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Progress in research on Fullerenes and PAHs in the interstellar and circumstellar medium.

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Abstract

Results on theoretical work, astronomical observations and laboratory measurements of the new form of carbon known as fullerenes and their hydrogenated forms (fulleranes) are reviewed. These molecules can be responsible for diffuse interstellar bands, for the UV *bump*, a prominent feature in the extinction curves observed in many lines of sight of our Galaxy and other galaxies, and the anomalous microwave emission discovered in several regions of star formation, in molecular clouds and HII regions. Recent detections of fullerene C_{60} and C_{70} in various astrophysical contexts from reflection nebulae to planetary nebulae and protoplanetary disks reinforce the hypothesis that fullerenes and fulleranes are common in the interstellar medium and could contribute significantly to extinction. Another potential agent of anomalous microwave emission processes and interstellar extinction bands are polycyclic aromatic hydrocarbons (PAHs). Identification of the simplest PAHs, naphthalene and anthracene, in the interstellar medium is also discussed.

1 Introduction

The experiments, carried out by Kroto and Smalley in 1985, aimed at reproducing the chemistry of giant red star atmospheres led to the discovery of a new form of carbon: the fullerenes, the third known allotropic form of carbon (the two others are graphite and diamonds). Laboratory experiments have shown that the most stable fullerene molecules are C_{60} and C_{70} and the most abundant is C_{60}, a hollow molecule with 60 carbon atoms distributed in 12 pentagons and 20 hexagons following the symmetry of truncated icosahedrons. The radius of this molecule is approximately 3.55 Å. The electronic structure of the C_{60} consists of 60 atomic 2pz orbitals and 180 sp^2 hybrid orbitals. The fullerenes with icosahedral symmetry I_h (C_{60}, C_{180}, C_{240}) have a high stability and are very stable against UV, gamma radiation and collisions. Fullerenes are efficiently formed in laboratory vaporization experiments of graphite [17] and could also be formed in asymptotic giant branch stars (AGB) where circumstellar molecular synthesis is very reach.

The fullerene family also includes the so-called buckyonions, conformed by several concentric fullerene shells with separations of order 3.4-3.5 Å. These molecules, which show an even greater stability than the individual icosahedral fullerenes, were first synthesized by electronic bombardment. Another very interesting form of fullerenes are fulleranes, hydrogenated fullerenes (C_nH_m), where the π electrons form a bond with hydrogen. The properties of fulleranes are not so well known as those of individual fullerenes, but on-going laboratory work is aimed to measure their optical and infrared spectra and molar absorptivity.

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. 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 and are also potential carriers of the anomalous microwave emission. Carbon ring based molecular forms are very stable against UV radiation. The stability of carbon ring structures, pentagons and hexagons, which conform fullerenes and PAHs is a remarkable property which may even have played a role in the development of life. The DNA bases are essentially conformed by combinations of such carbon rings and would also benefit from such stability properties.

2 PAHs

PAHs are widely distributed in the ISM and collectively detected in many galaxies, however, recognition of individual PAHs is difficult. The detection of discrete infrared emission bands near 3.3, 6.2, 7.7, 8.6, 11.3 and 12.7 μm in dusty environments excited by ultraviolet photons led to the suggestion that PAHs were present in the interstellar medium [15]. These infrared bands are due to C–C and C–H stretching and bending vibrations in an aromatic hydrocarbon material. Since these bands mostly probe specific chemical bonds and not any particular molecular structure, they cannot provide unambiguous identification of single PAHs. The naphthalene cation ($C_{10}H_8^+$) is the most simple PAH and one of the best characterized spectroscopically in low-temperature gas phase at laboratory [18]. The laboratory characterization, crucial for a potential identification in the interstellar medium, shows that the strongest optical band of the naphthalene cation is located at 6707.4 Åwith a full width at half-maximum (FWHM) of approximately 12 Å. Progressively weaker bands of similar width have been measured at 6488.9, 6125.2 and 5933.5 Å[2]. It has been reported the detection of weak absorption (less than 1.5 per cent of the continuum) broad optical bands in the spectrum of the star Cernis 52 (A3 V), a likely member of the very young star cluster IC 348, which appear to be consistent with the measured laboratory bands of the naphthalene cation [11]. Under the assumption that the bands are caused by naphthalene cations, a column density for Np^+ of order 1×10^{13} cm^{-2} was derived. A broad band at 7088.8 Å coincident to within the measurement uncertainties with the strongest band of the anthracene cation ($C_{14}H_{10}^+$) as measured in gas-phase laboratory spectroscopy at low temperatures is also detected in the line of sight of star Cernis 52 [12]. This is probably associated with cold absorbing material in an intervening molecular cloud of the Perseus star-forming region where various experiments have recently detected anomalous microwave emission. From the measured intensity and available oscillator strength it is implied that ∼0.008 per cent of the carbon in the cloud could be in the form of $C_{14}H_{10}^{+}$. A similar abundance was also claimed for the naphthalene cation in this cloud.

3 Fullerenes: theoretical and laboratory spectra, characterization and detection in space

Computation of the photoabsorption spectra of fullerenes using semiempirical models showed the potential role of these molecules to explain various interstellar absorption features [10]. The theoretical approach followed to compute photoabsorption cross sections was based in a Huckel 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. The spectral computations in the near UV and optical indicated strong absorption around 2175 Å and the formation of many weaker absorptions distributed through all the optical spectrum. Measurements of the extinction of radiation in the near UV/optical in different lines of vision of our Galaxy shows a main extinction feature in the range 2150-2190 Å, this so-called UV bump is very stable in wavelength. The calculated photoabsorption spectra of some individual fullerenes reproduce this feature of extinction curves remarkably well. If the abundance of fullerenes in the diffuse interstellar medium decreases as a function of size according to a power law, then it is possible to reproduce the UV bump with high precision for a power-law index in the range 3-4. From this comparison, it is possible to estimate the fraction of carbon locked in fullerenes and buckyonions in the ISM [10]. The numerical density of these molecules results in a range of 0.2-0.08 fullerenes per million hydrogen atoms. In the proposed scheme, small fullerenes would be the most abundant with abundances of order $n(C_{60})/n(H) \sim 10^{-6}$).

Laboratory studies have shown that hydrogenated fullerenes also reproduce well the peak and shape of the UV bump in the extinction curve. In particular, the electron absorption spectrum of $C_{60}H_{36}$, obtained in the laboratory using n-hexane (Fig. 1), shows maximum absorption precisely at 2175 Å with a molar absorption of 17140 L cm $^{-1}$ mol^{-1} corresponding to a cross section absorption of order 6500 Mbarn, approximately ten times higher than for C_{60}. It is very important to measure and characterize in the laboratory the transition bands of these molecules and carry out an extensive search in several phases of the interstellar medium.

Laboratory spectroscopy of the active IR bands of C_{60} and C_{70} at low temperatures is key to the search and identification of fullerenes in space. The main active bands of IR for the C_{60} are at 7.0, 8.5, 17.4 and 18.9 μm. These bands have been crucial in the search for fullerenes in space. Their detection led to the discovery of fullerenes C_{60} and C_{70} in the young planetary nebula Tc1 [3] with *Spitzer Space Telescope.* These molecules were subsequently identified in reflection nebulae [21], several planetary [8] and protoplanetary [22] nebulae, and in post-AGB stars [9].

Fullerenes are able to survive under the harsh conditions of the ISM as suggested by observations in several young stellar objects [20] and by the ubiquitous presence of the

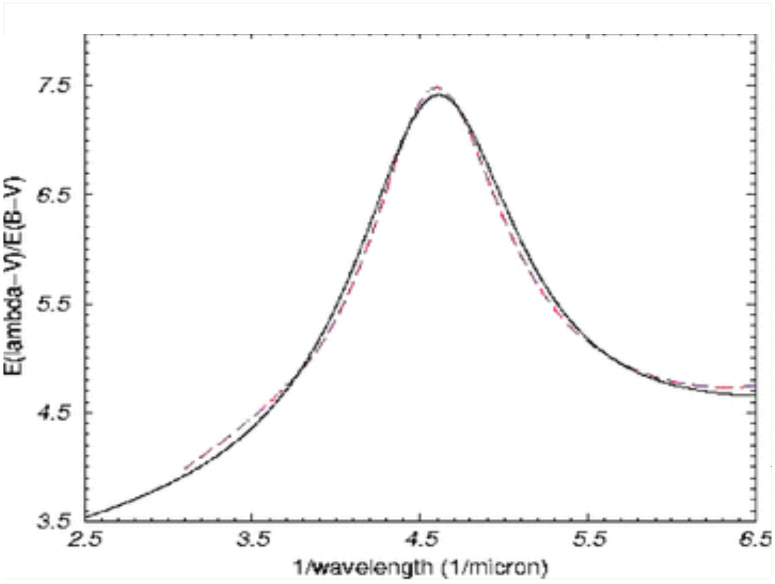

Figure 1: Comparison of the photoabsorption cross-section of fullerene $C_{60}H_{36}$ (continuous black line) with the interstellar extinction curve for a reddening factor RV= 3.1 (red dashed line) [6]. The vertical axis corresponds to normalized absorption at a certain wavelength, also known as reddening function.

diffuse interstellar bands at 957.7 and 963.2 nm which are associated to the cation C_{60}^{+} [7], [4]. These authors have inferred that a significant fraction of interstellar carbon is located in the C_{60} cation, although initial estimates of order 0.9% have been recently reduced to values of 0.1 % [1]. The cation bands were also detected in one protoplanetary nebula [13] deriving fullerene concentration values of order 0.05-0.1 ppm which are similar to values inferred from the UV bump at 217.5 nm under the assumption that this prominent feature of extinction is caused by fullerenes [10]. At such abundances, fullerenes can play an important role in interstellar chemistry [19], and given the stability of fullerenes against corpuscular and gamma radiation [5], it is likely that fullerenes originally formed in planetary nebulae later populate the interstellar medium and the clouds from which stars and planets form.

4 Fullerenes C_{60} and C_{70} in the circumstellar matter of stars with proto-planetary disks

I have carried out a systematic search of C_{60} and C_{70} in stars with protoplanetary disks in the young star cluster IC348 of the Perseus molecular complex. Here report results on a few selected stars (LRLL 1, LRLL 2 and LRLL 58)[16] with disk studies available in the literature. The spectra used in this work were obtained with the low resolution module-short wavelength (SL; 5-20 μm) and in one case with the high resolution short wavelength module (SH; 9.5-19.5 μm). The data processing is described elsewhere (see http://cassis.sirtf.com/).

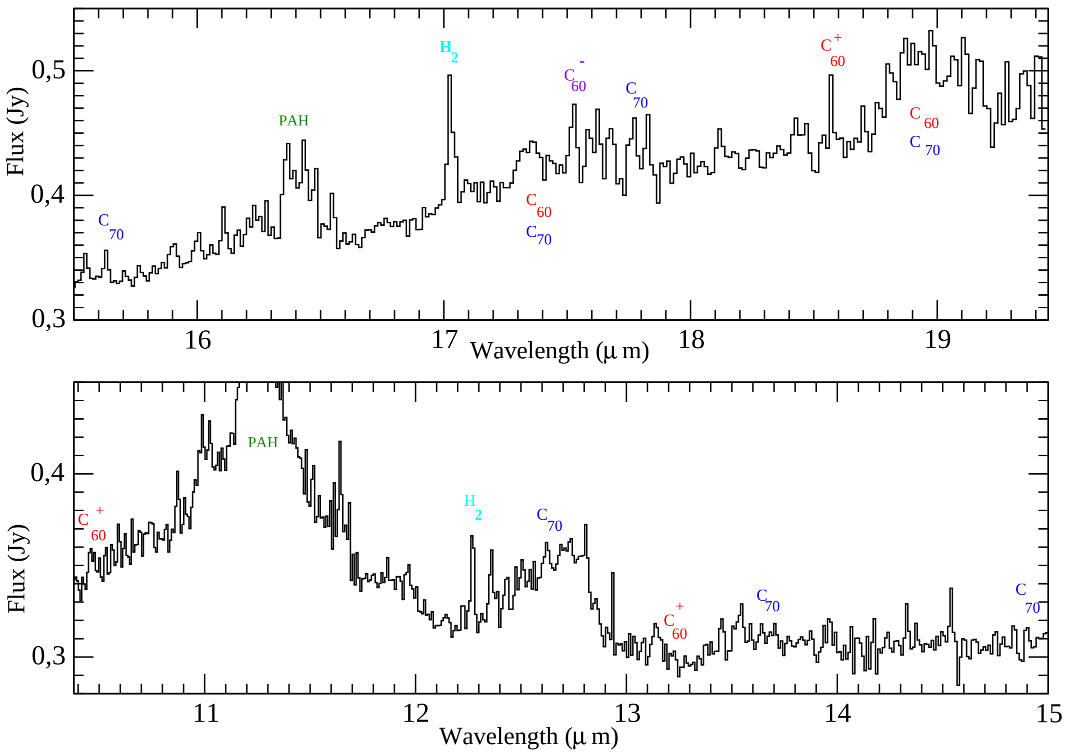

Figure 2: Mid-IR spectrum of star LRLL 2 obtained with Spitzer/IRS high resolution mode. Lines marked: C_{60} and C_{70} (17.4 and 18.9 μm), C_{70}(12.62, 13.83, 14.9,15.63 and 17.77 μm), C_{60}^+ cation (10.47, 13.22,18.58 μm), C_{60}^- anion (17.51 μm), H2 (12.28, 17.03 μm)

The package CASSIS [14] was used to inspect and extract the spectra. The spatial scale of the IRS (approximately 5 arcsec per pixel) does not allow to disentangle emission lines originating in the disk from emission lines produced in the reflection nebulae surrounding the stars under consideration. It was adopted the integrated spectra as a suitable description of the emission line spectrum in the region around each star.

In the range 16-20 μm a prominent emission spectral band system is present in each star which has a well sampled band at 18.9 μm of C_{60} with contribution of C_{70} and a blended feature of PAHs at 16.4 μm, H_2 (17 μm) and fullerenes C_{60} and C_{70} at 17.4 μm.

In Fig. 2 we plot the IRS spectrum of the IC 348 LRLL 2 star obtained by Spitzer with the high spectral dispersion module (R=600) showing details of the bands and the continuum emission. The positions of known bands of C_{60} (17.4 and 18.9 μm) and C_{70} (17.4, 17.8 and 18.9 μm) are marked. Weak features of C_{70} appear to be present in the spectrum, remarkably at 17.8 and 21.8 μm (which is important in order to ascertain the relative contribution of this molecule to the strong bands at 17.4 and 18.9 μm. The spectrum also shows evidence for the C_{70} vibrational bands at 12.6, 14.9 and 15.6 μm and the C_{60}^{+} bands at 10.5, 13.2 and 18.6 μm.

The C_{60} features in the range 17-19 μm have a typical width of 0.3-0.4 μm, wider than the spectral resolution of the instrument and similar to the widths observed in planetary nebulae (like Tc 1). The contribution of C_{70} to the total emission of the bands observed at 18.9 μm and 17.4 μm has been established using the information provided by other bands of this molecule assuming a simple model to describe band ratios, and resulting C_{70} contributions are in the range 10-30% of the total band strengths.

The total flux of the band at 18.9 μm is rather stable among the observed circumstellar material ranging from 3×10^{-16} to 1×10^{-15} W m^{-2}, in spite of the very different luminosity and temperature of the studied disk host stars. Interestingly, I find the 16.4μm PAH emission in LRLL 58 is significantly enhanced with respect the 18.9 μm C_{60} band, contrary to what is observed in the other two targets of the sample where this PAH band appears weaker relative to fullerene emission. It is proposed that the relative enhancement of the PAH emission in this cooler object is a consequence of the higher sensitivity of PAHs to the physical conditions of the environment and in particular to the stellar radiation field. LRLL 58 has the lowest luminosity and the coolest effective temperature of the stars in the sample and this may favour the survival of PAHs. Fullerenes are expected to be more robust against radiation than PAHs.

5 Conclusions

- (i) Fullerenes and its hydrogenated forms could be responsible of the UV bump 2175 Å, a remarkable feature of interstellar absorption, and for several important diffuse interstellar bands.

- (ii) Fullerenes have been detected in planetary nebulae, 0.3-0.02 % of total carbon seems to be in the form of C_{60}.

- (iii) The cation C_{60} is detected in one protoplanetary nebulae and in the line of sight of many hot stars: 0.1-0.9% of total carbon appears to be in the form of ${C_{60}}^{+}$ in these environments.
- (iv) Fullerenes C_{60} and C_{70} are detected in the circumstellar matter of Perseus stars with protoplanetary disks where they coexist with PAHs. These fullerenes appear to lock 0.1-1 % of the carbon available in these regions. Cation and anions of C_{60} are also detected at 5-10 times lower abundances.
- (v) The cations of the most simple PAHs naphtalene and anthracene are present in the Perseus region with abundances 10-100 times lower than the neutral form of the most simple fullerene C_{60}.

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