Laboratory study of carbonaceous dust and molecules of astrochemical interest

F Cataldo\textsuperscript{1,2}, D A Garcia-Hernandez\textsuperscript{3,4}, A Manchado\textsuperscript{3,4,5} and S Kwok\textsuperscript{6}

\textsuperscript{1} Actinium Chemical Research srl, Via Casilina 1626A, 00133 Rome, Italy
\textsuperscript{2} INAF-Osservatorio Astrofisico di Catania, Via S. Sofia 78, 95123 Catania, Italy
\textsuperscript{3} Instituto de Astrofisica de Canarias, Via Lactea s/n, 38205 La Laguna, Spain
\textsuperscript{4} Departamento de Astrofisica, Universidad de La Laguna (ULL), 38206 La Laguna, Spain
\textsuperscript{5} Consejo Superior de Investigaciones Cientificas, Madrid, Spain
\textsuperscript{6} Laboratory for Space Research, Faculty of Science, The University of Hong Kong, Hong Kong, China

E-mail: \textsuperscript{1} franco.cataldo@fastwebnet.it

Abstract. In this paper are reviewed some research works dedicated to the study of carbonaceous dust and molecules of astrochemical interest. First of all it is discussed the carbon arc through which it is possible to produce carbon soot and fullerenes under helium but also many other different products just changing the arcing conditions. For example, when the carbon arc is struck in an hydrocarbon solvent it is possible to produce and trap polyynes in the solvent. Monocyanopolyynes and dicyanopolyynes can be produced as well by selecting the appropriate conditions. Amorphous carbon soot or partially graphitized carbon black can be produced with the carbon arc. Fullerenes were found in space thanks to the reference infrared spectra and the absorption cross sections which were determined in laboratory. Fullerenes are readily reactive with hydrogen yielding fulleranes the hydrogenated fullerenes. Furthermore fullerenes react with PAHs and with iron carbonyl yielding adducts. All these fullerene derivatives were synthesized and their reference spectra recorded in laboratory. It was proposed that petroleum fractions can be used as model substrates in the explanation of the carriers of the AIB (Aromatic Infrared Bands) observed in protoplanetary and planetary nebulae and the UIE (Unidentified Infrared Bands) found in the interstellar medium.

1. Introduction
In recent years we were fascinated and involved in the research on topics of astrochemical interest which developed on laboratory scale. In most cases the ambition was to reproduce as closer as possible the astrophysical conditions were carbonaceous dust and molecules are formed and detected for instance by radioastronomy or by infrared spectroscopy.

2. Carbon vapor as the key source of carbon-rich molecules and carbon dust
It is well known that huge amounts of carbon dust are released in the space by carbon rich stars [1-4]. The elemental carbon is accompanied by carbon rich molecules like polyynes and cyanopolyynes [1-4]. Please refer to the contributions of Millar and Chernicharo to this conference issue for further details and references. The key molecule responsible for the formation of carbon dust and other molecules in circumstellar environment is C\textsubscript{2}. This molecule can be viewed as an acetylenic diradical •C≡C•and can be produced in laboratory for example with
a carbon arc [5] or by laser ablation of carbonaceous targets [6]. The simplest approach to produce C\(_2\) in laboratory is through a carbon arc and C\(_2\) can be recognized by its electronic absorption spectrum [7]. A carbon arc is ignited when two carbon electrode are put in contact and then slightly separated each other. The intensity of the arc is governed by the electric current flowing in the arc. In our experiments the minimal electric current used was about 10 A in the submerged electric arc [8], but it can reach 100 A in the production of fullerenes, when the arc is ignited in an helium atmosphere [9]. Higher arc regimes are needed in the production of exotic carbon nanostructures like carbon nanohorns [10]. The electronic absorption spectrum of the carbon arc reveals always the presence of the C\(_2\) molecule and the mass spectrometry of the gas phase carbon arc reveals the tendency of the C\(_2\) molecule to polymerize into longer carbon chains which are acetylenic in nature [11,12]. At this point is only matter of the environment surrounding the carbon arc as summarized in Fig.1. If the arc is struck in an helium atmosphere carbon dust will be produced almost exclusively. However, this carbon dust contains fullerenes and for this reason is also called “fullerene black” [9]. The amount of fullerenes (mainly C\(_{60}\) and C\(_{70}\) fullerenes with trace amounts of higher fullerenes) can reach up to 10\% by weight of the “fullerene black” carbon dust and must be extracted with an appropriate fullerene solvent like for instance benzene or toluene to remove C\(_{60}\) and C\(_{70}\) fullerene from the carbon dust matrix [9]. Thus, what we are learning from this laboratory experiment? That C\(_{60}\) and C\(_{70}\) fullerenes cannot be easily produced in pure form in space but they are produced necessarily mixed and adsorbed in carbon dust. Of course, there is also the possibility of fullerene desorption from the carbon dust by sublimation and we know that temperatures as high as 700\(^\circ\)C are necessary to cause the sublimation of C\(_{60}\) [13]. Helium is an essential gas in favoring the fullerene formation in high yields and this is attributed to its uniquely high thermal conductivity which favors the rapid temperature quench of the products [14]. In fact when the carbon arc is struck in argon or other inert gases having lower thermal conductivity than helium, once again the fullerene yield drops almost to zero and only the carbon dust is the reaction product [14].

Another important thing we learn from the study of the carbon arc is the inhibiting effect of hydrogen in fullerene formation. When the carbon arc is struck in a hydrogen atmosphere, the fullerene yield drops nearly to zero and instead the resulting products may be polycyclic aromatic hydrocarbons (PAHs), polyynes carbon dust and carbon nanotubes, depending on the conditions adopted [15]. Reactive gases in the arc are able to orient the reaction products toward new and unusual products. For example, as shown in Fig. 1, the presence of ammonia or acetonitrile leads to the formation of a mixture of polyynes and monocyanopolynyes [12,13] while when the carbon arc is struck in liquid nitrogen a mixture of dicyanopolyynes are obtained [16]. Another reactive gas is chlorine, its presence in the carbon arc favors the formation of chlorinated PAHs [9].

In summary, the general view is that C\(_2\) polymerizes into longer polyynes chains. These chains are stabilized if end-capped by hydrogen atoms and nitrogen atoms yielding polyynes and cyanopolyynes. If instead there is an inert gas, C\(_2\) may undergo a cyclization and crosslinking reaction producing fullerenes and carbon dust. In this process the eventual presence of hydrogen is crucial because it can orient the reaction products toward PAHs, polyynes, carbon nanotubes. The formation of carbon dust in an arc regime under He is the most common product. As already said, the dust consists -almost exclusively- of amorphous carbon (see Fig. 2 for a TEM image), in other words by carbon black with a certain amounts of fullerenes, the so-called “fullerene black”, but in special carbon regimes also unique carbon nanostructures known as “carbon nanohorns” are produced (see Fig. 1) [10]. On the other hand, when acetylene or methane are cracked in a carbon arc, then a large amount of carbon soot is produced together with polyynes and PAHs [17]. In this case the carbon soot rather than amorphous it appears partially graphitized at the transmission electron microscope as shown in Fig. 2 (right).
From $C_2$ to complex carbon structures

Figure 1. Different products obtainable from the carbon arc or by laser ablation of graphite under different conditions.

Figure 2. Transmission Electron Microscopy (TEM) images of amorphous carbon black (left) and partially graphitized carbon black from methane-acetylene arc (right).

3. Synthesis of polyynes, cyanopolyynes and other products through the submerged electric arc

Polyynes are acetylenic carbon chains derived for example from the polymerization of the $C_2$ unit in a carbon arc condition or in circumstellar medium conditions [5,11,12]. The hydrogen terminated carbon chains are the canonical polyynes but are known also nitrogen-terminated acetylenic chains known as monocyanopolyynes and dicyanopolyynes:
reactions like  is found respectively at 4100 K and at 4400 K. Thus, thermodynamics tells us that the such threshold temperature is even higher for monocyanopolyynes and dicyanopolyynes which of polyynes becomes negative at the threshold temperatures above 3500 K as shown in Fig. 4. stars [11,12].

In each cases polyynes, monocyanopolyynes and dicyanopolyynes are produced all together as mixture of products. The HPLC (High Pressure Liquid Chromatography) analysis on a normal C8 column in reversed phase was an excellent tool in the separation of the polyynes and the collection of their electronic absorption spectra by a DAD (Diode Array Detector) coupled with the HPLC apparatus [5]. In this way we have available the individual electronic absorption spectra of each polyyne, monocyanopolyyne and dicyanopolyyne produced with the submerged arc approach [5].

From the electronic absorption spectra it is possible to determine the relative abundance of the polyynes produced in laboratory with the electric arc and expressed in terms of the molar ratio C\textsubscript{8}H\textsubscript{2}/C\textsubscript{10}H\textsubscript{2}, C\textsubscript{10}H\textsubscript{2}/C\textsubscript{12}H\textsubscript{2} and so on. It was shown that the relative abundance of the polyynes generated with the arc is practically the same as that determined in the circumstellar environment by Chernicharo et al. [18] suggesting a similar mechanism of formation of these molecular species both in the electric carbon arc and in the circumstellar medium of carbon rich stars [11,12].

Thermodynamic calculations show that the Gibbs free energy of formation from the elements of polyynes becomes negative at the threshold temperatures above 3500 K as shown in Fig. 4. Such threshold temperature is even higher for monocyanopolyynes and dicyanopolyynes which is found respectively at 4100 K and at 4400 K. Thus, thermodynamics tells us that the reactions like nC+H\textsubscript{2} → H-(C≡C)n-H or the analogous for cyanopolyynes: nC+1/2H\textsubscript{2} + 1/2N\textsubscript{2} → H-(C≡C)n-C≡N and nC+2N\textsubscript{2} → H-(C≡C)n-C≡N become possible only at very high temperatures which in laboratory can be reached quite easily with the carbon arc. Once the polyynes are formed in the high temperature of the arc, they are ejected in the solvent and quenched to much lower temperature and then preserved in the solvent .

The formation of polyynes in the submerged electric arc is always accompanied by the formation of a mixture of polycyclic aromatic hydrocarbons (PAHs) and by the formation of carbon soot [20]. In general the latter component is just a by-product while the PAHs formation is quite appreciable. There are available chemical methods to separate the polyynes from the PAHs in solution. One method consists in the precipitation of polyynes as copper or silver acetylides and, after filtration, their re-solubilization in a fresh solvent by the action of a mineral acid [5].
Another interesting aspect about the polyynes chemical properties which may have astrochemical implications, regards the fact that they are reactive with atomic hydrogen. In laboratory the hydrogenation of polyynes is accessible under mild conditions and does not lead to fully hydrogenated products but to partially hydrogenated polyynes which are better described as ene-yenes, where the polyynes after the partial hydrogenation can be described as a sequence of conjugated acetylenic and ethylenic units displaying very rich and complex electronic absorption spectra [21].

4. Carbon arc in gas phase

Gas phase carbon arc is another interesting tool to simulate certain astrophysical conditions. Cracking of methane in a carbon arc (for example with a diluting inert gas like argon) is an excellent way to produce acetylene, polyynes and an important amount of carbon dust which we call acetylene black and whose microstructure is shown in Fig. 2 (left) [17]. Thermodynamics calculations show that above 1500K methane is unstable toward its reaction into acetylene and hydrogen: \(2\text{CH}_4 \rightarrow \text{HC}≡\text{CH}+3\text{H}_2\).
Together with acetylene we have detected a mixture of polyynes as secondary products, while the acetylene black is formed for example by the thermal decomposition of acetylene into the elements which is thermodynamically allowed at temperature below 3500 K. Simple PAHs were found as well as secondary products and adsorbed on the carbon black, after solvent extraction [22]. The best way to produce in high yield carbon soot in a carbon arc is by arcing halomethanes like CCl₄, CHCl₃ and CH₂Cl₂ [23].

5. **Fullerenes, fulleranes and other derivatives**

C₆₀ fullerene was expected to be present in space since the time of its discovery, but only in 2010 it was discovered through its infrared spectral signature in a young planetary nebula [24]. Later, C₆₀ was found in other astrophysical environments including the interstellar medium [25,26]. Recently, C₆₀ as radical cation was recognized as contributor to the DIBs in the gas phase [27]. The stability of C₆₀ toward high energy radiation was demonstrated suggesting an high permanence of this molecule in the harsh space conditions [28]. In laboratory the infrared spectra of C₆₀ and C₇₀ fullerenes were recorded in a wide range of temperatures [29]. The position of certain infrared bands of fullerenes are sensitive to temperature and undergo a shift as function of temperature [29]. These properties are useful for searching and recognizing fullerenes in space as well as the determination of the absorption cross section of each absorption band which is a useful property for the determination of column density in space. Other spectral properties of fullerenes were determined in a strong oxidizing medium like oleum. In such an environment C₆₀ and C₇₀ fullerenes are losing one electron and oxidized to the radical cations [30,31]. The optical spectra of these species were recorded but unfortunately, because of the strong interaction between solute and solvent the electronic transitions were found blue shifted and broadened with respect to the radical cation band position in the gas phase [30,31].

C₆₀ and C₇₀ fullerenes are readily reactive with atomic hydrogen yielding fulleranes the hydrogenated fullerenes [32]. The fullerenes are so avid of hydrogen that the hydrogenation in the laboratory conditions leads directly to C₆₀H₁₈ and C₆₀H₃₆ [33]. Thus, it is completely reasonable to think that hydrogenated fullerenes may be present in space. Indeed a tentative detection of hydrogenated fullerenes was made by Kwok et al in the PNPN IRAS 01005+7910 [34]. Hydrogenated fullerenes are releasing molecular hydrogen when irradiated with UV light playing a role in the conversion of atomic hydrogen to molecular hydrogen in space [35]. Furthermore, C₆₀H₃₆ presents a unique absorption band at 217 nm resembling the UV “bump” absorption observed in the interstellar light extinction curve [35]. When irradiated with UV light C₆₀H₃₆ loses hydrogen and the maximum of absorption is gradually shifted towards longer wavelengths [35]. Thermal treatment of fulleranes causes the release of hydrogen and the restoration of the pristine C₆₀ although the yield is not quantitative and also carbon soot as by-product is obtained [36].

Fullerenes were found in various space environments, sometime mixed with other complex molecules like PAHs or metals. Since it is known that fullerenes form adducts with PAHs through the Diels-Alder reaction, the synthesis of all the series of C₆₀ and acenes (anthracene, tetracene and pentacene) was performed and the infrared spectra of the adducts were recorded together with the electronic absorption spectra (see Fig. 5) [37-40]. The reference spectra are now available for searching such adducts in space although the fullerene-acene adduct show just a few new infrared bands different than the two reactants which are of diagnostic utility for the identification.

In another work [41], C₆₀ and C₇₀ fullerenes were irradiated with visible light in presence of iron pentacarbonyl (Fe(CO))₅ yielding the respective iron tetracarbonyl adducts (see Fig. 5). Iron is one of the most abundant metal in the universe and CO is ubiquitous. Fe and CO can react in mild conditions to produce Fe(CO)₅ which is a highly volatile iron compound. When irradiated with C₆₀ or C₇₀ the iron carbonyl compound forms adducts of the type shown in
Fig. 5. The fullerene-iron carbonyl adduct present a moderate thermal stability but a very characteristic infrared spectra.

**Figure 5.** Fullerene C\textsubscript{60}-pentacene adduct (left); Fullerene C\textsubscript{60}-iron carbonyl adduct (right).

6. Petroleum fractions as model of the structures of mixed aliphatic-aromatic compounds observed in PPNe

The protoplanetary nebulae show a series of distinctive infrared emission features which are certainly due to aromatic components [2,4]. These emission features are known as AIB (Aromatic Infrared Bands) and are not seen in AGB stars [2]. This means that the carriers of the AIB are synthesized in the circumstellar envelope during the post-AGB phase. The AIB of protoplanetary nebulae suggest a mixed aliphatic aromatic structure of the carriers. Instead, in planetary nebulae the AIB suggest essentially aromatic carriers [2]. This implies an increased UV processing of the carriers of the AIB on the passage from protoplanetary to planetary nebulae with elimination of hydrogen and aliphatic chains [2]. Some of the AIB bands of PPNe are also found in the interstellar medium for example in the Orion Nebula or in various reflection nebulae [2]. The AIB bands suggest a mixture of different carriers and the individual molecules of these carrier should be complex. For these reasons it was proposed as model of the AIB the infrared spectra of certain heavy petroleum fractions [42-44]. These heavy petroleum fractions are the bottom residue of the petroleum distillation and are made by a mixture of relatively large and complex molecules which can be described as mixed aliphatic-aromatic-naphthenic, containing also some heteroatom as shown in Fig. 6 [45,46].

The petroleum fractions proposed as model spectra of protoplanetary nebulae can be distinguished into two classes: the lighter types which are shown in the left of Fig. 6, which are soluble in n-pentane. The “core” of these molecule is made by an aromatic and cycloaliphatic (naphthenic) ring with some side alkyl chains. To this type belong the petroleum fractions called DAE and RAE [45,46].

**Figure 6.** Examples of “average molecules” in heavy petroleum fractions and asphaltenes.

The other class is the heavier type which is insoluble in n-pentane and which belongs to the asphaltenes, represented by the average molecule in the right of Fig. 6 characterized by a “core”
of the molecule made by two or three condensed aromatic rings \[45,46\]. To this type belongs the petroleum fraction called BQ-1. In Fig. 7 (left) it is shown that the infrared emission of the PPNe IRAS 22272+5435 is matched by the petroleum fraction DAE and MF2 and partially matched also by anthracite coal sample [42-44]. In Fig. 7 (right) it is shown that the infrared emission of the young PNe IRAS 21282+45050 is partially matched the BQ-1 petroleum fraction [46].

The model of petroleum fractions meets quite in full the model of MAONS (Mixed Aliphatic-Aromatic Organic Nanoparticles) proposed by S. Kwok and colleagues [4,47].

**Figure 7.** (Left) Infrared emission of the PPNe IRAS 22272+5435 (bottom) compared with the infrared spectra of petroleum fractions DAE and MF2 and by coal. (Right) Infrared emission of the PPNe IRAS 22272+5435 (top) compared with the spectra of petroleum fractions BQ-1 type.

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Franco Cataldo.