Review
Interstellar Carbon Dust

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Abstract: In the ranking of cosmic abundance of the elements, carbon is the second element, after oxygen, able to form multiple bonds propagating the formation of a network, thus playing an essential role in the formation of nanometer- to micrometer-sized interstellar dust grains. Astrophysical spectroscopic observations give us remote access to the composition of carbonaceous and organic interstellar grains. Their presence and abundances from spectroscopic observations and the phases of importance for the Galactic carbon budget are considered in this article.

Keywords: interstellar medium; dust grains; organic matter

1. Introduction

The interstellar space is filled with gas and dust grains. Interstellar carbonaceous large molecules and dust grains hold a large fraction of the available carbon abundance in the Galaxy. Various forms of carbon are observed and measured, the most recent allotropes observed are space fullerenes. The different potential carriers are traced via spectroscopic specific bands observed in emission and/or absorption. They are related to various allotropic forms of carbonaceous dust present in the interstellar medium and around young and old stars, ranging from purely carbon forms to carbon dust containing hydrogen and heteroatoms. The observations are compared to experiments conducted for identification and interpretation of these astronomical spectra. The several observed forms of carbon in space include (nano-)diamonds, fullerenes, polyaromatic structures, amorphous carbon and their hydrogenated amorphous carbon forms (generally named HAC in astrophysics and a-C:H in physics), as well as by extension the organic matter that originates from the energetic processing of ice mantles in dense cloud regions of the Galaxy and/or from the possible condensation in dense and chemically-rich stellar wind around evolved stars [1,2]. These dust grains are immersed in harsh astrophysical environments including vacuum ultraviolet photons and high energy accelerated particles (the cosmic rays), thermal evolution and will thus be processed.

In many astrophysical environments where they reside, the question of their contribution to the enrichment of the medium with complex organic molecules by top down chemistry (i.e., the destruction in smaller entities of initially very large size molecules or even grains) must thus be raised and assessed.

2. Observations of Interstellar Carbons

The vast majority of the information on interstellar space comes from spectroscopy for the obvious reason of the distance to the studied astrophysical objects. The solar system is the exception, for which samples can be examined by space probes carrying more than spectroscopic instruments or in favourable cases, extraterrestrial matter can be studied in the laboratory, for example, meteorites and interplanetary dust particles captured by Earth or sample return missions to comets and asteroids. The physico chemical composition of carbon based large molecules and dust grains can be observed either in emission or in absorption, depending on the astrophysical environment, size of the molecules and excitation source. The main components observed in emission in the Galaxy consist

of emission bands in the mid infrared, peaking around 3.3, 6.2, 7.7, 8.6, 11.3, 12.7 μm, characteristic of a polyaromatic component, the so-called aromatic infrared bands (AIBs) or Polycyclic aromatic hydrocarbon hypothesis ("PAHs") (Figure 1, lower right). Some specific environments also show emission spectra with an aliphatic character, in addition to the polyaromatic structure. Broad continua emission is also often present under these bands and extending to longer wavelength. In absorption, characteristic absorptions are observed in the mid infrared at about 3.4, 6.85 and 7.2 μm along long distant lines of sight (Figure 1, upper left), characteristic of hydrogenated amorphous carbons. Another spectroscopic signature occurs in the vacuum ultraviolet, with a broad absorption band around 217.5 nm, accompanied by a rise in the deep ultraviolet. These absorptions are related to the electronic absorption of carbon based species.
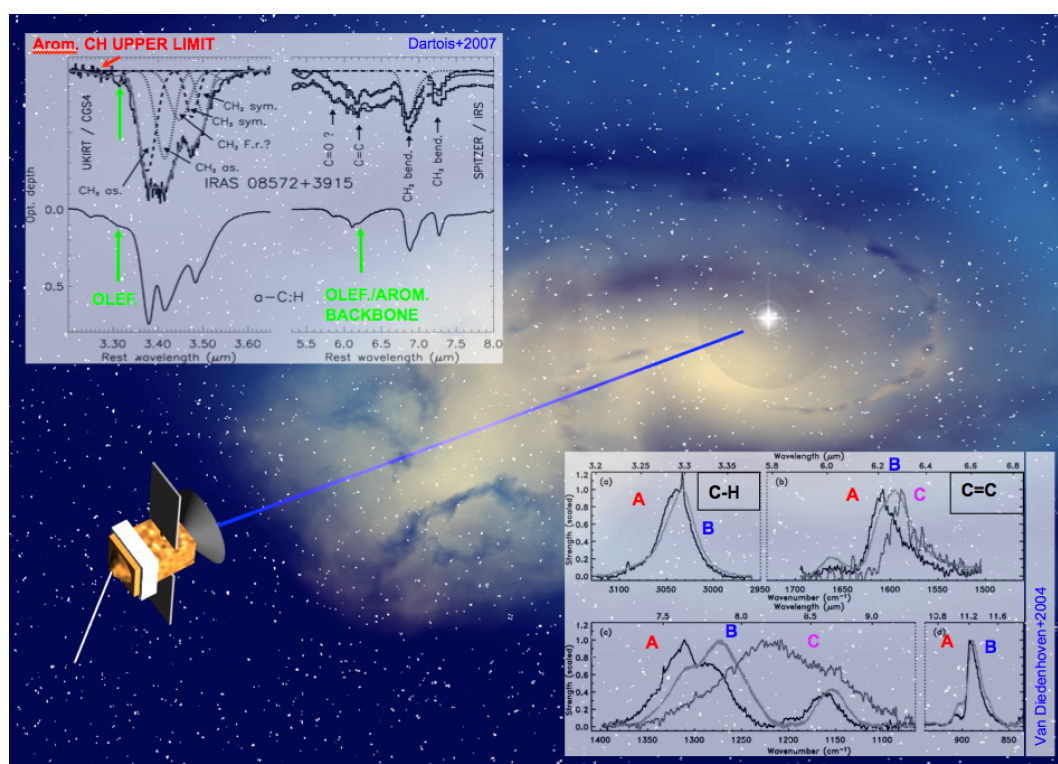

Figure 1. Observations along lines of sight toward the Galactic center or, even looking at other galaxies, allow one to probe interstellar dust. Using a bright distant infrared background source, the diffuse interstellar medium dust grain infrared signatures of hydrogenated amorphous carbons can be probed in absorption (e.g., shown in the upper left panel, compared to laboratory experiments). Another component of the diffuse medium, aromatic infrared bands can be observed in emission in many distinct lines of sight (e.g., lower right signatures). See References [3–5] for details of the inserts. Inserts from Dartois et al., A&A. 463, p637, 2007, reproduced with permission © ESO, and from Van Diedenhoven et al., ApJ 611, p933, 2004, reproduced with permission © AAS.

2.1. (Nano-)Diamonds

The existence of diamonds in interstellar space was postulated after the detection of small diamonds of presolar origin in meteorite extracts, with abundances sometimes almost approaching the part per thousands in some carbonaceous chondrites meteorites. Some of these diamond phases are truly attributed to a presolar origin based notably on their isotopic anomalies, others may be readily explained by high temperature and/or shock processing of carbon containing parent bodies or meteorites during solar system evolution [6–14]. The first detection of nanodiamonds in space have been performed by Reference [15] and unambiguously confirmed by comparing emission spectra of the dust grains evolving in circumstellar environments around the intermediate mass (a few $M_\odot$) Herbig Ae-Be stars to laboratory spectra [16]. These authors identified specific infrared emission bands

at 3.43 and 3.53 μm attributed to the vibrational CH elongation modes of hydrogenated diamond nanoparticle surfaces. These interstellar medium (ISM) nanodiamonds spectra are different from the one recorded for meteoritic extracted nanodiamonds [17]. Laboratory approaches to reproduce the observed ratios of the ISM observed bands have followed a top down (nanostructures are synthesized starting from big units, reducing their size and following the spectral evolution associated) or bottom up approach (starting from the molecular world, following the spectral evolution using small diamondoid molecules that are grown in size and measured experimentally and/or explored bigger and bigger also by quantum calculation) to constrain the sizes of these remotely observed hydrogenated diamond terminations [16,18,19]. The top down nano-diamond approach led to an estimate of relatively large sizes for the interstellar nano-diamonds and they were found to be related to the non relaxed surfaces for nano-diamonds in the experiments for sizes below 35 nm. The bottom-up molecular approach, combined with density functional calculations demonstrated that the observed intensity ratio of the two bands observed at 3.53 μm and 3.43 μm would imply a much lower size, with about 136 carbon atoms (∼1.5 nm). A few sources display the characteristic emissions attributed to CH diamond terminations [20]. An observational survey of about thirty lines of sight with expected similar astrophysical environments have been conducted by Reference [21], with no additional detections of the presence of these nanodiamond emission bands. Several observations have also succeeded in resolving spatially these emission bands [22–24] to understand the underlying physical conditions for their formation. In resolved sources they appear relatively close to the stars, closer than other carbon dust emission bands associated with polyaromatic materials. Observations at higher spatial resolutions will help in better defining where these diamonds reside and emit, and put additional constraints on their sizes. Their detection in only a handful of sources questions their overall importance in the carbon budget of the Galaxy. These interstellar nanodiamonds are among the best identified spectroscopic features for interstellar dust emission bands, from the spectroscopic point of view and are a potential probe of very specific carbon allotrope forming environments. Pushing the detection capabilities of space telescopes will assess to what extent these nanodiamonds should be considered as widespread.

2.2. Fullerenes

The existence of fullerenes in space has been postulated since their discovery by Reference [25]. A long search started in the visible to the infrared range. Reference [26] found that two interstellar absorption bands observed in lines of sight probing the diffuse intertellar medium almost matched to C_{60}^{+} absorptions recorded by Reference [27] in matrix isolation spectroscopy experiments. Reference [28], looking at absorption in the optical along lines of sight toward distant massive stars, probing the diffuse interstellar medium, could not find electronic absorptions of neutral C_{60}, estimating that $C_{60}^{+}/C_{60} \geq 100$. Reference [29] reported upper limits on the detection of both species in emission in the vibrational infrared. The first detection of C_{60} (single molecular species in vacuum) was reported by [30,31] through the main vibrationally active modes of C_{60}, spatially resolved in emission in a reflection nebula. Reference [32] reported the detection of C_{60} and C_{70} in emission around a protoplanetary nebula particularly poor in hydrogen. In the infrared, it has been reported in many other astrophysical lines of sight [33–49], mainly in protoplanetary nebulae sources, but also many other objects such as reflection nebulae, Asymptotic Giant Branch (AGB) and Herbig Ae/Be stars. In recent years, ion trap action spectroscopy allowed the measurement of almost unperturbed free flying C_{60}^{+} molecule electronic transitions in the laboratory [50,51]. They allowed the assignment of diffuse interstellar bands to C_{60}^{+}. Other fullerene cations have been measured in the laboratory [52–54], and investigated observationally but their lower intensity makes them often too difficult to observe astronomically. From laboratory experiment [55] the intrinsic strength of the transitions can be estimated. The corresponding amount of carbon locked in C_{60} or C_{60}^{+} is relatively low, of the order of a few 10^{-5} to 10^{-4} of the carbon cosmic abundance [56,57].

2.3. Graphite

Graphite is often referred to as an interstellar component. Its presence in the interstellar medium has been supported initially by the ultraviolet extinction observations (e.g., References [58–61]) and the hypothesis reinforced by the finding of some preserved presolar graphite grains in some meteorites. It has been used to fit the ultraviolet extinction curve observed in the diffuse medium. The model requirements to obtain a good fit imply a precise knowledge on the optical constants to be used [62]. Critical adjustments on the aspect ratio of pure graphite grains, as well as their size distribution are required to adjust the extinction curves [63–69] and it is thus considered by some authors as too demanding, a too narrow parameter space with respect to the diversity of environments expected in astrophysics. Many other carbon based material combinations can produce an extinction in the same wavelength range, offering alternatives to "pure" graphite grains [70–82]. Graphite is still used in some astronomical models as a template carbon base, sometimes denominated "interstellar graphite" [83] when it is adjusted based on observed interstellar extinction curves.

2.4. Silicon Carbide

Among Carbides, one of the most abundant expectation in the ISM is based on Silicon Carbide. While it is highly discussed in the meteorites community since a long time (see, e.g., Reference [84,85]), and some SiC dust particles are observed in emission or absorption around some C-rich stars (e.g., References [86–89]), it has not been detected in the diffuse ISM so far, whereas given the strength of the SiC vibrational mode, observable at 11.3 μm, in the shoulder of interstellar silicates, if present in abundance it should be observed, if it represents at least a few percents in abundance with respect to the silicates (e.g., References [90,91]). The reason of its absence in the diffuse ISM is the subject of a debate, including discussions on its survival after its formation in the envelopes of C-rich stars. Some observational constraints should be further pushed in the near future, but the vast majority of the silicon atoms seem engaged in the formation of silicates rather than SiC (e.g., Reference [92]).

2.5. The PAH Hypothesis

Among the most popular carbon based structures in space are the so-called Polycyclic Aromatic Hydrocarbons (PAHs). PAH refers to the infrared fluorescence of large free flying PAH-like entities, upon absorption and relaxation of a single energetic UV photon. This name follows the first description by References [93,94] to account for infrared emission bands observed at 3.3, 6.2, 7.7, 8.6, and 11.3 μm in many astronomical lines of sight, on the basis of laboratory PAH photophysics. This terminology is now part of a common language of astronomers, but should be more adequately stated as the "Polycyclic Aromatic Hydrocarbons hypothesis." A more suited term to name these emissions is probably Aromatic Infrared Bands (AIBs), as it is clear that these astrophysical bands arise in a polyaromatic system. However, such emissions are still unidentified with a definite carrier. The observed profile variations from source to source of these emission bands have been categorized [5,95] and named of classes $\mathcal{A}$,$\mathcal{B}$,$\mathcal{C}$. More recently a $\mathcal{D}$ class has been added [96]. The class $\mathcal{A}$ band positions display a highly aromatic character, whereas evolving toward the $\mathcal{C}$ and $\mathcal{D}$ classes, the emission bands also include some aromatic/aliphatic mixed character as seen in observations and experiments [96–103]. From an observational point of view, the class $\mathcal{A}$ emission bands are widespread and seen in many different observed source lines of sight, indicating that these AIBs carriers are present in distinct astrophysical environments and relatively easily excited by photons. If the changing profiles are associated with an evolution of the chemical composition of the carriers, the ubiquitous presence of class $\mathcal{A}$ emission is also attributed to a fluorescence mechanism, which is independent of the photon flux, and thus the distance to the photon source. Some of the class $\mathcal{C}$ and $\mathcal{D}$ emissions may be observed less frequently because they either are less represented in abundance, and/or are related to a thermal emission mechanism, active only relatively close to the photon sources. The observation statistics of

the different classes of AIBs is thus weighted by the variations of the astrophysical environments but also their intrinsic emitting mechanism efficiency.

2.6. Amorphous Carbon

There are not so many studies on the spectroscopy of astrophysical objects displaying amorphous (hydrogen-free) carbon dust. Such dust grains are injected into the diffuse medium, but then are difficult to observe, as generally they are only seen close to the stellar ejecta through a featureless blackbody-like continuum emission [86,104–107]. Once injected, such dust could be hydrogenated later, during its journey (e.g., References [97,108–110]) and irradiation in astrophysical atomic hydrogen dominated environments [111,112].

Hydrogenated amorphous carbons form another important carbonaceous species in the interstellar medium that is often overlooked because of the weaker intrinsic absorption features used to probe them. They however represent one of the major reservoirs of carbon based dust in galaxies. Observed for a long time from the ground through an absorption band at 3.4 µm in the direction of the Galactic center lines of sight, against bright infrared background sources [113], its observability requires a significant amount of column density, generally associated with distant lines of sight. The profile of the band can be assigned to methyl and methylene (sp^3 CH$_3$ and CH$_2$) elongation modes in a more complex dust grain [114]. Several suggestions have been made on the macromolecular structure supporting the spectroscopic observations. They evolved with time as the constraints from satellite observations yield data over a broader wavelength range, discarding some of the very first thoughts based on the 3.4 µm feature profile only [115–117]. The hydrogenated amorphous carbon signature is observed ubiquitously in the interstellar medium of extragalactic sources [3,4,118–120].

3. Evolution and Interaction with the Environment

The detection of large carbon molecules/radicals at the interfaces between the diffuse interstellar medium and dense cloud condensations is difficult to reproduce with astrophysical models including only gas phase chemistry. This questions the eventual proportions inherited from the destruction of carbonaceous dust grains, that is, the evolution and interaction with the environment of these grains [121–125].

Astronomical observations results from an equilibrium between destruction and production of species. The AIBs (PAHs) and a-C:H at the interface of Photon Dominated Regions (PDRs), transition regions between a diffuse (a few hydrogen per cubic centimetre) to denser medium (typically above a thousand hydrogen molecules or atoms per cubic centimetre) and exposed to harsh VUV photons generating an active photochemistry) are invoked to explain the observation of numerous hydrocarbon molecule detections and suggest the possibility of a top-down chemistry in such environments. These environments as well as the diffuse medium are also exposed to high energy atomic ions interacting with the astrophysical solids. Some laboratory experiments aim at constraining the observation of the evolution of such carbonaceous species within the ISM and at PDRs interfaces with denser regions and interactions with the radiative environment they are immersed in References [78,126–132]. A typical setup to monitor the species produced by interaction with astrophysical environments is shown in Figure 2. The laboratory photolytic and/or radiolytic rates, discussed in the above cited references, can be implemented in astrophysical models and provide a better match to observations of the gas phase abundances, in particular for large carbonaceous species, as well as evolution time scales that are in accordance with the expected diffuse-to-dense interface advection, that is, the speed at which the dense cloud interface is moving because of the strong UV field nibbling the dense interface. Both cosmic rays and VUV photons release carbonaceous species, feeding the ladder of large carbon species observed in astronomy. The laboratory experiments support the production of species from the solid phase and the evolution toward reactive and bigger species [133] detection is an active field of research.
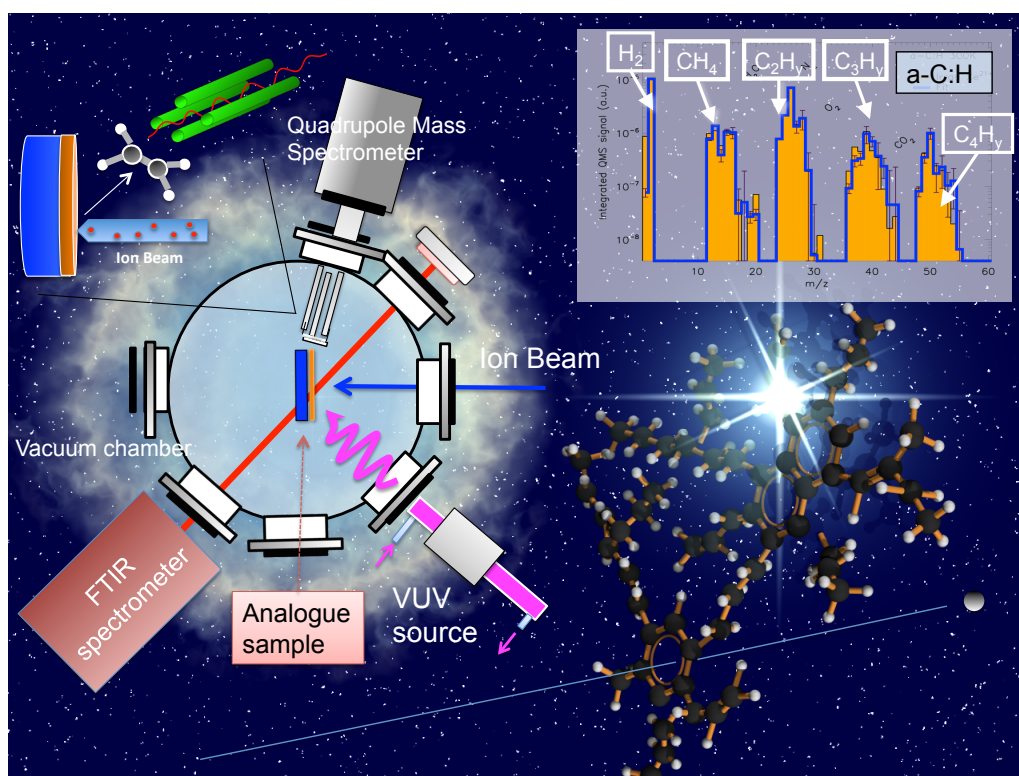
Figure 2. Typical scheme of experiments aiming at following the evolution of a dust analogue subjected to either ion irradiation simulating cosmic rays [126] or energetic VUV photons [127] from the interstellar radiation field. An interstellar analogue is placed at the center of the chamber, maintained at interstellar low temperatures and the evolution and products of the photolysis and or radiolysis are monitored both in the solid phase and the gas phase. Insert QMS spectrum from Dartois et al., A&A. 599, A130, p6, 2017, reproduced with permission © ESO.

4. Which Carbonaceous Solids Are Ingredients for Interstellar Models?

Observational biases, underlying emission mechanisms and spectroscopic contrasts favour the visibility of some of the carbonaceous dust components. When one examine the mass balance, based on the previously discussed astronomical observational *spectroscopic* constraints, neither (nano-)diamonds nor fullerenes seem abundant enough to validate the claim that they are major carbonaceous interstellar dust grains components. However, their presence reflects important evolutionary paths in the interstellar physico-chemistry, and they are of relevance to provide constraints on the astrochemistry at work. Focusing on the vast majority of interstellar grains, that is, the most abundant ones, then (hydrogenated) amorphous carbons and AIBs (polyaromatic) carriers dominate, carrying a large fraction of the available cosmic carbon. The carriers of the AIBs constitute an important part of astrophysical models, as they must account for the emission bands observed in the mid infrared. The requirements in models are around five percent of the available cosmic carbon abundance [134–142]. The hydrogenated amorphous carbon absorptions trace a material that represents an abundance higher than what the AIBs emission bands imply. The exact abundance will vary according to the dust grain carrier network adopted in the experiments and modeling, but are not less than a few percent and maybe up to about 40% of the available cosmic carbon abundance [3,143–146]. Some models are now including these alternative forms of carbon including polyaromatic and/or hydrogenated amorphous carbons, gradually abandoning models dominated by graphite as a proxy for carbon dust grains [147–149].

Conflicts of Interest: The author declares no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

AIBs   Aromatic Infrared Bands
PDR   Photon or Photodissociation dominated region
ISM   Interstellar Medium
PAHs   Polycyclic aromatic Hydrocarbons

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