) can be ruled out as the carrier the 21 \( \mu m \) feature due to the lack of features lying between the 18–23 \( \mu m \) wavelength range. C\(_{60}\)H\(_m\) with \( m = 2–8 \) is unlikely responsible for the 21 \( \mu m \) feature because their strong features have peak wavelengths shorter than 20 \( \mu m \). Moreover, C\(_{60}\)H\(_2\) can produce a strong feature around 27 \( \mu m \), which has never been detected. Figure 2 presents the contributions from each C\(_{60}\)H\(_m\) isomer to the total intrinsic strength of the features lying in the 18–23\( \mu m \) range. Except C\(_{60}\)H\(_2\) and C\(_{60}\)H\(_{36}\), the strengths increase with increasing \( m \) values, suggesting that moderately hydrogenated C\(_{60}\) among fulleranes produce the strongest vibrational bands in the wavelength range encompassing the 21 \( \mu m \) feature.

In Figure 3 we examine the intensity-weighted wavelengths (\( \lambda_{21} \)) of C\(_{60}\)H\(_m\) as a function
of $m$, which is defined as

$$\lambda_{21} = \frac{\sum_i \lambda_i F_i}{\sum_i F_i}$$

(1)

for $18 \mu m \leq \lambda_i \leq 23 \mu m$, where $F_i$ is the intrinsic strength of the $i^{th}$ mode at the wavelength of $\lambda_i$. An inspection of Figure 3 reveals that there is an approximately linear trend of longer intensity-weighted wavelengths with increasing hydrogenation degrees. This is in agreement with the predictions by the force-field model of [Webster (1995)](Webster_1995). Comparing with the observed peak wavelength ($20.1 \mu m$), we infer that moderately hydrogenated fulleranes with $10 < m < 20$ are the promising carrier for the $21 \mu m$ feature.

While the existence of fulleranes in astronomical environments seems plausible, there is as yet no unambiguous detection. [Díaz-Luis et al. (2016)](Diaz-Luis_2016) failed to detect the C-H stretching bands at 3.4–3.6 $\mu m$ in two PNe exhibiting strong C$_{60}$ emission, suggesting that fulleranes might have been destroyed by strong UV radiation or mostly ionized. Based on a comparison between the laboratory spectrum of gaseous C$_{60}$H$^+$ and the observations, [Palotás et al. (2019)](Palotas_2019) speculated that C$_{60}$H$^+$ might contribute to the spectra of two C$_{60}$-containing PNe. Presumably, exposed on very strong UV radiation, moderately and heavily hydrogenated fulleranes cannot survive in PNe. This is compatible with the non-detection of the $21 \mu m$ feature in PNe. [Zhang, & Kwok (2013)](Zhang_Kwok_2013) reported a tentative detection of fulleranes in the C$_{60}$ source IRAS 01005+7910, which is a PPN about to enter the PN stage. IRAS 01005+7910 is not assigned as a $21 \mu m$ source in the previous literature. However, a closer view of its infrared spectrum clearly reveals a faint feature exactly peaking at 20.1 $\mu m$ (Figure 4). This feature is much weaker than the C$_{60}$ bands, and has not been noted previously. If attributing it to fulleranes, we can hypothesize that fulleranes in this PPN are undergoing dehydrogenation, resulting in a transition from moderately hydrogenated C$_{60}$ to slightly and none hydrogenated C$_{60}$. The enrichment of slightly hydrogenated C$_{60}$ may partly explain the 15–20 $\mu m$ plateau emission in the spectrum of IRAS 01005+7910.

A criticism of the fullerane hypothesis was advanced by [Posch et al. (2004)](Posch_2004), who pointed out that the actual wavelength of the C$_{60}$ feature is not coincident with that of the emission band in the meteoritic nanodiamonds shown by [Hill et al. (1998)](Hill_1998). The argument stems from the fact that nanodiamonds and fulleranes have a similar hybridization structure. However, it is not always appropriate to expect that nanodiamonds and fulleranes emit bands at the same wavelength positions. The fullerane hypothesis refers to a combination of numerous C$_{60}$H$_m$ isomers with different $m$ values, making it sufficiently flexible to match the observational spectrum.

A significant criteria for band identification to examine whether associated subfeatures
from the carrier candidate are visible in observed spectra. The C-H stretching mode around 3.4 μm has been detected in almost all the 21 μm sources. However, the theoretical spectra of fulleranes imply that there is no correlation between the intensities of the 3.4 μm and the 21 μm features, as shown in Figure 5. The 3.4 μm/21 μm intensity ratios largely vary among different isomers, and strong 21 μm sources might exhibit weak features at 3–4 μm. This is conceivable since the 21 μm feature dominantly arise from C-C deformation vibrations. Therefore, the feature around 3.4 μm is not an ideal proxy to test the fullerane hypothesis.

The theoretical spectra of fulleranes reveal that the 5–10 μm feature has an intensity positively correlating with that of the 18–23 μm feature (Figure 6). This makes the fullerane hypothesis plausible since 21 μm sources exhibit prominent 5–10 μm feature as well. However, the 5–10 μm feature has been commonly detected in various circumstellar envelopes, and thus it cannot been entirely attributed to fulleranes.

A critical issue of the fullerane hypothesis is that the 13–17 μm feature arising from fulleranes is hardly visible in the observational spectra. As shown in Figure 7, the 13–17 μm feature should have a comparable intensity with the 21 μm one, which is in contrast to the observations. Nevertheless, it is notable that the band strengths reproduced by the DFT calculations are much less accurate than the wavelengths. The laboratory spectrum of C_{60}H_{18} (Iglesias-Groth et al. 2012, see their Figure 3) shows that the 13–17 μm feature is much weaker than the features lying in the 10 μm and 18–13 μm range. Moreover, an appropriate excitation model needs to be employed to accurately predict the observed intensities. As a result, the non-detection of the 13–17 μm feature is insufficient to invalidate the fullerane hypothesis. Although no strong band has been detected in the 13–17 μm range, a weak feature at 15.8 μm appears in the spectra of all the 21 μm sources (Hrivnak et al., 2008). Zhang & Kwok (2011) found that there is a loose correlation between the intensity of the 15.8 μm and 21 μm features (Figure 7), suggesting that the two features may arise from the same material. This gives a seemingly plausible support for the fullerane hypothesis.

The theoretical spectra of fulleranes do not exhibit strong bands around 30 μm. Therefore, the 30 μm feature detected in AGB stars, PPNe, and PNe is unlikely due to fulleranes. While the 21 μm feature, without exception, is accompanied by the 30 μm feature, the number of the 30 μm sources is much larger, and the strengths of the two features are not correlated with each other. A common property of the two features is that both are detected in C-rich environments. Strikingly, the 30 μm feature was also viewed in the spectra of the PPNe and PNe detected in C_{60} (Zhang, & Kwok, 2013). It is tempting to conjecture that the carrier of the 30 μm feature can be synthesized during the AGB stage, and then when exposed on UV radiation at PN and PPN stages it is fragmented and partly converted into fullerenes and fulleranes through a top-down scenario.
4. Conclusions

We investigated the theoretical spectra of C$_{60}$H$_m$ with the aim of examining whether fulleranes are responsible for the 21 $\mu$m feature in PPNe. Based on a comparison of wavelengths and intensities, we infer that moderately hydrogenated C$_{60}$ are a promising carrier material producing this feature. A mixture of specific C$_{60}$H$_m$ isomers is required to fit the observed profile of the 21 $\mu$m feature. The survive of fullerane is very sensitive to the UV radiative field, and thus can give a natural explanation for the emergence of the 21 $\mu$m feature on very short timescales. The main issue is that the theoretical spectra of fullerane pose strong features in the 13–17 $\mu$m range which are absent in 21 $\mu$m sources. However, given the limits of computation and model complexity, this is no enough to completely rule out the fullerane hypothesis. The analysis and results proposed here can provide a guideline for future experimental efforts on the identification of the 21 $\mu$m feature.

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Fig. 1.— The Spitzer/IRS spectrum of the PPN IRAS 04296+3429 (upper panel) and the theoretical spectra of $\text{C}_{60}\text{H}_m$ (lower panel). Note that the continuum has not been subtracted for the observational spectrum. The vertical lines mark the wavelength range of the observed 21 $\mu$m band.
Fig. 2.— Intrinsic strengths of the C\textsubscript{60}H\textsubscript{m} features lying in the wavelength range of 18–23 \(\mu\)m versus the \(m\) values. The filled circles, squares, triangles represent the slightly (\(m = 2–10\)), moderately (\(m = 12–20\)), and heavily (\(m = 36\)) hydrogenated C\textsubscript{60}, respectively.
Fig. 3.— The intensity-weighted wavelengths of the features lying in the wavelength range of 18–23 µm versus the $m$ values of $C_{60}H_m$. Symbols are the same as those in Figure 2. The horizontal line denotes the wavelength position of the 21 µm feature.
Fig. 4.— The Spitzer/IRS spectrum of the PPN IRAS 01005+7910. The vertical solid and dashed lines mark the positions of the 21 \(\mu\)m feature and the four C\(_{60}\) bands, respectively. The lower-right panel shows the continuum-subtracted spectrum.
Fig. 5.— Intrinsic strengths of the C$_{60}$H$_m$ features lying in the wavelength range of 3–4 $\mu$m versus those of 18–23 $\mu$m. Symbols are the same as those in Figure 2.
Fig. 6.— Intrinsic strengths of the C\textsubscript{60}H\textsubscript{m} features lying in the wavelength range of 5–10 µm versus those of 18–23 µm. Symbols are the same as those in Figure 2.
Fig. 7.— Intrinsic strengths of the C₆₀H₆ features lying in the wavelength range of 13–17 µm versus those of 18–23 µm. Symbols are the same as those in Figure 2. The insert shows the correlation between the strengths of the 15.8 µm the 21 µm features, as found by Zhang et al. (2010).