

Fullerenes and fulleranes in circumstellar envelopes

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Abstract. Three decades of search have recently led to convincing discoveries of cosmic fullerenes. The presence of C_{60} and C_{60}^+ in both circumstellar and interstellar environments suggests that these molecules and their derivatives can be efficiently formed in circumstellar envelopes and survive in harsh conditions. Detailed analysis of the infrared bands from fullerenes and their connections with the local properties can provide valuable information on the physical conditions and chemical processes that occurred in the late stages of stellar evolution. The identification of C_{60}^+ as the carrier of four diffuse interstellar bands (DIBs) suggests that fullerene-related compounds are abundant in interstellar space and are essential for resolving the DIB mystery. Experiments have revealed a high hydrogenation rate when C_{60} is exposed to atomic hydrogen, motivating the attempt to search for cosmic fulleranes. In this paper, we present a short review of current knowledge of cosmic fullerenes and fulleranes and briefly discuss the implications on circumstellar chemistry.

1. Introduction

Fullerenes are carbon cage molecules consisting of pentagons and hexagons. C_{60} , the best known fullerene, was first discovered in the experiments of understanding the carbon-chain chemistry in circumstellar environments [1]. Given their remarkable stability, fullerenes have been long suspected to exist in the Universe. The detections of fullerenes in terrestrial rocks and meteorites [2, 3, 4] suggest that they can be formed in nature, although the formation mechanisms in various geological environments are still in considerable debate. However, albeit with extensive efforts, search for fullerenes in deep space has been frustrating until recently.

The electronic spectrum of C_{60} is dominated by a few UV features, and its visible bands are relatively weak. Highly reddened O-type stars can be targeted to search for electronic transitions from interstellar C_{60} . However, no positive detection has yet been made. Unsuccessful attempts [5, 6] only set an upper limit to the C_{60} abundance in the interstellar medium (ISM). C_{60} has a low ionization potential (7.6 eV), and thus its singly-ionized species, C_{60}^+ , might be more abundant in the ISM. It has been long conjectured that two diffuse interstellar bands (DIBs) at 9632 Å and 9577 Å can be attributed to C_{60}^+ [7]. This was recently verified by experimental spectra of gas-phase C_{60}^+ [8]. The gas-phase laboratory spectra also exhibit two weaker bands at 9428.5 Å and 9365.9 Å, which were soon discovered in the spectra of DIBs [9]. The identification of C_{60}^+ as the carrier of four DIBs re-raises the possibility that fullerene derivatives might be responsible for the DIB phenomenon.

In infrared spectra, many vibrational modes of C_{60} are degenerate, resulting in four major features at 7.0, 8.5, 17.4, and 18.9 μm . Early attempts did not yield in certain detections [10, 11].



The first detection of C_{60} infrared bands was made in a young planetary nebula (PN) by the *Spitzer* Space Telescope [12]. Soon thereafter, C_{60} was detected in a variety of circumstellar environments [13, 14, 15, 16, 17, 18, 19, 20, 21], suggesting that it is a common molecule in the Universe and can survive in high-UV environments. About 5 percent of Galactic C-rich PNe have found to contain C_{60} , while Magellanic Cloud PNe show higher detection rate [22]. Infrared bands from the cation form C_{60}^+ were also detected in some of the C_{60} sources [23, 24, 25]. There is no firm detection of the other charge states, although some efforts have been devoted to search for circumstellar C_{60}^{2+} and C_{60}^- [24, 25].

2. The Formation of Fullerenes

The discovery of C_{60} in a proto-PN [18] suggests that fullerenes can be formed on a timescale of 10^3 years. In low-density environments, fullerenes are unlikely to be formed through assembly of small carbon species on such a short timescale (i.e. the bottom-up process). Although fullerenes can be experimentally synthesized via several different routes, observations point to a top-down scenario in astronomical environments [14, 26]. In this scheme, photon- or shock-induced processes cause dehydrogenation and ejection of C_2 of large hydrocarbon molecules, providing a pathway for the formation of closed-caged carbon molecules. Spatially resolved observations of reflection nebulae and H II regions indicate that the formation of C_{60} is related to the radiation fields [13, 26, 27]. However, the detection of C_{60} in various evolved stars suggests that strong UV irradiation is not necessary for fullerene formation [17, 24].

What is the precursor of fullerenes? Hydrogenated amorphous carbon (HAC) particles and polycyclic aromatic hydrocarbons (PAHs) have been presented as the starting materials [14, 15, 26, 28]. All the C_{60} sources exhibit prominent plateau emission [22, 24], which can be attributed to stretching and bending modes of mixed aromatic-aliphatic organic nanoparticles (MAONs, [29]). Therefore, we propose that fullerenes might be formed through the sp^3 to sp^2 transformation in MAONs. MAONs have a three-dimensional structure, and thus can be processed into multi-layered fullerenes (buckyonions), which have been suggested as the carrier of the 217 nm extinction bump [30] and some DIBs [31].

3. Search for Fullerenes

When mixed with atomic hydrogen, fullerenes can be readily hydrogenated into fullerenes ($C_{60}H_m$). In experiments, $C_{60}H_{36}$ and $C_{60}H_{18}$ are the most significant products of the hydrogenation of C_{60} . Induced by UV photons or thermal energy, $C_{60}H_m$ can be converted back to C_{60} by releasing molecular hydrogen. Fullerenes and fullerenes, therefore, may play a crucial role in the formation of H_2 in astronomical environments [32]. However, a search for fullerenes in two PNe showing strong C_{60} emission has not met with success [33].

Early studies indicate that the experimental spectrum of $C_{60}H_{36}$ is able to match several infrared emission bands in proto-PNe [34]. IRAS 01005+7910, a C_{60} -containing proto-PN, shows a few features around $3.4\mu m$ which have been tentatively ascribed to C-H stretching modes of $C_{60}H_m$ ($m \approx 36$) [24]. In the present work, we calculate the theoretical infrared ($5\text{--}20\mu m$) spectra of several $C_{60}H_m$ using the quantum chemistry method [35], and compare the results with the observed spectrum of IRAS 01005+7910, as shown in Figure 1. Our theoretical calculations are reasonably close to the experimental spectra [36]. For slightly hydrogenated C_{60} , the four carbon skeletal vibration modes are still visible, but the relative intensities might vary compared to those of C_{60} . Therefore, it is possible that the previously detected C_{60} features actually stem in part from $C_{60}H_m$. This might help account for the discrepancy between the observed intensities and the predictions from excitation models of C_{60} [24]. For highly hydrogenated C_{60} , the carbon cage is significantly distorted by the repulsion between the hydrogen atoms, and can be disrupted if $m > 36$. The four features from the skeletal vibrations are relatively inconspicuous or substantially invisible in highly hydrogenated C_{60} , partly because the energy

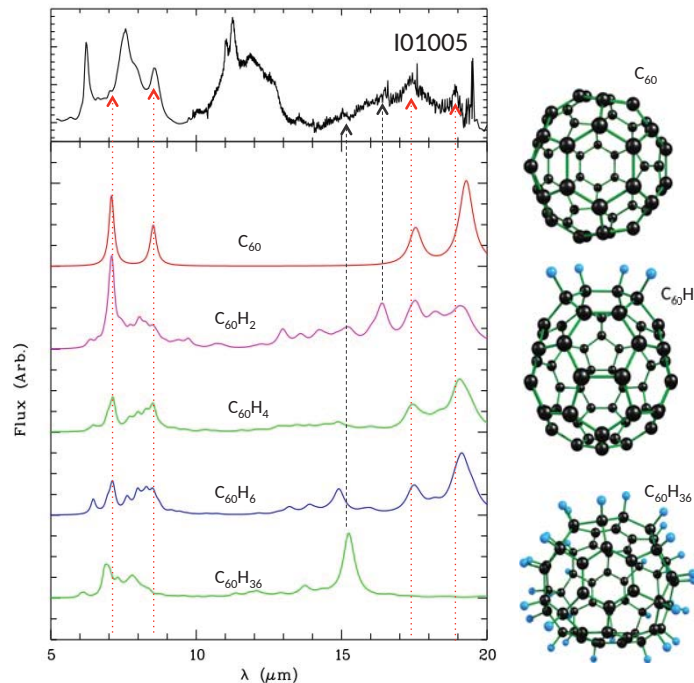


Figure 1. The graph on the left shows the observed spectrum of IRAS 01005+7910 (upper panel) and theoretical spectra of C_{60} and $C_{60}H_m$ (lower panel). The dotted arrows mark the four features arose from the skeleton vibrations of C_{60} . Hydrogenated C_{60} might be responsible for some weak features, as indicated by the dashed arrows. The energetically optimized structures of C_{60} , $C_{60}H_4$, and $C_{60}H_{36}$ are shown on the right.

is released largely through C-H vibrational modes. We therefore conjecture that fullerenes and fullerenes are rather common species in circumstellar envelopes, but hydrogenation will limit their detectability in infrared spectra. The main challenge in searching for circumstellar $C_{60}H_m$ is that the exact m value is unspecified and there are many isomers for a given m value. Nevertheless, we find that the observed spectrum might exhibit bands originating from $C_{60}H_m$ (Figure 1). In addition, it should be noted that many $C_{60}H_m$ have a ionization potential of < 10 eV, and might exist as cation form in the ISM.

4. Summary and Perspectives

The detections of C_{60} and C_{60}^+ in circumstellar and interstellar environments indicate that fullerenes and their derivatives are abundant and widespread in the Universe. Given their high chemical activity and physical stability, fullerene-related compounds (FCs) are promising candidates for the carrier of DIBs. There are some potential matches between the properties of FCs and DIBs [37]. Strong C_{60}^+ absorption bands at 9632 Å and 9577 Å have been detected towards IRAS 01005+7910 [38]. Two DIBs are found to be enhanced in C_{60} -containing PNe [39]. These observations support the view that some of the DIB carriers might be FCs and have a circumstellar origin. Except fullerenes, some other FCs such as metallofullerenes [40] and fullerene/PAH adducts [41] can readily form together with fullerenes in experiments. Furthermore, if molecules like CO and H_2 are trapped inside the fullerene cage, their vibrational and rotational spectra may be strongly affected by the interaction with the wall. Future experimental and theoretical works on these FCs are highly valuable.

Acknowledgments

Financial support for this work was provided by the Research Grants Council of the Hong Kong under grants HKU7073/11P and HKU7062/13P.

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