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Are Fullerenes Responsible for the 21 Micron Feature?[†]

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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) shows a number of unidentified bands in their infrared spectra, among which a small sample exhibits an enigmatic feature at $\sim 21 \mu\text{m}$. Hydrogenation converts fullerenes into fullerenes, which breaks the symmetry of fullerene molecules and produces new infrared bands. In this work, we investigate the possibility of fullerenes ($C_{60}H_m$) as the carrier of the $21 \mu\text{m}$ feature in terms of theoretical vibrational spectra of fullerenes. The evidences favoring and disfavoring the fullerene hypothesis are presented. We made an initial guess for the hydrogen coverage of $C_{60}H_m$ that may contribute to the $21 \mu\text{m}$ feature.

Key words: Fullerenes, Infrared, Asymptotic giant branch and post-asymptotic giant branch, Circumstellar matter, Stars

I. INTRODUCTION

The “ $21 \mu\text{m}$ ” feature refers to an infrared emission band peaking at $20.1 \mu\text{m}$, which was first discovered by Kwok *et al.* [1] in four circumstellar envelopes of evolved stars based on a measurement of the *Spitzer*/IRS spectra. Sloan *et al.* [2] derived a longer central wavelength of $(20.47 \pm 0.10) \mu\text{m}$. 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 Magellanic Clouds [3]. The $21 \mu\text{m}$ 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), and usually are denoted as protoplanetary nebula (PPN). All the $21 \mu\text{m}$ sources are carbon rich, exhibiting absorption features from C_2 , C_3 , and CN [4] as well as the aromatic C–H bands at 3.3 and $11.3 \mu\text{m}$ [5]. Moreover, a broad emission band around $30 \mu\text{m}$ always appears along with the $21 \mu\text{m}$ feature [5]. The identification of the $30 \mu\text{m}$ feature is another unsolved problem [6]. It is worth noting that the spectra of two supernova remnants show a strong dust feature exactly peaking at $21 \mu\text{m}$ [7]. Although its peak

wavelength slightly differs from the $21 \mu\text{m}$ feature, it would be interesting to investigate whether their carriers belong to a similar molecular family.

Identification of the $21 \mu\text{m}$ feature is vital for understanding circumstellar chemistry and matter cycle in galaxies. Although a number of candidate materials have been proposed as its carrier [6], no consensus emerges. Some of them can be rejected. Zhang *et al.* [8] found that S-, Si-, and Ti-containing compounds are unlikely responsible for the $21 \mu\text{m}$ feature as a cause of low abundances of these elements. The strength of the $21 \mu\text{m}$ feature suggests that its carrier is composed of rich elements. Fe oxides can be ruled out because they would emit too broad $21 \mu\text{m}$ feature or some subfeatures that were never detected [8, 9]. A carrier candidate that has not been adequately examined by these authors is hydrogenated fullerene (fullerane).

Since the discovery of C_{60} [10], fullerenes or their derivatives have been long conjectured to be ubiquitous throughout interstellar and circumstellar space. This was subsequently confirmed by the detection of C_{60} and C_{70} in PNe [11, 12], and the convincing assignment of a few diffuse interstellar bands as C_{60}^+ [13]. C_{60} can be rapidly formed in PPN stage [14]. García-Hernández *et al.* [12] suggested that the environments of forming fullerenes could be hydrogen-rich. Fullerenes have high proton affinities. When mixed with atomic hydrogen, C_{60} can be efficiently hydrogenated into fullerenes in laboratory [15, 16]. 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 fullerenes and search for their existence in circumstellar envelopes.

Based on a simple force-field model, Webster [17] found that fullerenes can radiate a broad band in the

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wavelength range of 19–23 μm , and raised the possibility of fullerenes as the carrier of the 21 μm feature. In laboratory environments, only specific fullerenes 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 fullerenes can account for the 21 μm feature.

II. COMPUTATIONS

In order to test the proposal of C_{60}H_m as the carrier of the 21 μm feature, we calculated the vibrational spectra of selected C_{60}H_m with even numbers of hydrogen atoms [18]. It is computationally impossible to derive the spectra of all C_{60}H_m because of the enormous isomer numbers. In laboratory conditions, C_{60} can be readily hydrogenated into $\text{C}_{60}\text{H}_{36}$ and then form $\text{C}_{60}\text{H}_{18}$ through thermal annealing [16]. With increasing hydrogen coverage, the carbon hybridization goes from sp^2 to sp^3 . This reduces the stability of the carbon cage. Moreover, fullerenes 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 to exist in PPNe. A total of 55 isomers belonging to 11 kinds of C_{60}H_m species ($m=2, 4, 6, 8, 10, 12, 14, 16, 18, 20,$ and 36) were selected for the computations. These isomers should represent those with lowest energy and thus be the most stable ones for a given m number. For computational convenience, we did not consider fullerenes 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 study.

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-factor scheme [19]. This method can well reproduce the experimental spectrum of C_{60} [18]. Assuming that C_{60}H_m infrared spectra thermally were excited in circumstellar environments, we derived the fluxes through scaling the computed intrinsic strengths by a Boltzmann factor at 300 K. A Drude profile with a fixed width of 0.3 μm 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.

III. RESULTS AND DISCUSSION

The theoretical spectra of C_{60}H_m in the 5–30 μm range are presented in FIG. 1. Although the vibrational modes are spread out over a wide wavelength

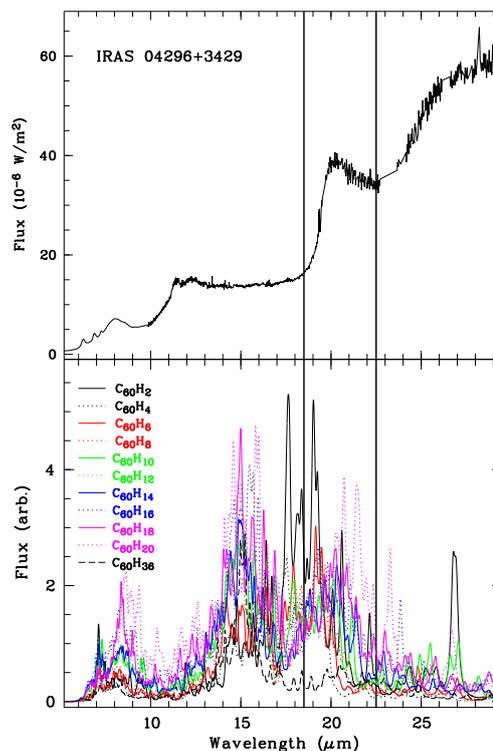


FIG. 1 The *Spitzer*/IRS spectrum of the PPN IRAS 04296+3429 (upper panel) and the theoretical spectra of C_{60}H_m (lower panel). Note that the continuum has not been subtracted for the observational spectrum. The vertical lines mark the wavelength range of the observed 21 μm band.

range, strong emission features mainly concentrate between 5–10, 13–17, and 18–23 μm . The 3–4 μm wavelength range, where the C–H stretching modes can produce strong features, has been extensively discussed in a previous paper [18], 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 [20]. As shown in FIG. 1, a strong 21 μm emission band exists in the spectrum of IRAS 04296+3429, which is well confined in the wavelength range of 18–23 μm . It is clear that a weighted combination of different C_{60}H_m spectra provides a potential to reproduce the 21 μm feature. The features grouping in the wavelength of 5–10 μm are also detected in the observational spectrum, providing a further support for C_{60}H_m as the carrier of the 21 μm feature. However, no strong feature in the 13–17 μm range is detected in the observational spectrum, which instead exhibits features in 10–13 μm range. The 10–13 μm features are not seen in the theoretical spectra of C_{60}H_m , and usually are attributed to silicon carbides in the literature [11].

Any single C_{60}H_m spectrum is unable to reproduce the observed 21 μm feature. Fullerenes, if being responsible for the 21 μm feature in PPNe, should be a mixture

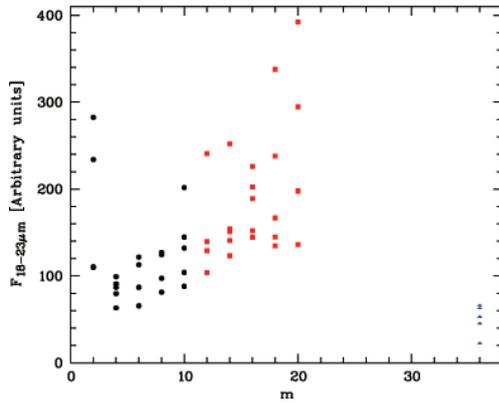


FIG. 2 Intrinsic strengths of the $C_{60}H_m$ features lying in the wavelength range of 18–23 μm versus the m values. The filled circles, squares, and triangles represent the slightly ($m=2-10$), moderately ($m=12-20$), and heavily ($m=36$) hydrogenated C_{60} , respectively.

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 μm features have a remarkably consistent profile [21]. 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 [22]. In order to explain the observations, we conjecture that only a 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 fullerenes, or even break the carbon cage. The rigorous environments required for the existence of fullerenes are compatible with the rareness of the 21 μm feature in astronomical objects.

FIG. 1 indicates that $C_{60}H_{36}$ can be ruled out as the carrier from the 21 μm feature due to the lack of features lying in the 18–23 μm wavelength range. $C_{60}H_m$ with $m=2-8$ is unlikely responsible for the 21 μm feature because their strong features have peak wavelengths shorter than 20 μm . Moreover, $C_{60}H_2$ can produce a strong feature around 27 μm , which has never been detected. FIG. 2 presents the contributions from each $C_{60}H_m$ isomer to the total intrinsic strength of the features lying in the 18–23 μm 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 fullerenes produces the strongest vibrational bands in the wavelength range encompassing the 21 μm feature.

In FIG. 3, we examine the intensity-weighted wavelengths (λ_{21}) of $C_{60}H_m$ as a function of m , which is

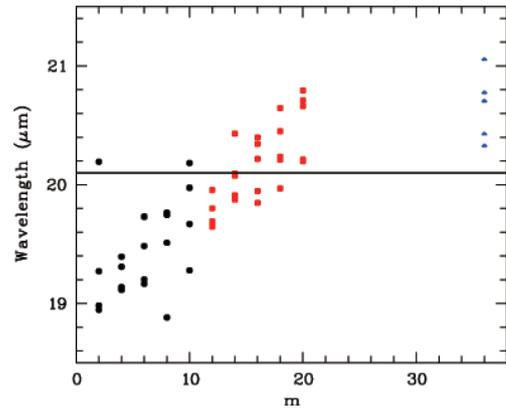


FIG. 3 The intensity-weighted wavelengths of the features lying in the wavelength range of 18–23 μm versus the m values of $C_{60}H_m$. Symbols are the same as those in FIG. 2. The horizontal line denotes the wavelength position of the 21 μm feature.

defined as

$$\lambda_{21} = \frac{\sum_i \lambda_i F_i}{\sum_i F_i} \quad (1)$$

for $18 \mu\text{m} \leq \lambda_i \leq 23 \mu\text{m}$, where F_i is the intrinsic strength of the i th mode at the wavelength of λ_i . An inspection of FIG. 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 [17]. Comparing with the observed peak wavelength (20.1 μm), we infer that moderately hydrogenated fullerenes with $10 < m < 20$ are the promising carriers for the 21 μm feature.

While the existence of fullerenes in astronomical environments seems plausible, there is as yet no unambiguous detection. Díaz-Luis *et al.* [23] failed to detect the C–H stretching bands at 3.4–3.6 μm in two PNe exhibiting strong C_{60} emissions, suggesting that fullerenes 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.* [24] speculated that $C_{60}H^+$ might contribute to the spectra of two C_{60} -containing PNe. Presumably, exposed to very strong UV radiation, moderately and heavily hydrogenated fullerenes cannot survive in PNe. This is compatible with the non-detection of the 21 μm feature in PNe. Zhang and Kwok [25] reported a tentative detection of fullerenes 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 μm source in the previous literature. However, a closer view of its infrared spectrum clearly reveals a faint feature exactly peaking at 20.1 μm (FIG. 4). This feature is much weaker than the C_{60} bands, and has

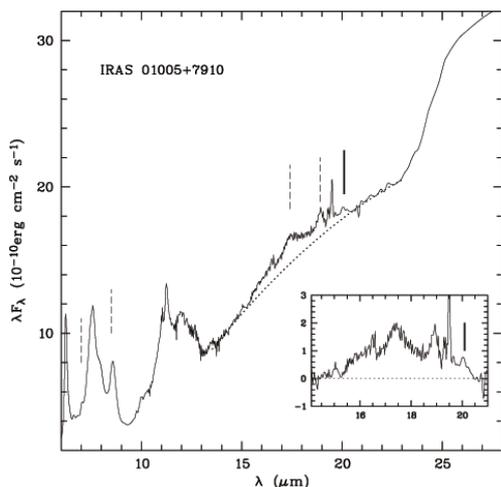


FIG. 4 The *Spitzer*/IRS spectrum of the PPN IRAS 01005+7910. The vertical solid and dashed lines mark the positions of the 21 μm feature and the four C_{60} bands, respectively. The inset panel shows the continuum-subtracted spectrum.

not been noted previously. If it is attributed to fullerenes, we can hypothesize that fullerenes 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 μm plateau emission in the spectrum of IRAS 01005+7910.

A criticism of the fullerane hypothesis was advanced by Posch *et al.* [26], 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.* [27]. The argument stems from the fact that nanodiamonds and fullerenes have a similar hybridization structure. However, it is not always appropriate to expect that nanodiamonds and fullerenes 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 criterium for band identification is 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 fullerenes imply that there is no correlation between the intensities of the 3.4 μm and the 21 μm features, as shown in FIG. 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 arises from C–C deformation vibrations. Therefore, the feature around 3.4 μm may not serve as a good tracer to examine the fullerene hypothesis.

The theoretical spectra of fullerenes reveal that the

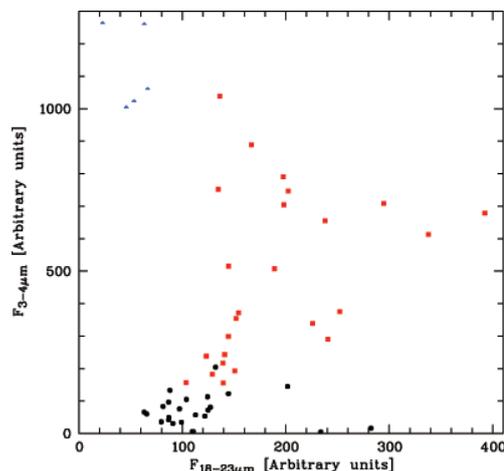


FIG. 5 Intrinsic strengths of the C_{60}H_m features lying in the wavelength range of 3–4 μm versus those of 18–23 μm . Symbols are the same as those in FIG. 2.

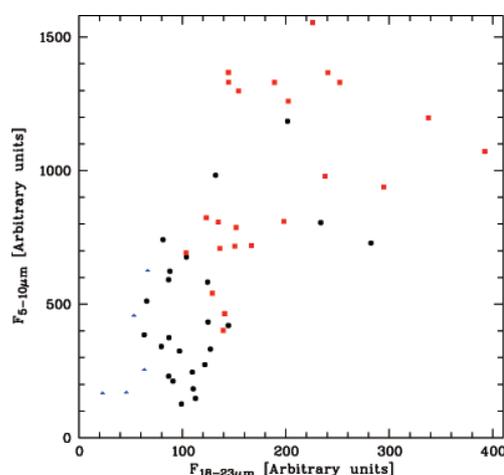


FIG. 6 Intrinsic strengths of the C_{60}H_m features lying in the wavelength range of 5–10 μm versus those of 18–23 μm . Symbols are the same as those in FIG. 2.

5–10 μm feature has an intensity positively correlating with that of the 18–23 μm feature (FIG. 6). This is in good agreement with the observational results that the spectra of 21 μm sources usually show a broad peak at 7–9 μm as well [2]. This makes the fullerane hypothesis quite plausible. However, the 5–10 μm feature has been commonly detected in various circumstellar envelopes, and cannot be entirely attributed to fullerenes.

According to our calculations, an issue of the fullerane hypothesis is that the 13–17 μm feature arising from fullerenes is hardly visible in the observational spectra. As shown in FIG. 7, the 13–17 μm feature should have a comparable intensity with the 21 μm one, which is in contrast to the observations. FIG. 7 shows that the 13–17 μm feature is likely to peak at 15 μm . Zhang *et al.* [18] examined the spectra of all C_{60} -containing objects, but did not make any unambiguous detection of

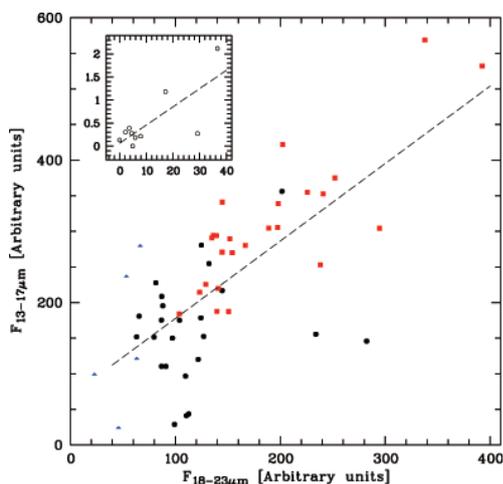


FIG. 7 Intrinsic strengths of the $C_{60}H_m$ features lying in the wavelength range of 13–17 μm versus those of 18–23 μm . Symbols are the same as those in FIG. 2. The insert shows the correlation between the strengths (in arbitrary units) of the 15.8 μm and the 21 μm features, as found by Zhang *et al.*[20]. Dashed lines represent the linear fittings.

the 15 μm feature (this feature was marginally seen in only two C_{60} -containing objects, which cannot be considered as a solid detection). It doesn't seem to support the expect that fullerenes coexist with fullerenes. Nevertheless, it is notable that DFT calculations reproduce the spectra of free-flying molecules, which can interpret the band wavelengths of experimental spectra much better than the band strengths. If the material is in condensed phase, some prominent bands in the theoretical spectra may be strongly suppressed. From a close inspection of the laboratory spectrum of $C_{60}H_{18}$ (see FIG. 3 in Ref.[16]), we can see some bands lying in the 13–17 μm range with wavelengths coincident with the theoretical calculations. But these bands appear much weaker than those lying in the 5–10 μm and 18–13 μm ranges, contrary to the theoretical results. Furthermore, 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 in astronomical objects, a weak feature at 15.8 μm appears in the spectra of all the 21 μm sources [5]. Zhang and Kwok [14] found that there is a loose correlation between the intensity of the 15.8 μm and the 21 μm features (FIG. 7), suggesting that the two features may arise from associated materials. Sloan *et al.* [2] presented that the associated 15.8 μm feature may arise from aliphatic chains with alkyne bonds, and thus the carrier of the 21 μm feature should be related to aliphatic hydrocarbons. This favors the fullerane hypothesis.

The theoretical spectra of fullerenes do not exhibit strong bands around 30 μm . Therefore, the 30 μm fea-

ture detected in AGB stars, PPNe, and PNe is unlikely due to fullerenes. 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} [25]. It is tempting to conjecture that the carrier of the 30 μm feature can be synthesized during the AGB stage, and then when exposed to UV radiation at PN and PPN stages it is fragmented and partly converted into fullerenes and fullerenes through a top-down scenario.

IV. CONCLUSION

We investigated the theoretical spectra of $C_{60}H_m$ with the aim of examining whether fullerenes are responsible for the 21 μm feature in PPNe. Based on a comparison of wavelengths and intensities, we infer that moderately hydrogenated C_{60} is 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 μm feature. The survival of fullerane is very sensitive to the UV radiative field, and thus can give a natural explanation for the emergence of the 21 μm feature on very short timescales. The main issue is that the theoretical spectra of fullerane pose strong features in the 13–17 μm range which are absent in 21 μm sources. However, given the limits of computation and model complexity, this is not complete enough to 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 μm feature.

V. ACKNOWLEDGMENTS

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