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Fullerenes, PAHs, Amino Acids and High Energy Astrophysics

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Abstract

We present theoretical, observational and laboratory work on the spectral properties of fullerenes and hydrogenated fullerenes. Fullerenes in its various forms (individual, endohedral, hydrogenated, etc.) can contribute to the UV bump in the extinction curves measured in many lines of sight of the Galaxy. They can also produce a large number of absorption features in the optical and near infrared which could be associated with diffuse interstellar bands. We summarise recent laboratory work on the spectral characterisation of fullerenes and hydrogenated fullerenes (for a range of temperatures). The recent detection of mid-IR bands of fullerenes in various astrophysical environments (planetary nebulae, reflection nebulae) provide additional evidence for a link between fullerene families and diffuse interstellar bands. We describe recent observational work on near IR bands of $C_{60}{}^{+}$ in a protoplanetary nebula which support fullerene formation during the post-AGB phase. We also report on the survival of fullerenes to irradiation by high energy particles and gamma photons and laboratory work to explore the chemical reactions that take place when fullerenes are exposed to this radiations in the presence of water, ammonia and other molecules as a potential path to form amino acids.

Keywords: ISM - molecules: fullerenes, PAHs - nebulae.

1 Introduction

The discovery of fullerenes in 1985 when trying to reproduce the chemistry of the atmospheres of red giant stars (Kroto et al., 1985) led to the identification of the third allotropic form of carbon. The most abundant fullerene molecule produced in those experiments was C_{60}, a hollow molecule with 60 carbon atoms distributed in 12 pentagons and 20 hexagons (truncated icosahedron symmetry). Comparetively, we recall Polycyclic Aromatic Hydrocarbons (PAHs) are planar molecules consisting of carbon rings and hydrogen, these rings are similar to benzene. The naphthalene and anthracene are the most simple PAHs with two and three benzene rings, respectively. These molecules 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). Similarly, fullerenes and their hydrogenated forms, are potential carriers of the interstellar bands. Several studies have shown that carbon ring based molecular forms are very stable against UV radiation. This is remarkable because the basic structures of amino acids and in general of the molecular basis of life are essentially conformed by such carbon rings making them rather stable against possible mutations. Laboratory work byChen et al. (2008) have demonstrated that under strong UV radiation a mixture of naphthalene, ice and methane at low temperature, it is possible to form a large variety of amino acids. Fullerenes with carbon atom number of 20 (m^2 + n^2 + nm) where n and m are integers have icosahedral symmetry groups I_h and exhibit high stability. These molecules are very stable against UV/gamma radiation and collisions with other particles. Fullerenes have been detected in carbonaceou chondrites, a type of meteorite that originated in the early Solar System,with abundances of the order of 0.1 ppm (Pizzarello et al. 2000). On Earth, fullerenes have been detected in sedimentary layers of the Cretaceous-Tertiary boundary (KTB) in China and Bulgaria and in the mineral shunghite of the region of Karelia (Russia). In the various phases of the interstellar medium it is likely the presence of both, fullerenes and hydrogenated fullerenes, the so-called fulleranes (C_nH_m). A review of the properties of fullerenes and fulleranes can be found in Cataldo & Iglesias-Groth (2009, 2010). Here, recent developments on the astrophysical search for ionised fullerenes and on the properties of fullerenes when exposed to high energy radiation.

2 Astrophysical Searches for Fullerenes

Theoretical work on the photoabsorption spectrum of icosahedral fullerenes suggests that these molecules can be responsible of the strongest feature in the interstellar extinction curve, the UV bump at 2175 Å. For large fullerenes and buckyonions the experimental photoabsorption spectrum is very poorly known and the potential role of these molecules in interstellar absorption has been explored on a theoretical basis (see, for example, Iglesias Groth et al., 2002, 2003). In these works a theoretical approach to the photoabsorption specturm was based on a Hückel and Pariser-Parr-Pople (PPP) model. Fits of the computed spectra to measurements of the interstellar extinction in the UV/Optical for different lines of sight in our Galaxy (Fitzpatrick, 1999) were obtained (see details of the model can be found in Iglesias-Groth, 2004). Very good fits to the extinction curves are provided by the photoabsorption cross sections computed for both individual fullerenes and buckyonions. The comparison of these models with the observed UV bump leads to an estimate of the number density of these molecules (in the range 0.2-0.08 ppm) and of the percentage of carbon locked in fullerenes and buckyonions in the ISM (Iglesias-Groth 2004, 2007) which depending the size distribution of these molecules could reach up to 25 % of all carbon in the ISM.

Fullerenes C_{60} and C_{70} present active vibrational bands in the near infrared (3-20 μm) which have been key for their identification in planetary nebulae, reflection nebulae and post-AGB stars (see e.g. Cami et al. 2010, Zhang and Kwok, 2011). Experimental measurement of the molar absorptivity for these infrared transitions is essential for the determination of fullerene abundances in such astrophysical contexts. Laboratory work is being conducted to measure the dependence of the molar absorptivity of fullerene infrared bands with temperature from approx. 100 K to 500 K to cover a variety of conditions in the interstellar medium (Iglesias-Groth et al. 2011).

2.1 New results on ionised fullerenes: C_{60}^+

Recently, it was reported the detection of mid-IR vibrational transitions of the fullerene C_{60} in a carbon rich protoplanetry nebula, IRAS 01005+7910 (Zhang and Kwok 2010). We recorded the spectrum of this object between 5500 and 10000 Å with resolving power of 57,000 and detected two bands at 9577 and 9632 Å which are consistent with laboratory measurements of the C_{60} cation (See figure 1. Iglesias-Groth and Esposito, 2013). If these two bands were produced by C_{60}^+ in the material surrounding the central post-AGB star we could infer that $\sim$ 1 % of carbon is trapped in this ionized form of fullerenes and that the cation abundance is much higher than that of the neutral fullerene species. It appears that ionized fullerene species in this protoplanetary nebula are significantly more abundant than in neutral form, which is consistent with the predictions of ionization models of PAHs (Bakes and Tielens 1995, Salama et al. 1996) for irradiated clouds near a hot star.

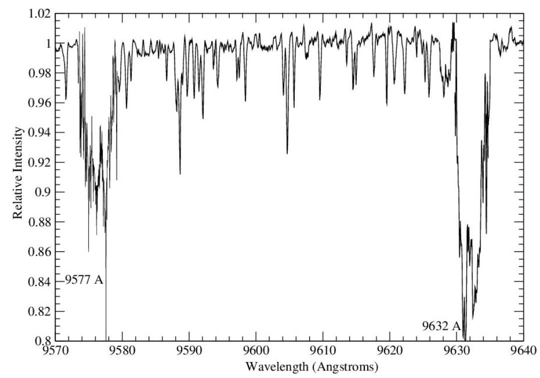

Figure 1: The two near IR bands in the spectrum of IRAS01005+7910, attributed to the cation of C_{60} (Iglesias-Groth & Esposito 2013)

These observations provide additional evidence for the presence of fullerenes in protoplanetary nebulae and suggest that a significant production takes place in this late stage of stellar evolution. Mid-IR bands of C_{60}^+ could be present in the 7-20 μm spectrum of IRAS 01005+7910 and are also likely to be detected in the spectra of planetary nebulae. Accounting for the ionized species of fullerenes appears necessary in nebulae with a nearby source of ionizing photons. A caveat: the derived abundances and excitation temperatures of planetary nebulae with claimed detections of fullerenes may have to be revised if indeed there is a significant contribution of cations to the formation of the bands used in these analyses. High resolution spectroscopy will be required for a reliable determination of the relative abundance of neutral and ionized fullerenes in these objects.

2.2 The stability of C_{60} and C_{70} towards copuscular and γ radiation

The stability of C_{60} and C_{70} fullerenes in the interstellar medium and embedded in meteorites and comets has been investigated with γ irradiation and with He^+ ion bombardment. The radiation dose generated by radionuclides decay expected to be delivered to fullerenes buried at a depth of $\geq$ 20 m in comets and meteorites is about 3 MGy per million years. We have exposed fullerenes to various radiation doses and found that these molecules are by far resistant to this type of radiation. Laboratory measurements on the concentration of samples of fullerenes exposed to strong radiation doses indicate that these molecules can survive millions of years inside comets and meteorites (Cataldo et al. 2009). This provides a natural explanation to their presence inside certain carbonaceous chondrites. In this laboratory experiments, fullerenes were also exposed to intense particle bombardment. Fullerens adsorbed or deposited on the surface of carbon are exposed to cosmic ray bombardment with estimated doses of radiation comprised between 30 and 65 MGy per 10^6 years. We carried out experiments to test the survival of both C_{60} and C_{70} fullerenes and found that the complete amorphization occurs at about a radiation dose of 250 MGy. Thus we infer that after 4-8 millions of years exposure to cosmic rays it is expected to producce a complete amorphization (Cataldo et al. 2009).

2.3 Gamma Radiolysis of C60 fullerene in water and water/ammonia mixtures; relevance of fullerenes fate in ices of interstellar medium

In order to explore the potential astrochemical role of fullerenes,Iglesias-Groth et al. (2013) have explored the radiolysis of fullerene C_{60} dispersed in H_2O, H_2O/NH_3, H_2O/methanol and H_2O/NH_3/methanol under gamma radiation doses of 250 and 500 kGy. It was found that C_{60} originally insoluble in the above mentioned hosting matrix became soluble as a consequence of multiple hydroxylation and oxidation reaction produced by the free radicals generated by the radiolysis of the hosting matrix. The changes undergone by C_{60} were studied by infrared spectroscopy (FT-IR) and by electronic absorption spectroscopy. The astrochemical consequences of the present study are that C_{60} ejected in the interstellar medium for instance from protoplanetary and planetary nebulae can condense together with water and other ices in dense molecular clouds. Under the action of high energy radiation C_{60} reacts with the free radicals generated from the matrix where it is embedded it is solubilized and consequently its carbon content becomes available for further abiotic processes of synthesis of molecules of astrobiological interest. The behavior of C_{60} appears comparable to that of common PAHs which are also hydroxylated and oxidized under similar conditions.

3 Stability Toward High Energy Radiation of Non-Proteinogenic Amino Acids: Implications for the Origins of Life

In order to investigate the response of amino acids to high energy radiation, Cataldo et al. (2013) have taken a series of non-proteinogenic amino acids, most of them found frequently in carbonaceous chondrites, and exposed them to solid state radiolysis in vacuum to a total radiation dose of 3.2 MGy. This corresponds to 23% of the total dose expected to be taken by organic molecules buried in asteroids and meteorites since the beginning of the Solar System in 4.6 x 10^9 years. The radiolyzed amino acids where studied by FT-IR spectroscopy, Differential Scanning Calorimetry (DSC) and by polarimety and Optical Rotatory Dispersion (ORD). It is found that an important fraction of each type of amino acid is able to "survive" to the massive dose of radiation and also the enantiomeric excess is partially preserved. Based on these results it is concluded that it is not a surprise to find amino acids even in enantiomeric excess in carbonaceous chondrites.

4 Conclusions

The astrochemical consequences of the recent discoveries of fullerenes in various astrophysical contexts are not fully understood yet. Fullerenes are far resistant to high doses of gamma radiation and bombardment by high energy particles. It is likely that fullerenes ejected in the interstellar medium,for instance from protoplanetary and planetary nebulae can condense together with water and other ices in dense molecular clouds. Under the action of high energy radiation fullerenes react with the free radicals generated from the matrix where they are embedded. If C_{60} is trapped in water ices it is hydroxylated and oxidized by the radiolysis products of water. The oxidation of C_{60} makes this molecule hydrophilic and hence soluble in water. The same phenomenon occurs in water/ammonia, in water/methanol and in water/ammonia/methanol mixtures. Thus, C_{60} which in the solid state displays a considerable radiation resistance, when embedded in radiolytic sensitive matrices like those just mentioned, it reacts swiftly, it is solubilized and consequently its carbon content becomes available for abiotic processes of synthesis of other molecules of astrobiological interest. This compares well with the behavior of PAHs which are also hydroxylated and oxidized by the free radicals produced by the radiolysis of the hosting matrix (Gudipati & Allamandola 2006, Ricca et al. 2007, Ashbourn et al. 2007, Cuylle et al. 2012, Nuevo et al. 2012).

It is known that PAHs and ices exposed to strong UV radiation can lead to the formation of amino acids. Fullerenes exposed to gamma radiation provides a path for a variety of astrochemical reactions which have to be explored in much more detail, which ultimately could lead to the formation of amino acids, which are likely to survive under the intense gamma radiation. Further laboratory work is essential to explore the role of high energy radiation in astrophysical sources and carbon molecules as a route to prebiotic molecules.

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