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FULLERENES AND ASTRONOMY

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Abstract. The astrophysically motivated investigations of the chemistry of carbon stars resulted with the discovery of the C_{60} molecule, first and the most interesting representative of fullerenes molecules. Here is presented a review of astronomical researches connected with fullerenes as for example the search for interstellar and circumstellar ones or presence of such molecules in meteorites brechias of impact craters on Earth and impact traces on spacecrafts. Also, their connection with the problem of the diffuse interstellar and circumstellar absorption lines is discussed. Particular attention is payed to the search for polyynes in interstellar space which resulted in the formulation of investigation of chemistry of carbon stars and in discovery of fullerenes.

1. INTRODUCTION

Possibilities which provides the new C_{60} molecule and variety of the possible new compounds with this molecule as the basis, will result possibly in the birth of a new chemistry. The basic impulse, resulting with the discovery of this new molecule, came from astrophysics, from the attempt to explain the origin of unexplained bands and lines in emission and absorption spectra from interstellar space. It was first of all the intensive absorption band at 217 nm. It was supposed that its origin is connected with small graphite particles (Hufman, 1977). Also a group of interstellar diffuse absorption lines in the visible part of the spectrum, was an unexplainable puzzle for more than 70 years (Hufman, 1977; Herbig, 1975; Krätschmaher et al, 1990a). There were as well several intensive emission bands, with polycyclic aromatic hydrocarbons as carriers (Léger et al, 1984; Allamandola et al, 1985).

We will present shortly here, the development of investigations related to the astrophysical spectra, motivating researches resulting in the discovery of fullerenes.

2. INTERSTELLAR MOLECULES

The development of interstellar spectroscopy was particularly stimulated by the question of the origin of life on Earth. Chemists and biologists belived that a lot of complex organic molecules in the warm sea of the young Earth is needed for that. In 1923., russian scientist A. I. Oparin, supposed that the spontaneous creation of the first primitive single-celled organisms two billion years ago, was the result of the accumulation of biologically important molecules in microscopic coloidal droplets. But which is the origin of such complex organic molecules? Charles Townes, who in the 1964 obtained the Nobel Prize for the invention of the maser, discovered with coworkes (Cheung et al, 1968) in 1968 the ammonia molecule (NH_3) in space. The ammonia molecules in interstellar space, coming from a dense cloud lying in the direction of the galactic center, were discovered with the help of the microwave radiation with a wavelength of 1.25 cm, observed by the Hat Creek radio telescope. It was the first polyatomic molecule (a molecule with more than two atoms) found in the interstellar space, and it was only the beginning. During the next three years approximately twenty molecules have been identified in the interstellar space, water, formaldehyde, hydrogen cyanide, and acetylene among them. The astrochemistry was born, and it was the beginning of the identification of more and more complex organic molecules in space.

It was assumed that the majority of the observed molecules originate in a series of reactions between molecular ions and molecules, combined with reactions on the surfaces of interstellar dust particles (Turner, 1989).

3. CARBON ATOM CHAINES - POLYYNES IN INTERSTELLAR SPACE

The new breakthrough in the investigation of the interstellar polyatomic molecules was when Barry Turner, an astronomer at the National Radio Astronomy Observatory at Green Bank in West Virginia detected microwave signals identified as due to cyanoacetylene HC_3N. The fact that interstellar clouds where such complex organic molecules have been found, are in the same time the places of the condensation of new stars with planetary systems, was in favour of the hypothesis that complex organic molecules, needed for the creation of life, were present in the warm sea of the young Earth, and that they are maybee of cosmic origin. The question was if even more complex molecules are present in interstellar space. Namely the last identified complex molecule belonged to the carbon chain molecules of the general form HC_nN (where n is equal to or larger than three), named cyanopolyynes (see e. g. Bell et al, 1982; Čelebonović, 1992). But in order to answer on this question one needs the good knowledge of their microwave spectra, and exotic cosmic conditions held the promise of the presence of molecules which are not present on Earth and which have not been synthesized in laboratories.

In 1975, Harry Kroto, a young chemistry lecturer at the University of Sussex, who was an expert in microwave spectroscopy, was very interested by the problem of organic molecules in space. Together with his colleague David Walton, he decided to investigate the existence of cyanobutadiyne (HC_5N) in interstellar clouds. An undergraduate student Antony Alexander, was engaged to synthesize cyanobutadiyne under Kroto and Walton's supervision, in order to measure its microwave spectrum and search for similar signals in space. Alexander synthesized cyanobutadiyne and measured its microwave spectrum between 26.5 and 40.0 gigahertz (Alexander et al, 1976). Than, Kroto asked his colleague Takeshi Oka from Ontario in Canada, and Oka with Lorne Avery, Norman Broten and John MacLeod, with the help of Kroto's data discovered HC_5N in Sagittarius B2 using the 43-metre diameter radio telescope at Algonquin Park in Ontario (Avery et al, 1976).

Does in interstellar space exists and more complexe molecule cyanohexatriyne HC_7N? Kroto and Walton engaged a new graduate student Colin Kirby to synthesize this molecule. It was not an easy task but after a lot of difficulties it was done (Kirby et al, 1980) and the result enabled to identify and this molecule in space (Kroto et al, 1978). How far one can continue in this manner? It was obvious that an attempt to synthesize further members of the series will be an extremely difficult task. But Oka suggested to estimate the microwave spectrum of HC_9N molecule by extrapolation on the basis of the properties of preceeding members of the series. This attempt was successful and this molecule (Broten et al, 1978) and soon $HC_{11}N$ (Bell et al, 1982) as well, joined to the list of molecules identified in space.

4. CHEMISTRY OF THE CARBON STARS AND DISCOVERY OF FULLERENES

It was of little probability that chains of carbon atoms originate in ion - molecule reactions as it is with simpler molecules. Polyynes and small carbon clusters have been found not only in interstellar clouds (C_3) but as well in the shell around carbon star IRC+10^o216 (Turner, 1989). Kroto (1981) assumed that the source of carbon chain molecules and clusters are carbon rich red giant stars, which by radiation pressure pour in interstellar space dust containing carbon grains, mostly in the form of amorphous graphite. Kroto (1982) supposed that carbon chains may be synthesized in reactions between carbon clusters made by the vaporization of graphite from carbon grains, and simpler molecules. Together with Robert Curl and Richard Smalley, Kroto formulated a project on the simulation of carbon star chemistry and included also students Jim Heath and Sean O'Brien. The result of this project was the synthesis of C_{60} (Kroto et al, 1985) which led to the Nobel prize for Chemistry for Kroto, Curl and Smalley in 1996. They showed that by laser vaporization of graphite, carbon clusters C_n with n from 1 up to 190 are formed, with C_{60} as dominant one (Kroto et al, 1987). Due to the similarity of the structure of C_{60} and domes constructed by the architect Buckminster Fuller, such clusters obtained the name buckminsterfullerenes or simply fullerenes.

It is interesting that Andrew Kaldor from an oil company in New Jersey obtained molecules C_{60} and C_{70} during plasma graphite formation, still in 1984, but has not remarked and identified them on the spectrogram (Cheush, 1999).

Krätschmer et al. (1990)demonstrated that in sooth obtained by electric arc with graphite electrodes with helium as the working gas, are present C_{60} and C_{70}. The fullerenes are a new cristal allotropic modification of the carbon, besides graphite and diamond.

We have also hiperfullerenes with onion type structure where e.g. a C_{60} molecule is within C_{240}. This one within C_{540} and this one within C_{960}. Such multishell fullerenes or buckyonions suggested by Kroto and McKay (1988) are firstly synthetized in laboratory by Ugarte (1992, 1993)

In the spherically symmetrical vacuum hole within a C_{60} molecule, one can put different atoms and ions. For example Weiss et al. (1988), obtained with an arc

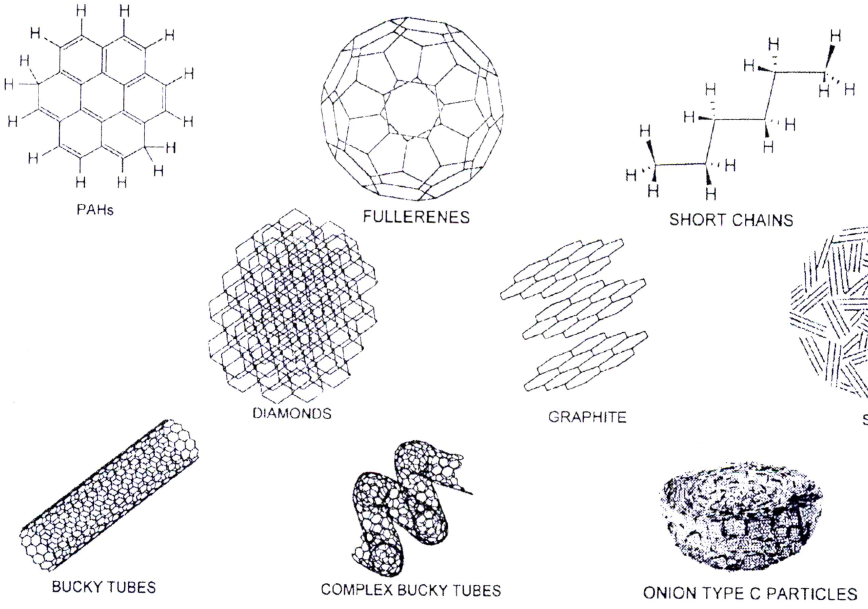

Figure 1: Some of the various forms of carbon that are likely present in gaseous and solide state in the interstellar matter and in solar system material (from Ehrenfreund and Charnley, 2000).

where kalium nitrate has been added to graphite electrodes, that some of K atoms finished in C_{60} molecules and the new compound is named K@C_{60}. One of interesting properties of complex carbon forms is also possibility of six angles graphite structure to form nanotubes (see Ebbesen and Ajayan, 1992). Consequently, carbonaceous dust in the interstellar medium may show strong diversity. In Fig. 1 (from Ehrenfreund and Charnley, 2000) are shown the chemical structures of some carbon compounds that are likely present in space.

Later, C_{60} and C_{70} have been identified on Earth in shock produced brechias of the Sudbury impact structure in Ontario (Becker et al, 1994), and in the geological strata of the Cretaceous-Tertiary and the Permian-Triassic boundary layers, associated with bolide impacts (Becker, 1999; Becker et al, 2000, 2001, Botta and Bada, 2002; Pizzarellos et al, 2001). Fullerenes have been detected as well in an impact crater on a spacecraft (Di Brozolo et al, 1994) and in meteorites (see de Vries et al, 1993; Becker et al, 1993; Foing and Ehrenfreund, 1997, Becker and Bunch, 1997; Becker, 1999 and Becker et al. 1999).

The presence of carbon onions in acid residues of the Allende meteorite (see e.g. Ehrenfreund and Charnley, 2000)suggested that higher fullerenes or nanotubes may be present in meteorites. In this meteorite Becker et al. (1999) have found C_{100} and C_{400}. The higher fullerenes have also been isolated from the Murchinson carbonaceous residue, and measurements of noble gases (helium, neon, and argon) in both the Murchinson and Allende fullerenes by Becker et al. (2000) indicate that these molecules are extraterrestrial in origin.

It was supposed that hydrogen may inhibite the fullerenes growth mechanisms so that one should search C_{60} in hydrogen depleted space regions (Goeres and Sedlmayr, 1992). It has been shown in Gerhardt et al. (1987) however, that fullerenes may be formed when H and O are present. It has been pointed out as well (Kroto and Jura, 1992) the formation of fullerenes in space in relation to carbon dust.

Fullerenes may be formed in small amounts in envelopes of R Coronae Borealis stars (Goeres and Sedlmayr, 1992). Theoretical models show the possible formation of fullerenes in the diffuse interstellar gas with the help of formation of C_2-C_{10} chains from C^+ insertion, ion-molecule reactions, and neutral-neutral reactions (Bettens and Herbst, 1996, 1997).

Interstellar hydrogenated fulleranes (molecules such as family $C_{60}H_m$, m=1,2,...) have been discussed in Webster (1995), and C_{60}^+H was proposed to be most abundant of such molecules in space (Kroto and Jura, 1992). Iglesias-Groth and Breton (2000) suggested that suitable astronomical targets to search for fullerenes are not only carbon stars but also post-AGB stars, protoplanetary nebulae and dusty regions in the Galaxy.

5. DIFFUSE INTERSTELLAR BANDS, SPECTRA AND FULLERENES

One of the great unsolved astrophysical problems is the problem of the identification of the Diffuse Interstellar Bands (DIB) carriers (see Herbig, 1995 for a review). It was proposed in Kroto et al. (1985) and Leger et al. (1988) that the ion C_{60} is a possible DIB carrier. Foing and Ehrenfreund (1994, 1997) searched for C_{60}^+ in the diffuse medium in the infrared. They found two diffuse bands at 957.7 nm and 963.2 nm, in the spectra of 7 carbon rich stars, and in 1997 they proved that the positions of these bands in stellar spectra are coincident within 0.1 percent with laboratory measurements of C_{60}^+ in neon matrix, obtained by Fullara et al. (1993). This was the first evidence of the possible presence of C_{60}^+ around carbon rich stars.

This result motivated Moutou et al. (1999) to use ISO data to search for 7.1 and 7.5 micrometers vibrational emission lines of C_{60}^+ in NGC 7023. They placed an upper limit on C_{60}^+ in NGC 7023 of ¡ 0.3% of interstellar carbon (Moutou et al, 1999; see also Sellgren, 2001). Searches for C_{60} in the interstellar matter throught its UV absorption band at 386 nm, have placed limits of ¡ 0.01% of cosmic carbon abundance in C_{60} (Snow and Seab, 1989; Somerville and Bellis, 1989).

Garcia-Lario et al. (1999) attribute the 21 micrometer dust features observed in the C-rich protoplanetary nebula IRAS 16594-4656 to fullerenes, which may be formed during dust fragmentation. However, many different carrier species have been proposed for this broad strong emission band (e.g. Webster, 1991, 1993, 1995; Hill et al, 1998, see also Ehrenfreund and Charnley, 2000).

Another family of fullerenes which could be relevant to clarify the origin of the DIBs and the unidentified infrared emissions in astronomical objects are the buckyonions or multishell fullerenes (see e.g. Iglesias-Groth and Breton, 2000).

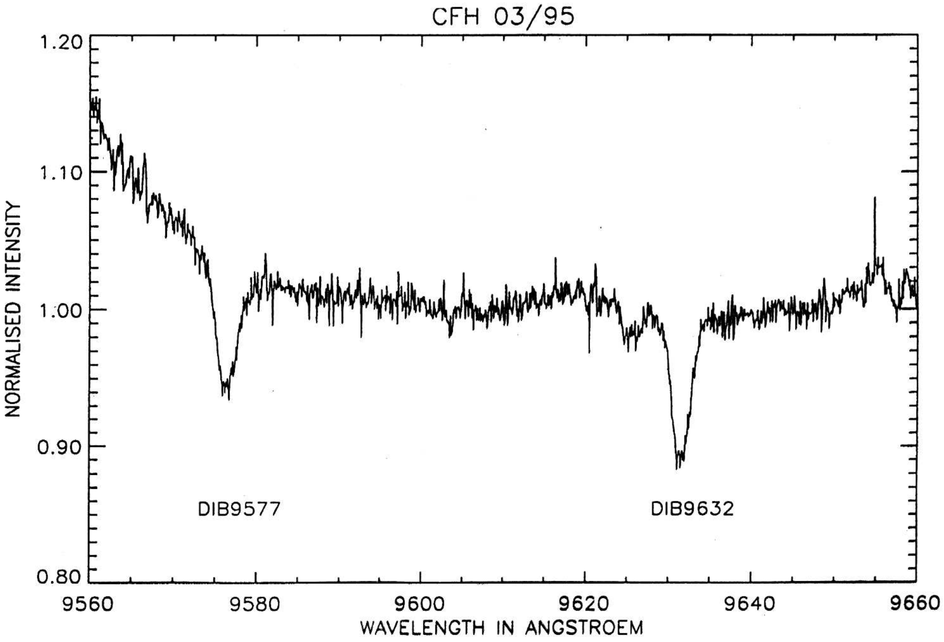

Figure 2: Telluric corrected spectrum of HD183143 carbon rich star observed by Canadian French Telescope at Hawai (CFT) in March 1995. The two DIB's at 9577 and 9632 Å are confirmed with the same width of 2.86 Å consistent with the C_{60}^{+} assignment and expected rotational contour broadening with temperature 60±10 K. This Fig. is from Foing and Ehrenfreund (1997) article with the first possible confirmation of the presence of C_{60}^{+} ion in carbon rich star spectra.

It was demonstrated as well that doping of C_{60} with C_{70} provokes interesting changements in the spectrum. It has been stated in Pichler et al. (1991), that the optical absorption spectrum of the C_{60}/C_{70} mixture is qualitatively similar with the interstellar extinction curve for photon energies less than 4 eV, so that carbon clusters might be present in space as well as C_{60} and C_{70} mixture. In any case, the investigation of the spectral properties of the C_{60} and C_{70} mixtures in different proportions, with eventual addition of other fullerenes, will contribute to to our knowledge on the fullerene abundance in space.

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