

Fullerenes and PAHs: from laboratory to the detection in interstellar space

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Abstract

We will review theoretical, experimental and observational work on the new form of carbon known as fullerenes and its hydrogenated forms (fulleranes). This type of molecules can be responsible for diffuse interstellar bands, for the UV “bump”, a remarkable feature of the extinction curve observed in many lines of sight of our Galaxy and other galaxies, and for the anomalous microwave emission detected in regions of star formation, in molecular clouds and HII regions. The recent detections of the fullerenes C₆₀ and C₇₀ in planetary nebulae of our Galaxy and in the Magellanic clouds provide further support to the hypothesis that these fullerenes are common in the interstellar medium. I will also review advances in the identification of polycyclic aromatic hydrocarbons (PAHs) which are also potential agents of the previous phenomena.

1 Introduction

Experiments aimed to reproduce the chemistry of the atmospheres of red giant stars led to the discovery of a new form of carbon: the fullerenes [17], the third known allotropic form of carbon (graphite and diamonds are the other two). In laboratory experiments, the most abundantly produced fullerene molecule is C₆₀, a hollow molecule with 60 carbon atoms distributed in 12 pentagons and 20 hexagons following the symmetry of truncated icosahedra (see Fig. 1). The radius of the molecule is approximately 3.55 Å. The electronic structure of the C₆₀ consists of 60 atomic orbitals 2p_z and 180 hybrid orbitals sp². Fullerenes (C₆₀, C₁₈₀, C₂₄₀...) with a number of atoms 20(m² + n² + nm), where n and m are integers, have icosahedral symmetry groups I_h and present high stability. Fullerenes are very stable against UV and gamma radiation and collisions.

The fullerene family includes nanotubes (fullerenes with cylinder symmetry), endohedral fullerenes with small atoms (He, Ne, etc.) inside the cage and the so-called buckyonions, conformed by several concentric shells of fullerenes (Fig. 1b) with separations of order

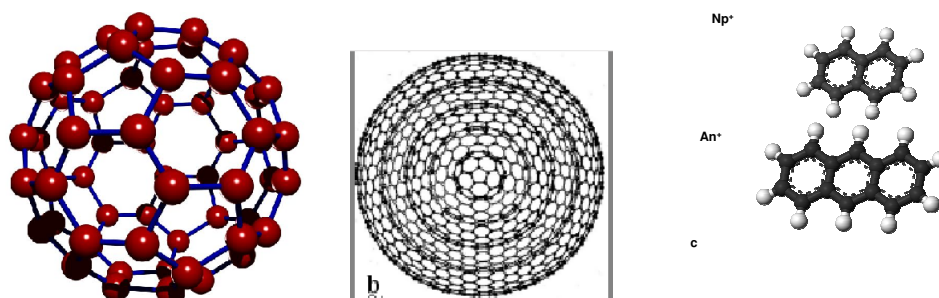


Figure 1: *Left panel:* Representation of the fullerene C_{60} . *Middle:* Representation of the buckyionon $C_{60}@C_{240}@C_{540}@C_{960}@C_{1500}$ with five layers. *Right panel:* Schemes of the naphthalene $C_{10}H_8^+$ (at the top) and anthracene cation $C_{14}H_{10}^+$.

3.4-3.5 Å. These molecules, which display even higher stability than individual icosahedral fullerenes, were first synthesized via electronic bombardment. Another very interesting form of fullerenes are the fulleranes, hydrogenated fullerenes (C_nH_m), where the π electrons form a bond with hydrogen. The properties of fulleranes are not as well determined as for single fullerenes but major effort is ongoing to measure their optical and infrared spectra and molar absorptivity [5].

Fullerenes have been detected in meteorites of the chondrite carbonaceous type. These meteorites were likely originated at the beginning of the Solar System. Mass spectroscopy of the Allende meteorite (Mexico 1969), the Murchinson meteorite (Australia 1969) and the Tagish Lake meteorite (Canada) reported fullerene abundances of order 0.1 ppm [1, 20]. On Earth, fullerenes have been detected in sedimentary layers of the cretaceous-Tertiary (KTB) boundary in China and Bulgaria and in shunghite mineral of the Carelia region (Russia).

1.1 Polycyclic Aromatic Hydrocarbons

PAHs are planar molecules consisting of carbon rings and hydrogen, these rings are similar to benzene. The most simple PAHs are naphthalene and anthracene with two and three benzene rings, respectively. In Fig. 1 (right) we show a representation of the cations. PAHs have been proposed as carriers of the Unidentified Infrared Emission bands and of the diffuse interstellar bands which are ubiquitous in the interstellar medium [18]. Carbon ring based molecular forms are very stable against UV radiation. A remarkable property which may have played a role in the development of life, as the DNA bases essentially conformed by combinations of such carbon rings would also benefit from this stability.

2 Fullerenes: theoretical remarks, laboratory characterization and detection in space

The photoabsorption spectrum of large fullerenes and buckyonions is not well known from the experimental point of view. Computations of the photoabsorption spectra using semiempirical models showed the potential role of these molecules to explain interstellar absorption phenomena [12]. The theoretical approach followed to compute photoabsorption cross sections was based in a Hückel and Pariser-Parr-Pople (PPP) models and took into account the strong electronic correlation and the screening effects associated to π electrons in these molecules [10, 11]. The spectral computations in the near UV and optical indicated strong absorption around 2170 Å and the formation of many weaker absorptions distributed through all the optical spectrum.

2.1 UV Bump

Measurements of the most intense feature associated to near UV/optical extinction of radiation in different lines of sight of our Galaxy [7] show that the main extinction feature in the optical and near UV is located in the range 2150-2190 Å, this so-called UV bump is very stable in wavelength. The computed photoabsorption spectra of some individual fullerenes reproduce remarkably well this feature of the extinction curves. If the abundance of fullerenes in the diffuse interstellar medium decreases for larger fullerenes according to a power-law of negative index with absolute value $\sim 3-4$, then it is possible to reproduce the UV bump with high precision.

From the comparison of these theoretical spectra with the observed UV bump in the extinction curves, it was possible to estimate what could be the fraction of carbon locked in fullerenes and buckyonions in the ISM [12]. The number density of these molecules resulted in the range 0.2-0.08 fullerenes per million hydrogen atoms. In the proposed scheme the small size fullerenes would be the most abundant with abundances of order $n(\text{C}_{60})/n(\text{H}) \sim 10^{-6}$. Similar values are reported for carbonaceous chondrites. From this, using the proposed size distribution of fullerenes in the interstellar medium, it was inferred that the abundance of carbon in fullerenes and buckyonions could reach values as high as $n(\text{C})/n(\text{H}) = 90-110 \times 10^{-6}$. Therefore, up to 25% of all the carbon could be locked in these molecules. Certainly a much lower contribution would be possible depending on the actual number density of the large size fullerenes, for the moment only detections of fullerenes with 60 and 70 carbon atoms have been reported.

2.2 Hydrogenated fullerenes and the UV bump

Considering the high abundance of hydrogen in the universe and also the π electron cloud in fullerenes, it is reasonable to expect that hydrogenated fullerenes represent the most common form of these molecules. Recent laboratory studies [5] have shown that hydrogenated fullerenes can reproduce well the peak and shape of the UV bump in the extinction curve. In particular, the electronic absorption spectrum of $\text{C}_{60}\text{H}_{36}$, obtained in the laboratory using

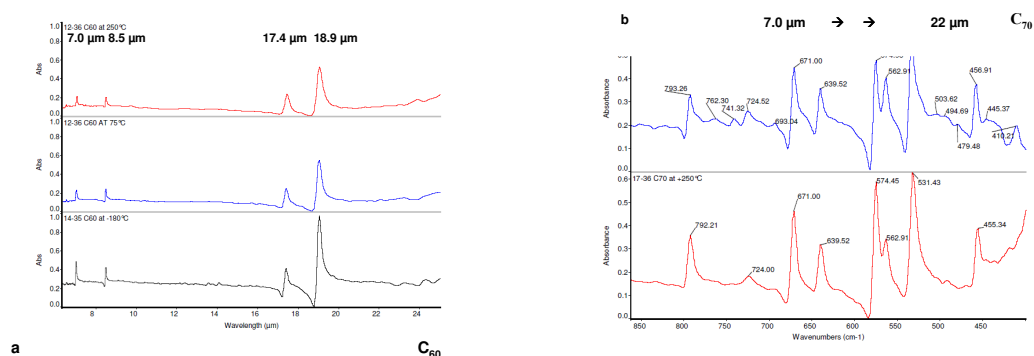


Figure 2: Laboratory spectroscopy of mid-IR active bands of C_{60} and of C_{70} at low temperatures [15].

n-hexane, shows a maximum absorption precisely at 2175 \AA with molar absorptivity of $\epsilon_{217} = 17140 \text{ L cm}^{-1} \text{ mol}^{-1}$ which corresponds to an absorption cross section of order 6500 Mbarn , about ten times higher than for C_{60} . It is therefore of the highest importance to measure and characterize at laboratory the transition bands of these molecules and carry out an extensive search in various phases of the interstellar medium.

2.3 Infrared spectroscopy of fullerenes and their discovery in space

Laboratory spectroscopy of mid-IR active bands of C_{60} and C_{70} at low temperatures [15] is key to the search and identification of fullerenes in space. The main IR active bands for the C_{60} are at 7.0 , 8.5 , 17.4 and 18.9 \mu m . The recent detection of fullerenes C_{60} and C_{70} in planetary nebulae [4] has generated a lot of momentum in the field and additional detections of fullerenes in planetary nebulae have been reported [8]. It seems that the late stages of the evolution of solar-type stars favour the production of fullerenes. These molecules are very resistant to UV radiation and therefore have long survival times in interstellar space. It is likely that fullerenes originally formed in planetary nebulae subsequently populate the interstellar medium and the clouds from which stars and planets form. It is important to extend the search for fullerenes and its derivatives in various phases of the interstellar medium: including other planetary nebulae, molecular clouds and very importantly protoplanetary disks, as the presence of fullerenes in protoplanetary disks may explain their existence in the meteorites of the Solar System. Measurements of absorptivities at low temperatures are key to derive the abundances of these molecules in the various phases of the interstellar medium.

3 Naphthalene and Anthracene in interstellar space

Gas phase laboratory spectroscopy of naphthalene and anthracene cations, at low temperatures provide precise wavelengths, widths and oscillator strengths of bands [2, 19, 21], which are useful to search for these molecules in the interstellar medium. The strongest vibronic

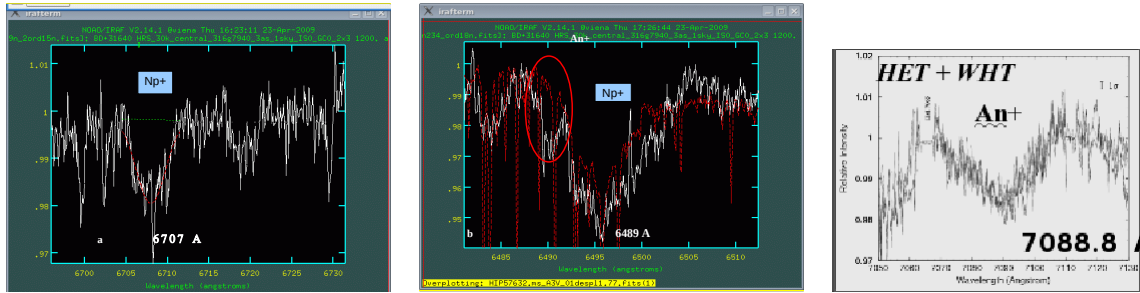


Figure 3: Spectra of star Cernis 52 in the Perseus molecular complex confirming the existence of broad band absorptions at 6707 Å, 6489 Å(naphthalene cation) and 7089 Å(anthracene cation).

band for the naphthalene cation the D2←D0 is at 6707.4 Å with a full width at half maximum of ~ 12 Å (uncertainty ± 1 Å) and oscillator strength $f=0.05$. Laboratory measurements show that the next three strongest naphthalene cation absorption bands are at: 6488.9, 6125.2 and 5933.5 Å, respectively. Along this series, the intensity decreases as we move to shorter wavelengths, with a ratio of a factor 2 between each two consecutive bands in wavelength. Studies of the absorption spectrum of the anthracene cation (An^+) in supersonic jet cavity ring-down spectroscopy [22] found only one transition in the optical region, with central wavelength for the D2←D0 transition of An^+ at 7087.6 ± 1.3 Å, with a FWHM 40 Å.

In Fig. 3 we display spectra of star Cernis 52 in the Perseus molecular complex showing independent detections of an interstellar band at 6707.4 ± 0.2 Å which could be associated to the naphthalene cation. The spectra were obtained with different telescopes.

The next most intense naphthalene cation band at 6488.7 Å is not easy to detect, because of a blend with another broad diffuse band (see Fig. 3) at 6494.2 Å that dominates the spectral region [16]. Using the published list of diffuse interstellar bands [9] and synthetic spectra to account for any possible stellar photospheric features, Iglesias-Groth et al. [13] concluded that there is evidence for a band at 6488.8 Å with a relative strength to the 6707 band which would be consistent with the expectations for the first two transitions of the D2←D0 system of the $C_{10}H_8^+$ naphthalene cation. Spectra of Cernis 52 obtained at HET and at WHT also show a very broad band at 7088.8 ± 2.0 Å which is consistent with the strongest band measured in the laboratory for the anthracene cation [14].

Adopting for the oscillator strength of the transition at 6707.4 Å a value of $f=0.05$ and using the measured equivalent width of the band, it was derived for $C_{10}H_8^+$ a column density of $N_{np^+}=1 \times 10^{13} \text{ cm}^{-2}$. For the anthracene cation $C_{14}H_{10}^+$, the column density obtained was $N_{an^+}=1.1 \times 10^{13} \text{ cm}^{-2}$

Assuming a ratio $C/H=3.7 \times 10^{-4}$ and hydrogen column density per unit interstellar absorption $N_H/A_V=2 \times 10^{21} \text{ cm}^{-2}$ (with $A_V=3 E(B-V)$) it was inferred that 0.002 % of the total carbon in the intervening cloud could be in the form of naphthalene cations and a value of 0.003 % for the anthracene cations.

3.1 A connection between naphthalene and amino acids?

Laboratory experiments combining naphthalene with water, ammonia and UV radiation at very low temperatures of order 15 K produced 13 amino acids [6]. The abundance of ammonia in Perseus is similar to that for naphthalene and anthracene cations in the line of sight investigated towards the Perseus molecular complex. Since the physical conditions in the intervening cloud are not far from those adopted in this laboratory experiment, it is therefore possible that in the intervening cloud a factory of amino acids could be at work. An ongoing program with IRAM 30m telescope aims to search for the amino acid glycine in the line of sight of Cernis 52 using well known transitions at 101.3-130.4 GHz.

4 Conclusions

i) The photoabsorption spectra of icosahedral fullerenes and buckyonions could explain the 2175 Å bump in the extinction curve of the interstellar medium. Based on absorption curves measured at laboratory, the fullerenes $C_{60}H_{36}$ and $C_{60}D_{36}$ also fit well the wavelength, width and shape of the UV bump in the extinction curve of the diffuse interstellar medium. It appears that fullerenes and related molecular forms could be responsible of the UV bump, a major feature of interstellar absorption. If so, fullerenes would be ubiquitous molecules in interstellar space. The recent detections of fullerenes in planetary nebulae of our Galaxy and in the Magellanic Clouds reinforce the view that a significant fraction of carbon is locked in fullerene based molecules. The contribution of these molecules to the total amount of carbon in the Galaxy is still rather uncertain and will require further studies. Hydrogenated forms of fullerenes have not been identified yet in space, but could be a major carbon reservoir.

ii) There is evidence for the most simple PAHs (naphthalene and anthracene) in the intervening translucent cloud toward star Cernis 52 in the Perseus molecular complex. The derived column densities for the cations of these two molecules are $1 \times 10^{13} \text{ cm}^{-2}$. This would be the first identification of individual PAHs out of the Solar System. Their detection adds support to electric dipole radiation from PAHs as responsible for the anomalous microwave emission detected in Perseus.

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