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Fullerenes and PAHs in space

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Abstract. Theoretical, observational and laboratory work on the new form of carbon known as fullerenes and its hydrogenated forms (fulleranes) are reviewed. These molecules can be responsible of diffuse interstellar bands, the UV bump, a major feature in the extinction curves measured in many lines of sight in our Galaxy and other galaxies and the anomalous microwave emission detected in several regions of star formation,in molecular clouds and HII regions. Recent detections of fullerenes C_{60} and C_{70} in planetary nebulae of our Galaxy and in the Magallanic cloud render support to the hypothesis that fullerenes and fulleranes are carriers of these processes. Other potential agents of these emission and absorption processes are the polycyclic aromatic hydrocarbons (PAHs). We also review observational efforts to identify the most simple PAHs, naphthalene and anthracene, in regions of anomalous microwave emission.

Key words. ISM – Molecules:Fullerenes, PAHs – Nebulae

1. Introduction

Fullerenes were discovered in 1985 in experiments aimed to reproduce the chemistry of the atmospheres of red giant stars (Kroto et al.,1985). Fullerenes, graphite and diamonds are the three alotropic forms of carbon. In laboratory, the most abundant fullerene molecule is C_{60}, a hollow molecule with 60 carbon atoms distributed in 12 pentagons and 20 hexagons following the symmetry of truncated icosahedra (see figure 1a). The radius of the molecule is approximately 3.55 Å. The electronic structure of the C_{60} consists of 60 atomic orbitals 2pz and 180 hybrid orbitals sp^2. Fullerenes (C_{60}, C_{180}, C_{240}...) with a number of atoms $20(m^2 + n^2 + nm)$, where n and m are integers, have icosahedral symmetry groups I_h and present high stability. Fullerenes are very stable against UV, gamma radiation and collisions. The fullerene family includes nanotubes (fullerenes with cylinder symmetry) and endohedrical fullerenes with small atoms (He, Ne, etc.) inside the cage. Other type of fullerenes are the so-called buckyonions, conformed by several concentric shells of fullerenes (fig1b) with separations of order 3.4-3.5 Å. These molecules, which display even higher stability than individual icosahedral fullerenes, were first synthesized via electronic bombardment on carbon soot (Ugarte, 1992). Other techniques to produce buckyonions are based on annealing of carbon soot and nanodiamonds at temperatures of ∼ 2000 K (Kuznetsov et al., 1994; Tomita et al., 1999, 2001) and by deposition of carbon ions on metallic substrates (Cabioch 1995; 1997). Another very interest-

Send offprint requests to: S.Iglesias-Groth ing 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 (see e.g. Cataldo and Iglesias-Groth 2010).

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 (Vries et al. 1993; Becker et al. 1994, 1997,1999; Pizzarello et al., 2000). On Earth, fullerenes have been detected in sedimentary layers of the cretaceous-Tertiary (KTB) boundary in China and Bulgary 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 figure 2 we show a representation of their respective cations. PAHs have been postulated as potential carriers of the Unidentified Infrared Emission bands and of the diffuse interstellar bands which are ubiquitous in the interstellar medium (see e.g. Léger and Puget 1984). Several studies (Europhysics 2006) have shown that carbon ring based molecular forms are very stable against UV radiation. This is remarkable because the basic structures of life are essentially conformed by many such carbon rings making them rather stable against possible mutations.

2. Anomalous microvawe emision and the identification of naphthalene and anthracene in space

Several experiments dedicated to the study of the anisotropy of the cosmic microwave back-

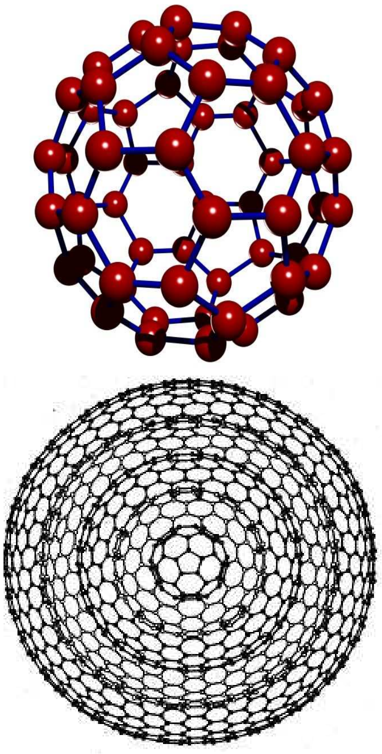

Fig. 1. Top: Representation of the fullerene C_{60}. **Bottom:** Representation of the buckyonion $C_{60}@C_{240}@C_{540}@C_{960}@C_{1500}$ with five layers.

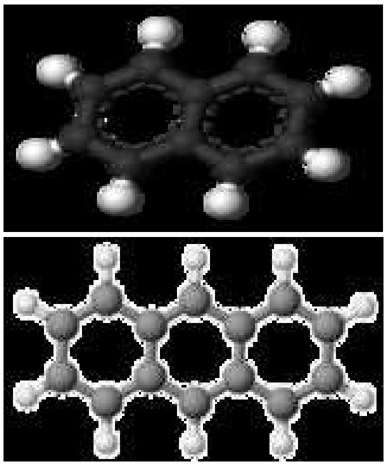

Fig. 2. Schemes of the naphthalene $C_{10}H_8^+$ (at the top) and anthracene cation, $C_{14}H_{10}^+$

ground have found evidence for microwave emission in the range 10–90 GHz correlated at high galactic latitudes with thermal emission from interstellar dust (COBE Kogut et al. 1996, Leitch et al. 1997; TENERIFE CMB experiment: de Oliveira-Costa et al. 1999, 2004). An explanation for this "anomalous" dust-correlated microwave emission based on electric dipole emission from fast rotating carbon-based molecules has been proposed by Draine & Lazarian (1998a,b). These models appear to reproduce the major features of the so-called anomalous microwave emission (Finkbeiner et al. 2004) but do not identify the actual carrier of the emission which is likely related to carbon-based molecules like PAHs and hydrogenated fullerenes which can spin faster than 10 GHz given the conditions of the interstellar medium.

The first unambiguous detection of anomalous microwave emission (AME) was reported in the Perseus star forming complex by Watson et al. (2005) who analysed data from COSMOSOMAS and WMAP. A good fit to the emissivity of the Perseus region (Watson et al 2005) was obtained considering model prescriptions by Draine and Lazarian (1998). The peak of AME is located at 22 GHz. A second firm detection was reported in the dark cloud LDN 1622 (Casassus et al. 2006). More recently many other AME regions have been detected, in particular several with the Planck satellite. The possibility that PAHs are carriers of AME can be explored with observations of absorption and/or emission bands of individual PAH molecules previously characterized in the laboratory.

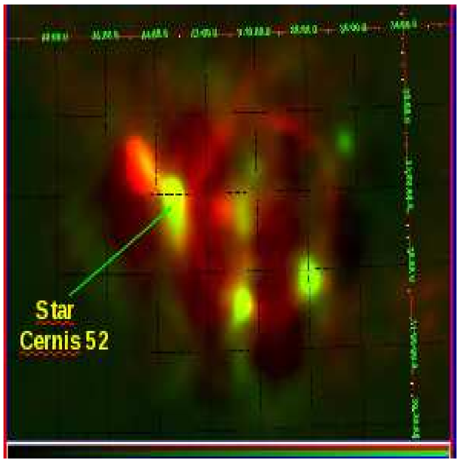

Fig. 3. Map of the Perseus molecular complex obtained by the interferometer VSA (33 GHz) superposed to IRAS 100 microns. The Star Cernis 52, spectral type A3V, is inside the most intense yellow spot

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2.1. Gas phase laboratory measurements of the most simple PAHs

Gas phase laboratory spectroscopy of naphthalene and anthracene cations, at low temperatures provide precise wavelengths, widths and oscillator strengths of bands (Pino et al. 1999, Romanini et al. 1999, Biennier et al. 2003) as required to search for these molecules in the interstellar medium. The strongest vibronic band for naphthalene cation the D2←D0 is at 6707.4 Å with a full width at half maximum of ∼12 Å (uncertainty ± 1Å) 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, with a precision of about 0.5 Å. 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. Sukhorukova et al. (2005) have studied the absorption spectrum of the anthracene cation (An^+) in supersonic jet cavity ring-down spectroscopy. They 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.

2.2. Observations

A search for transitions of these molecular species in the line of sight of regions with anomalous microwave emission has been conducted with four different instruments and telescopes: the SARG spectrograph (Gratton et al. 2001) on the 3.5 m Telescopio Nazionale

Galileo (TNG), at the Roque de los Muchachos Observatory (La Palma,Spain) ; ISIS at the 4.2 m William Herschel Telescope (WHT); the 2dcoudè cross-dispersed echelle (Tull et al.1995) on the 2.7 m Harlan J. Smith Telescope at McDonald Observatory (Texas, USA); and HRS at Hobby-Eberly Telescope 9m. McDonald Observatory (Texas, USA)

The selected star, Cernis 52, is a reddened star (excess colour E(B-V)=0.9, V=11.3 and spectral type star A3V) located at a distance of $230^{+135}{}_{-85}$ pc where most of the dust extinction is known to concentrate in the Perseus OB2 dark cloud complex. We determined as stellar parameters Teff = 8350 ± 200 K, logg (cms^{-2})= 4.2 ±0.4 dex, metallicity of [Fe=H] =-0.01 ±0.15 and atmospheric abundances of O, Mg, Si, S, Ca, and Fe. These stellar parameters are consistent with the star being in a pre-main-sequence evolutionary stage with an age < 9 Myr and a mass of 2 M_{solar}. This determination places the star at a similar distance than the young cluster IC 348. Radial velocity and proper motion are also consistent with membership in IC 348 (see, Gonzalez-Hernandez, et al. 2009). Since star Cernis 52 is either embedded or behind a cloud responsible for significant visible extinction (A_V=3) absorption bands caused by the intervening interstellar material were expected in the spectrum. The Na I doublet and the KI 7698 Å shows that the interstellar absorption towards Cernis 52 arises mostly in a discrete individual cloud. A high content of CH and CH^+ with values close to 2 x 10^{14} cm^{-2} was detected and observations of C_2 Phillips (2,0) and (3,0) bands has provided a determination of the kinetic temperature and density of the intervening gas (T= 40± 10 K n=250± 50 cm^{-3} (Iglesias-Groth 2010).

In Fig. 4 we present spectra of star Cernis 52 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 Figure 5) at 6494.2 Å (Jenniskens et al. 1994) that dominates the spectral region. Using the list of diffuse interstellar bands compiled by Hobbs et al. (2008) and synthetic spectra to account for any possible stellar photospheric features, Iglesias-Groth et al. (2008) 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.

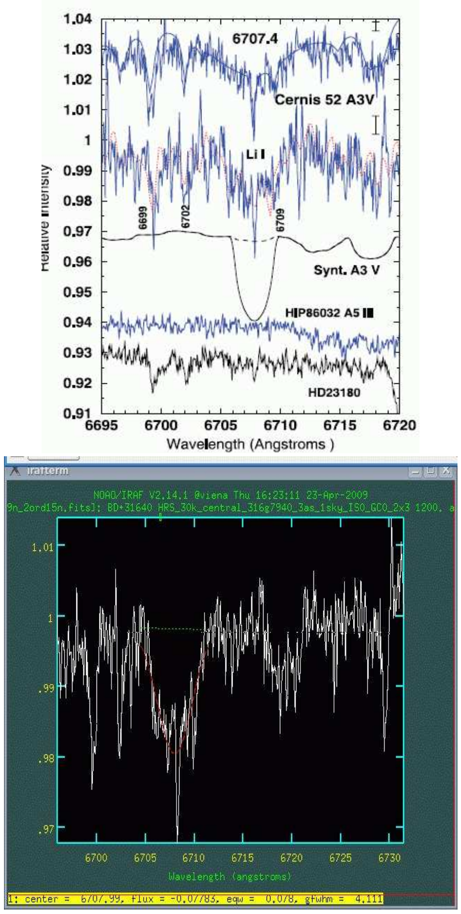

Fig. 4. Top: Two spectra at the top (blue lines) obtained with the 2D Coudé Spectrog. at Mc Donald Observatory . The red line in the second spectrum shows the lower resolution ISIS data obtained at the 4.2m WHT. The very narrow absorption feature at 6707.7 Å is due to interstellar lithium. (Iglesias-groth et al. 2008) **Bottom:** New 9m HET spectra of Cernis 52 confirming the existence of a broad band absorption at 6707 Å.

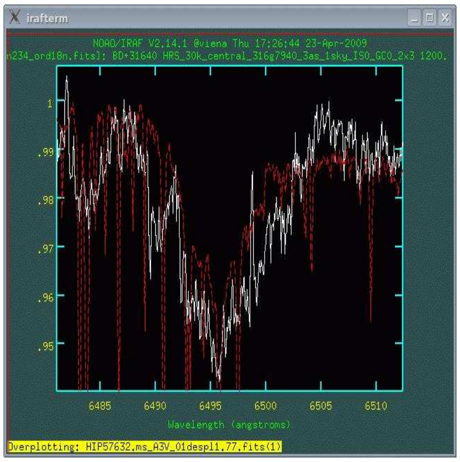

Fig. 5. A band at 6489 Å, which could be associated to the naphthalene cation. We show a comparison between Cernis 52 spectrum (white line) and a similar spectral type star (red line).

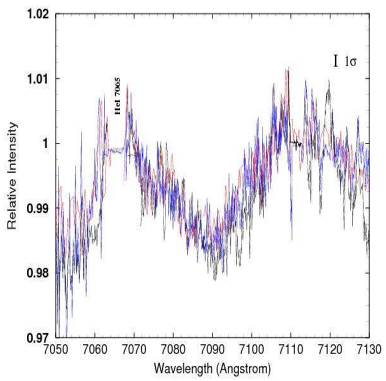

Fig. 6. Absorption band in star Cernis 52 which could be due to the anthracene cation.The spectr has been corrected for bands originating in the stellar photosphere, for known interstellar diffuse interstellar bands and for telluric bands (see details in Iglesias-Groth et al., 2010)

Spectra of Cernis 52 obtained at HET and at WHT also show a very broad band at 7088.8 ± 2.0 Å (see figure 6 and Iglesias-Groth et al. 2010) which is consistent with the strongest band measured in the laboratory for the anthracene cation by Sukhorukova et al. (2005).

2.3. Estimate of naphthalene and anthracene abundance

Adopting for the oscillator strength of the transition at 6707.4 Å a value of f=0.05 (Pino et al. 1999) and using the measured equivalent width of the band, it was derived for $C_{10}H_8{}^+$ a column density of $N_{np}{}^+$=1 x 10^{13} cm^{-2}. For the anthracene cation $C_{14}H_{10}{}^+$, the column density obtained was $N_{an}{}^+$=1.1 x 10^{13} cm^{-2}

Assuming a ratio C/H= 3.7 x 10^{-4} and hydrogen column density per unit interstellar absorption N_H/A_V = 2 x 10^{21} 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.

2.4. A connection between naphthalene and amino acids?

Chen et el al. (2008) reported on a laboratory experiment which combined naphthalene with water, ammonia and UV radiation at very low temperatures of order 15 K. They produced 13 amino acids which are involved in the development of life. The abundance of ammonia in Perseus is similar to that mentioned above for naphtahlene 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 there is a factory of amino acids and that naphthalene and other simple PAHs are key molecules for the formation in interstellar space of other molecular structures essential for life development. 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.

3. Fullerenes as carriers of UV bump extinction and their detection in space

The photoabsorption spectrum of large fullerenes and buckyonions is very poorly

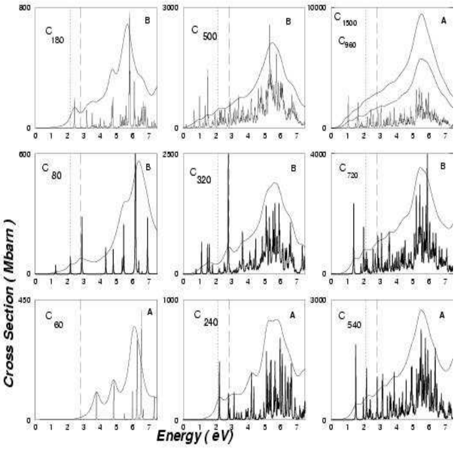

Fig. 7. Several theoretical spectra of fullerenes obtained with a PPP model.

known from the experimental point of view. In order to investigate the potential role of these molecules in interstellar absorption, as a first step it was necessary to use semiempirical models to compute the photoabsorption spectra of icosahedral fullerenes (see e.g. Iglesias-Groth 2004)

This theoretical approach was based in a Hückel and Pariser-Parr-Pople (PPP) model. It was necesary to consider the strong electronic correlation, because the screening effects associated to π electrons are relevant in these molecules. Use was made of the so-called random phase approximation to compute photoabsorption cross sections for some single fullerenes and buckyonions. Results can be seen in Fig. 7 and the details can be found in e.g. Iglesias-Groth et al., (2002) and Iglesias-Groth (2003).

3.1. UV bump

Measurements of the most intense feature associated to near UV/optical extincion of radiation in different lines of our Galaxy are presented in Fitzpatrick (1999). The wavelength of the peak extinction is in the range 2193 to 2157 Å, very stable and peak widths are in the range 0.96-1.55 eV. The usual reddening factor in the diffuse interstellar medium is R_V =3. In figures 8a and 8b theoretical fullerene spectra are plotted. We note the remarkably good fit to the extinction curves produced by the theoretical cross sections of the buckyonion C_{180}@C_{720} (solid line).

Based on comparisons with the observed UV bump in the extinction curves of the Galaxy, Iglesias-Groth (2004) inferred the porcentage of carbon locked in fullerenes and buckyonions in the ISM. The number density of these molecules resulted in the range 0.2-0.08 fullerenes per million hydrogen atoms. A value similar to what was measured in 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 be in the range n(C)/n(H) = 90-110 x 10^{-6} and that up to 25% of all the carbon could be locked in these molecules.

3.2. On the action of UV photons on hydrogenated fullerenes $C_{60}H_{36}$ and $C_{60}D_{36}$

Considering the high abundance of hydrogen in the universe and also the π electron cloud of fullerenes, we expect that hydrogenated fullerenes are widely spread in the interstellar medium. Recent laboratory studies (see the book by Cataldo and Iglesias-Groth 2010) have produced very interesting results which encourage the search for these molecules in interstellar space. In Fig. 9 we can see the very good fit of fully hydrogenated fullerene $C_{60}H_{36}$ to the Fitzpatrick UV extinction curve for reddening factor R_V=3.1. The electronic absorption spectrum of $C_{60}H_{36}$ was obtained in n-hexane. The absorption maximum is indicated by the vertical line and is located at 2175 Å with molar absorptivity of ε 217 = 17140 L cm^{-1} mol^{-1}. which corresponds to absorption cross sections of order 6500 Mbarn, about ten times higher than for C_{60}. It is therefore of the highest importance to measure transition bands of these molecules and carry out an extensive search in various phases of the interstellar medium. Additional laboratory spec-

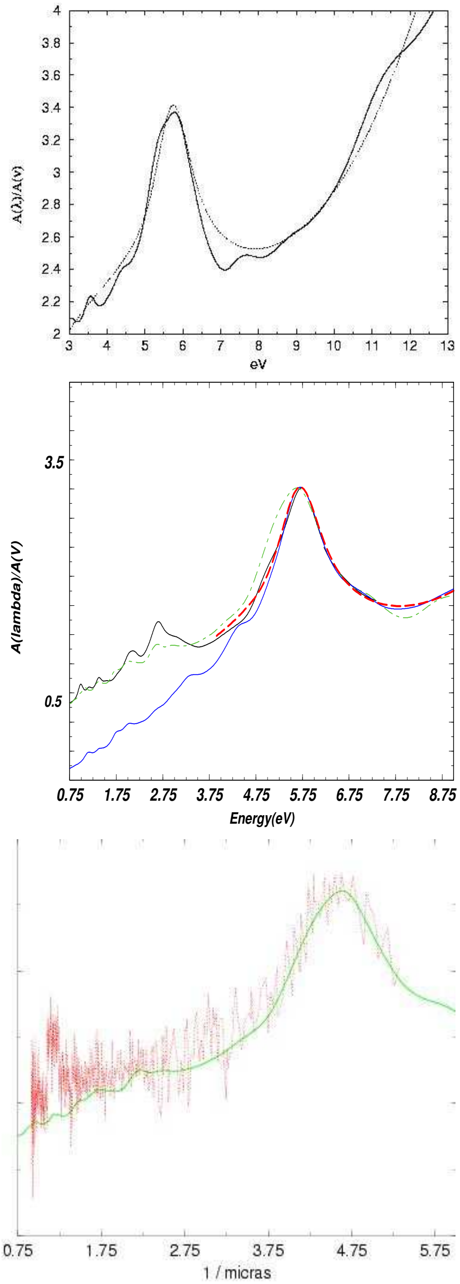

Fig. 8. **Top:** A comparison between theoretical spectra of the buckyonion,C_{60}@C_{180} and measurements of the UV bump. **Middle:** Best fit to the UV bump in the diffuse interstellar medium (R_V =3.1) obtained for a power law size distribution of fullerenes N(R) ~ $R^{-3.5\pm1.0}$. **Bottom:** A comparison between laboratory measurements for carbon onions (Red line: laboratory results obteined by Manisch et al. (2004) and theoretical calculations for a mixture of fullerenes (green line)

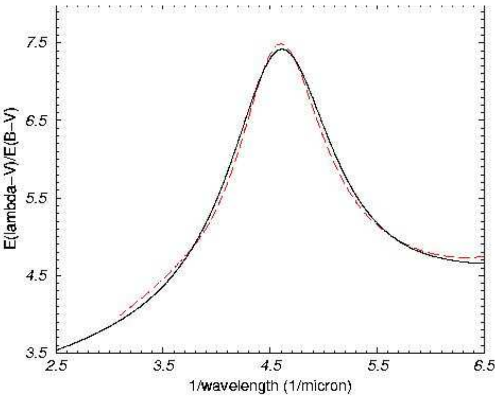

Fig. 9. Electronic absorption spectrum of $C_{60}H_{36}$ in n-hexane overplotted to the Fitzpatrick UV absorption curve (Cataldo and Iglesias-Groth,2009).

troscopy work is ongoing (Iglesias-Groth and Cataldo).

3.3. 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 (see e.g. Iglesias-Groth, Cataldo and Manchado, 2011) is central to the search and identification of fullerenes in space. The main IR features are shown in Fig. 10 for the C_{60} displaying active bands at 7.0, 8.5 , 17.4 and 18.9 μm. Measurements of absorptivities are also key to derive their abundances.

Camíet al. (2010) claimed the detection of fullerenes C_{60} and C_{70} in planetary nebulae. This detection has generated a lot of momentum in the field and additional detections of fullerenes in planetary nebulae have been reported (see e.g. by Garcia-Hernandez et al. 2011). In Fig. 11, we show the spectra for several planetary nebulae with the transitions abscribed to fullerenes. It seems that the late stages of the evolution of stars like the Sun 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 originated in planetary nebulae progressively populate the interstellar medium.

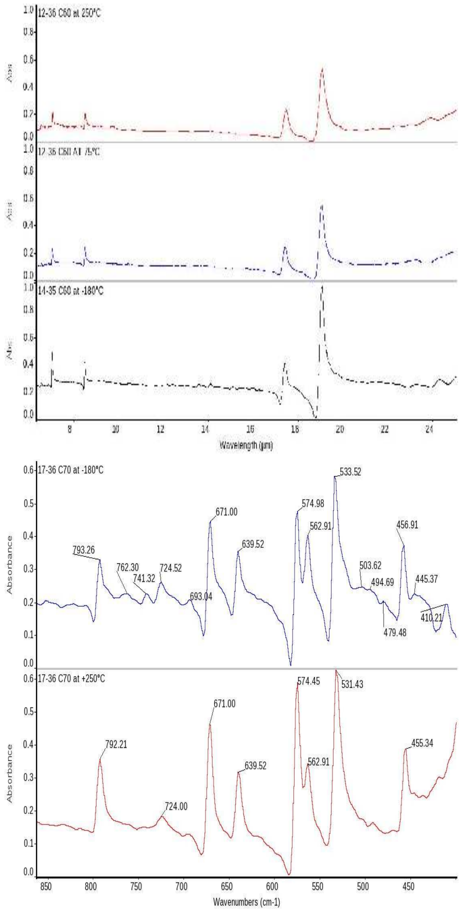

Fig. 10. top: Laboratory spectroscopy of mid-IR active bands of C_{60} at the top, and of C_{70} (bottom) at low temperatures (Iglesias-Groth et al. 2011).

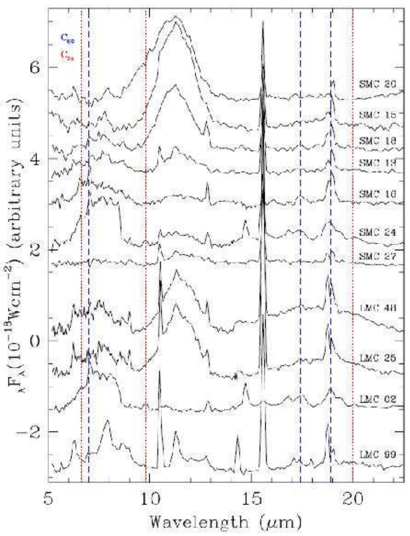

Fig. 11. Spitzer spectra for several Planetary Nebulae in the Magellanic Clouds with emission lines of fullerenes (from García-Hernandez et al. 2011)

4. Conclusions

i) There is evidence for the most simple PAHs (naphthalene and anthracene) in the intervening translucent cloud (E(B-V)=0.9) toward star Cernis 52 in the Perseus molecular complex. The derived column densities for the cations of these two molecules are 1 x 10^{13} 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.

ii) A study of C_2 population levels gives for the intervening cloud: Kinetic gas temperature of 40 ±10 K and density of collisional particles n=250 ± 50 cm^{-3}. This would be the first physical characterization of a cloud with anomalous microwave emission.

iii) This Perseus line of sight is among the most carbon rich so far detected in translucent clouds N(C_2)= 10 x 10^{13} cm^{-2}. It is also rich in ammonia. Well suited for production of interstellar amino acids. A search for transitions of glycine with the 30 m IRAM telescope is in progress.

iv) 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 fulleranes $C_{60}H_{36}$ and $C_{60}D_{36}$ 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 ubiquituous molecules in interstellar space.

v) The recent detection of fullerenes in planetary nebulae of our Galaxy and in the Magellanic Clouds adds support to the hypothesis 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 indentified yet in space, but could be a major carbon reservoir.

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