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# Structure and evolution of interstellar carbonaceous dust. Insights from the laboratory

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A large fraction of interstellar carbon is locked up in solid grains. The nature, origin and evolution of these grains have been investigated for decades. A combination of observations, models and experiments indicates that carbonaceous dust is mostly made of a mixture of grains composed almost exclusively of carbon and hydrogen. They have different proportions of aliphatic and aromatic structures, and a variable H/C ratio. Their sizes can vary typically between the nm and the hundreds of nm. Carbonaceous grains are largely formed in the envelopes of carbon rich asymptotic giant branch (AGB) stars and evolve in the interstellar medium, where they can be transformed or destroyed by the effects of hydrogen atoms, UV radiation, cosmic rays or shock waves from supernovae. Surviving grains eventually enter dense clouds and participate in the cloud collapse leading to star formation, closing thus their lifecycle. Within this general picture, there are doubts and issues that cannot be solved just by observation and modeling and require laboratory work. In this article we provide an overview of the development and present state of the field indicating open problems and debated questions. We stress recent experimental progress in the understanding of dust formation, both in circumstellar envelopes and the cold interstellar medium, and also in the energetic processing of dust analogs, that points to a possible top down chemistry in the diffuse medium, and especially in photon irradiated regions.

## KEYWORDS

interstellar medium, interstellar dust, carbonaceous solids, laboratory astrochemistry, spectroscopy, energetic processing

## 1 Introduction

Dust grains represent roughly one per cent of the mass of the Milky Way, but they are crucial in the physics and chemistry of the interstellar medium (ISM). Their interaction with stellar radiation is determinant for the optical and thermodynamic properties of the Galaxy, and they play a key role in the dynamics of star formation. They provide also the surfaces needed for the production of most of molecular hydrogen, and for the chemical reactions leading to many of the observed interstellar (IS) molecules. General reviews on interstellar dust can be found in [Draine. \(2003\)](#), [van Dishoeck. \(2014\)](#), [Hensley and](#)

Draine. (2021), Potapov and McCoustra. (2021), Suhasaria and Mennella. (2021), Tielens. (2022).

The presence of interstellar dust was inferred in the first decades of the 20th century from observations on the selective absorption (reddening) of starlight (Schalén, 1929; Timpler, 1930). Initially, metallic particles (Schalén, 1940) and then water ice particles with impurities like H<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, Fe (Oort et al., 1946) were suggested as possible dust constituents. The first IS molecules (CH, CN, CH<sup>+</sup>) were discovered at about the same time (Swings and Rosenfeld, 1937; McKellar, 1940; Douglas and Herzberg 1941). An overview of the knowledge on interstellar matter by the end of the forties can be found in Schalén. (1949). In the sixties, extensive studies of light extinction, including the UV region, and the use of laboratory measured optical constants, led to the formulation of a dust model based on graphite and silicate particles (Hoyle and Wickramasinghe, 1969). Since that time, observations have been much improved (Hensley and Draine, 2021), and models of interstellar dust have been substantially refined (Mathis et al., 1977; Draine and Lee, 1984; Zubko et al., 2004; Jones et al., 2013; Jones et al., 2017), but virtually all of them contain silicates and some sort of carbonaceous matter as the basic ingredients of interstellar grains. A detailed account and discussion of the evolution of dust models can be found in Jones et al. (2017).

Information about the composition, size, shape and optical properties of IS dust grains is mostly derived from remote measurements of light extinction (absorption plus scattering) and emission. Extinction data are now available over the whole range from X Ray to the radio frequencies, whereas emission is observed from the IR to the microwave domain. Polarization, observed both in extinction and emission, is also of help to constrain grain properties (Hensley and Draine, 2021). Some complementary information is gained from presolar dust grains in meteorites (Davies, 2011). As a result of cumulative investigations over decades, a picture of interstellar dust has emerged that can be summarized as follows: dust grains are mostly made of amorphous silicates and carbonaceous material, and they enclose a significant part of some of the most common elements. It is estimated that nearly all Fe, Si, and Mg, and approximately 35 per cent of oxygen and 40 per cent of carbon (both with large uncertainties, Hensley and Draine, 2021) are locked up in grains. Minor dust components, such as oxides, carbides, sulfides and metallic particles, can be present in very small proportions. Grains with a size of  $d \approx 100$  nm account for most of the dust mass, but much of the grain surface, which is determinant for light scattering, absorption and chemical reactions, corresponds to smaller grains, with sizes that can go down to the order of 1 nm. The most important clues about the chemical composition of the dust particles are provided by vibrational bands observed both in emission and extinction.

The presence of silicates in the grains is made manifest by two intense absorption bands, at 9.7  $\mu\text{m}$  and 18  $\mu\text{m}$ ,

corresponding respectively to Si-O stretching and O-Si-O bending vibrations. These features were first observed in circumstellar emission (Woolf and Ney, 1969; Forrest et al., 1979), but are also widespread in the diffuse ISM. The lack of fine structure in the IR bands suggests that silicate grains are mostly amorphous. It is estimated that only 1-2 per cent of the silicate mass is crystalline (Hensley and Draine, 2021).

Several spectral features are associated with IS carbonaceous matter different from small gas phase molecules. These features include the 217.5 nm extinction bump, the diffuse interstellar bands (DIBs), the extended red emission, and some characteristic infrared absorption and emission bands. The first two DIBs were detected a century ago, and their interstellar character was first recognized by Merrill. (1936). DIBs are a collection of more than 500 relatively broad bands observed mostly in absorption, between the UV and the IR. It is generally assumed that they are due to electronic transitions of large C-containing molecules in the gas phase, but most of them have not been assigned to a specific molecular carrier. Positive identifications of DIBs will be mentioned in the next section. The extended red emission was first observed in a planetary nebula (PN), the red rectangle, as a broad band extending from 540 to 760 nm with a peak near 660 nm (Schmidt et al., 1980). The feature is common in reflection nebulae, but it has also been detected in planetary nebulae, in H<sub>II</sub> regions, and in the diffuse ISM (Kwok, 2016; Witt and Lai, 2020). It is attributed to photoluminescence of some carbonaceous material, and it has been suggested that the species responsible for the extended red emission could be related to those responsible for the DIBs. Both, the nature of the possible carriers of the extended red emission, and the details of the excitation process, are still under debate (Witt and Lai, 2020). The 217.5 nm extinction bump and the IR absorption and emission bands are attributed to large molecules or solid grains of variable size containing aliphatic and aromatic carbon structures and a variable degree of hydrogenation. They will be discussed at length in the rest of this work. An assignment of these spectral features can be found in Table 1. Most of the following discussion is focused on the signatures of carbonaceous matter in the diffuse interstellar medium of the Milky Way, but other environments like circumstellar atmospheres, dense clouds or outer galaxies will also be mentioned.

At present, more than 250 molecules have been detected in the gas phase of the interstellar and circumstellar medium (McGuire, 2022), most of them through high resolution measurements of characteristic rotational transitions. In general, molecular detections, based on reliable spectroscopic constants, are undoubted, irrespective of the details and the history of the astronomical environment where a given molecule is found. This is unfortunately not the case of dust grains, whose spectroscopic signatures are broad, unspecific bands corresponding to generic functional groups. Since on many occasions unequivocal assignment is not possible, likely

TABLE 1 Summary of characteristic spectral features of carbonaceous matter observed in the ISM. Band assignments can be found for instance in Gavilan et al. (2017), Dartois et al. (2007), Chiar et al. (2013), Allamandola et al. (1989), Hudgins and Allamandola (1999), Tielens (2008), Peeters et al. (2021). The given band centers are approximate, and slightly different values can be found in the literature.

Band center (approx)	Type of compound	Observation	Assignment
217.5 nm/4.6 $\mu\text{m}^{-1}$	Aromatic	Absorption	$\pi$ - $\pi^*$ transition
3.3 $\mu\text{m}$ /3040 $\text{cm}^{-1}$	Aromatic/olefinic	Absorption/emission	CH stretch
3.38 $\mu\text{m}$ /2962 $\text{cm}^{-1}$	Aliphatic	Absorption/emission	CH <sub>3</sub> asym. stretch
3.41 $\mu\text{m}$ /2923 $\text{cm}^{-1}$	Aliphatic	Absorption/emission	CH <sub>2</sub> asym. stretch
3.48 $\mu\text{m}$ /2877 $\text{cm}^{-1}$	Aliphatic	Absorption/emission	CH <sub>3</sub> sym. stretch
3.52 $\mu\text{m}$ /2840 $\text{cm}^{-1}$	Aliphatic	Absorption/emission	CH <sub>2</sub> sym. stretch
6–6.4 $\mu\text{m}$ /1666–1562 $\text{cm}^{-1}$	Aromatic/olefinic	Absorption/emission	sp <sup>2</sup> C=C stretch
6.85 $\mu\text{m}$ /1460 $\text{cm}^{-1}$	Aliphatic	Absorption/emission	CH <sub>2</sub> def.+CH <sub>3</sub> asym. bend
7.25 $\mu\text{m}$ /1379 $\text{cm}^{-1}$	Aliphatic	Absorption/emission	CH <sub>3</sub> sym. bend
7.7 $\mu\text{m}$ /1299 $\text{cm}^{-1}$	Aromatic	Absorption/emission	sp <sup>2</sup> C-C stretch
8.6 $\mu\text{m}$ /1162 $\text{cm}^{-1}$	Aromatic	Emission	sp <sup>2</sup> C=C-H in plane bend
11.2 $\mu\text{m}$ /893 $\text{cm}^{-1}$	Aromatic	Emission	sp <sup>2</sup> C=C-H out of plane bending “solo” <sup>a</sup>
12.0 $\mu\text{m}$ /833 $\text{cm}^{-1}$	Aromatic	Emission	sp <sup>2</sup> C=C-H out of plane bending “duet” <sup>a</sup>
12.7 $\mu\text{m}$ /806 $\text{cm}^{-1}$	Aromatic	Emission	sp <sup>2</sup> C=C-H out of plane bending “trio” <sup>a</sup>
13.5 $\mu\text{m}$ /752 $\text{cm}^{-1}$	Aromatic	Emission	sp <sup>2</sup> C=C-H out of plane bending “quartet” <sup>a</sup>

<sup>a</sup>Solo, duet, trio and quartet refer to the number of exposed benzene ring sides (Hudgins and Allamandola 1999).

carriers proposed for the dust bands are often not only based on spectra, but also on assumed formation and evolution mechanisms. The elucidation of these mechanisms is now the subject of intense experimental investigation, and in this article we will try to highlight the fruitful interplay between laboratory and observations. Theoretical calculations and astrochemical models, which are also decisive for a sound understanding of interstellar dust, are beyond the scope of this work. The article is organized as follows: Section 2 deals with the structure and composition of grains. It is divided into three subsections corresponding to three kinds of observational information: ultraviolet extinction, infrared absorption, and infrared emission. In Section 3 the processes of dust formation and energetic processing of dust are analyzed, and, finally, in Section 4 the main conclusions of the work are summarized.

## 2 Structure and composition of carbonaceous grains

Carbon is the fourth element in order of abundance in the Universe. In a recent review Hensley and Draine. (2021), discuss ISM elemental abundances and propose a  $[C/H]_{\text{ISM}} = 324$  ppm value for the total carbon abundance, relative to hydrogen. The average values estimated in that work for carbon in the gas phase and in dust grains are  $[C/H]_{\text{gas}} = 198$  ppm and  $[C/H]_{\text{dust}} = 126 \pm 56$  ppm respectively. A similar cosmic abundance of carbon,  $[C/H]_{\text{ISM}} = 339 \pm 39$  ppm, is reported by Zuo et al. (2021). Both Hensley and Draine and Zuo et al. adopt a model based on protosolar abundances augmented by Galactic chemical

enrichment (GCE), and discard previous values based on solar and stellar sources (see for instance Gadallah, 2015 and the introduction of Günay et al., 2018 for a discussion on the previous estimates of  $[C/H]_{\text{ISM}}$ ). In the literature there are often estimates of fractional carbon abundances based on data from laboratory dust analogs. When considering these estimates, care should be given to the  $[C/H]_{\text{ISM}}$  assumed in each case. The electronic structure of carbon allows the formation of hybridized orbitals, which offer multiple bonding possibilities. As a consequence of its comparatively high abundance and flexibility for bonding, carbon is the element found in the largest number of existing compounds, and the one that allows the construction of the most complex chemical structures, including living beings. Complex carbon-based molecules and solids make much of interstellar dust. Progress in the study of IS carbonaceous dust and related species is reviewed in several recent works (Tielens, 2008; Kwok, 2016; Herrero et al., 2018; Dartois, 2019; Peeters et al., 2021; Hansen et al., 2022; Kwok 2022).

Elementary carbon has different allotropes and some of them are candidates for carriers of IS spectral features (Henning and Salama, 1998). Nanodiamonds have been found in meteoritic presolar grains (Davies, 2011) and also in astronomical observations. They were first identified in space through the 3.43  $\mu\text{m}$  and 3.53  $\mu\text{m}$  emission bands from circumstellar dust (Guillois et al., 1999). The two bands correspond to the CH stretching vibrations of hydrogen-terminated crystalline facets of diamond. Nanodiamonds have only been detected in a few sources and, most probably, they are not relevant for the carbon budget in the Galaxy (Dartois, 2019). Fullerenes have

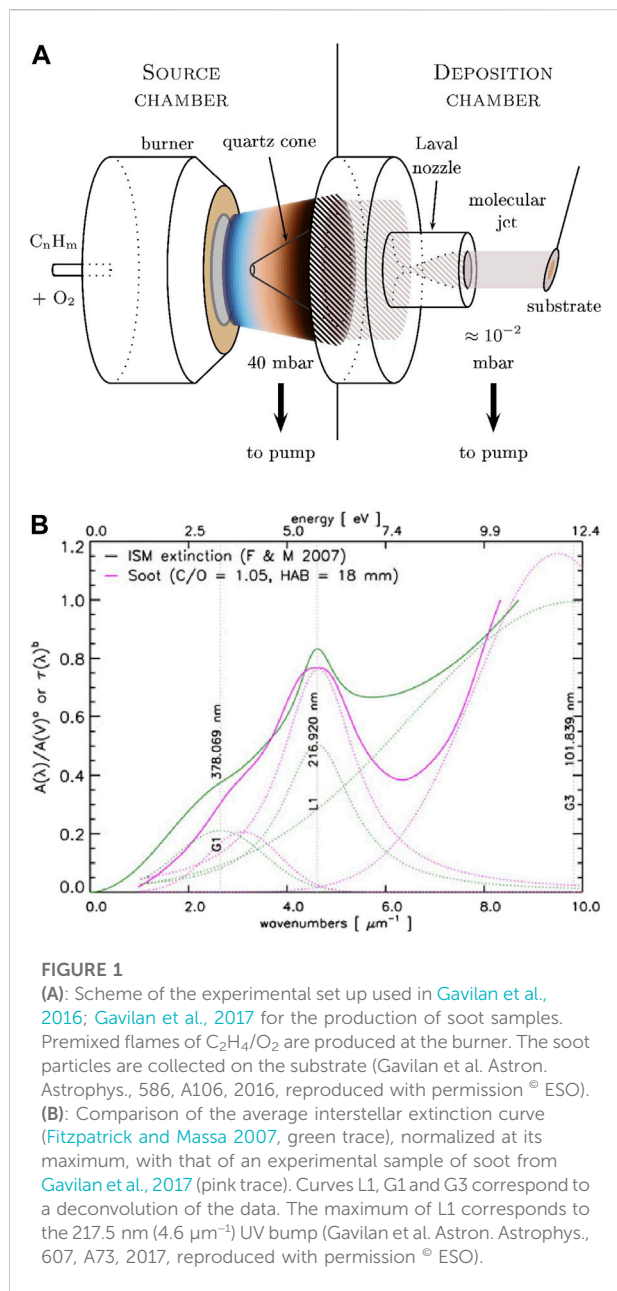
also been detected in the ISM. The first detection of  $C_{60}$  was reported by [Sellgren et al. \(2010\)](#). The authors of that work detected IR features at 7.4  $\mu\text{m}$ , 17.4  $\mu\text{m}$  and 18.9  $\mu\text{m}$ , corresponding to the main vibrationally active modes of  $C_{60}$ , in the emission spectrum of a reflection nebula.  $C_{60}$  and  $C_{70}$  were then observed around a hydrogen poor protoplanetary nebula ([Cami et al., 2010](#)), and, since then, many more detections have been reported in protoplanetary nebulae, reflection nebulae, asymptotic giant branch (AGB) stars and Herbig Ae/Be stars (see [Dartois, 2019](#) for references). The ionized fullerene  $C_{60}^+$  was shown by [Campbell et al. \(2015\)](#) to be the carrier of the DIBs at 963.2 nm and 957.7 nm. The assignment was based on refined cryogenic ion trap measurements and constitutes to date the only positive identification of a DIB carrier. Estimates based on laboratory intrinsic transition strengths indicate that the fraction of IS carbon locked in  $C_{60}$  or  $C_{60}^+$  should be in the  $10^{-3}$ – $10^{-4}$  range ([Berné et al., 2017](#)). In contrast to diamonds and fullerenes, graphite has been traditionally considered an important component of IS grains. We include it in the following discussion dedicated to the likely carriers of the most important spectral features associated with carbonaceous dust. As for graphene, an upper [C/H] limit of 20 ppm has been derived from the absence of the 275.5 nm  $\pi$ - $\pi^*$  inter-band transition resonance ([Li et al., 2019](#)).

## 2.1 The carriers of the 217.5 nm ( $4.6 \mu\text{m}^{-1}$ ) ultraviolet extinction bump

In the diffuse interstellar medium, UV extinction shows a pronounced and broad feature (“bump”) at 217.5 nm ( $4.6 \mu\text{m}^{-1}$ ) protruding from an otherwise monotonic curve that rises steeply towards short wavelengths in the far ultraviolet (FUV). The UV bump was discovered by [Stecher \(1965\)](#) and, considering the optical properties of graphite, [Stecher and Donn. \(1965\)](#) indicated that small graphite particles would produce the observed absorption. The assignment of the UV bump to pure graphite particles was successfully used in dust models ([Mathis et al., 1977](#)) and refined and adapted over the years to the growing body of experimental data ([Draine and Lee, 1984](#); [Draine 1989](#); [Mathis 1994](#)). Within this model, the bump would be due to the absorption produced by  $\pi$  plasmons in small graphitic grains. Over the years, the UV bump was observed in the diffuse ISM towards many Galactic lines of sight. A detailed analysis of 328 Galactic interstellar extinction curves from the IR to the UV was presented by [Fitzpatrick and Massa. \(2007\)](#). These authors concluded that the peak position of the 217.5 nm feature was fairly stable (typically within 1 per cent), whereas its full width at half maximum (FWHM) could vary between 80 and 125 nm depending on the source. No correlation was found between peak position and width. The pure graphite model cannot easily explain the high variety of extinction values and variable widths for the 217.5 nm feature, and other carbonaceous

solids have been suggested as alternative. The presence of presolar graphite grains in meteorites ([Davies, 2011](#)) indicates that pure graphite particles exist in the ISM, but it is difficult to estimate their relative abundance. A characteristic lattice line of graphite at 11.53  $\mu\text{m}$  ([Draine 2016](#)) has been sought in IR observations, but it has not been found (see next subsection).

The various carbonaceous solids suggested as carriers of the 217.5 nm bump are often based on dust analogs produced in the laboratory. These carrier candidates are disordered solids containing C and H and, in analogy with graphite, have a more or less extensive  $C_{sp^2}$  network. [Sakata et al. \(1983\)](#); [Sakata et al. \(1994\)](#) used an expanding hydrocarbon plasma to generate an amorphous carbonaceous material denominated quenched carbon composite, QCC. By suitably modifying the experimental conditions, they obtained QCC samples with an absorption band peaking at 217–220 nm and with a shape roughly similar to that of the IS extinction curve. Electron microscopy of these QCCs showed that they were made of particles with diameters smaller than 4 nm. [Joblin et al. \(1992\)](#) used synchrotron radiation to measure the UV extinction of mixtures of polycyclic aromatic hydrocarbons (PAHs) evaporated from natural terrestrial mixtures. The estimated masses of the evaporated PAHs ranged between 170 and 550 u. The extinction curves from different PAHs mixtures showed consistently an absorption maximum at 205 nm and smaller, mixture-specific bands, at lower wavelengths. A steep extinction rise was also observed towards the FUV. The authors concluded that PAHs could not fully account for the astronomical 217.5 nm bump, but could contribute appreciably to the bump intensity, especially at its short wavelength side. Using UV absorption cross sections determined in the same work, [Joblin et al.](#) estimated that roughly 18 per cent of interstellar carbon could be in the form of PAHs. Later estimates from infrared emission give smaller values (see below). [Mennella et al. \(1996\)](#) proposed an analog based on hydrogenated amorphous carbon (generally abbreviated a-C:H, and often HAC in the astrophysical literature) as the possible carrier of the UV bump. Samples of a-C:H, made of chainlike structures of aggregates composed of spheres with an average diameter of 11 nm were produced in an arc discharge between two graphite rods in a  $H_2$  atmosphere at 10 mbar. Hydrogenated amorphous carbon is a disordered material that contains a mixture of aliphatic and aromatic structures ([Robertson, 1986](#); [Schultrich, 2018](#)). It will be described in more detail in the next subsection. Solids made of a-C:H are semiconductors. Their band gap,  $E_g$ , and their electronic  $\pi$ - $\pi^*$  transitions, that take place between  $\approx 190$  and 270 nm, are largely determined by the size of the aromatic units. Irradiation of a-C:H samples with UV photons leads to dehydrogenation and graphitization, which results in a decrease of  $E_g$  and in changes in the UV-Vis spectra. The extinction curve of the freshly deposited a-C:H samples in the experiments of [Mennella et al. \(1996\)](#) showed a monotonic



growth with decreasing wavelength down to 200 nm. However, upon UV irradiation with a hydrogen lamp, a resonance was activated in the spectrum of the a-C:H grains at 215 nm, close to the position of the interstellar bump. Mennella et al. attributed the 215 band to  $\pi$ - $\pi^*$  transitions in the  $sp^2$  ringed clusters forming the grains, made possible by structural changes induced by the UV irradiation. Note that this interpretation is in contrast with the collective plasmon excitation assumed in the graphite model of the UV bump carriers (Draine and Lee, 1984).

More laboratory analogs of the carriers of the 217.5 nm bump were subsequently generated. Interstellar dust analogs based on a-C:H were generated through evaporation or laser ablation of a

carbon target in the presence of hydrogen (Schnaiter et al., 1998; Gadallah et al., 2011; Duley and Hu, 2012), and polyaromatic soot-based analogs through  $CO_2$  laser pyrolysis of gas phase hydrocarbons (Steglich et al., 2010). Comparison with astronomical data showed that the 217.5 nm bump can be approximately reproduced with the UV spectra of PAHs with 50–60 carbon units or with nanometric particles of hydrogen poor a-C:H with a high  $C_{sp^2}$  content. Considering the measured absorption strengths, if the UV bump were due to particles like those produced by Schnaiter et al. (1998), the IS abundance of carbon contained in this kind of dust would be  $[C/H]_{dust} = 84$ –114 ppm, and the dust analogs from the experiment of Gadallah et al. (2011) would lead to  $[C/H]_{dust} = 108$ –269 ppm. These abundances are compatible with the  $[C/H]_{dust} = 126 \pm 56$  ppm proposed by Hensley and Draine. (2021) and suggest that these materials are realistic candidates for carriers of the astronomical UV bump, especially those from the experiments of Schnaiter et al. In recent works, Gavilan et al. (2016); Gavilan et al. (2017) have also used polyaromatic soot and a-C:H as analogs for IS dust. Films of soot nanoparticles and a-C:H were deposited on suitable substrates, and transmission spectra were recorded over a wide spectral range from the FUV to the IR. The soot deposits were prepared using a premixed flame of oxygen and  $C_2H_4$  (see Figure 1A), and the a-C:H layers were generated with RF discharges of  $CH_4$  or toluene. The largely polyaromatic and H poor soot samples were found to reproduce better the region of the 217.5 nm bump (as expected), but more hydrogenated carbons seem to contribute to the spectrum in the FUV. A comparison of the UV spectrum of a soot sample with the average interstellar extinction curve of Fitzpatrick and Massa. (2007) is shown in the Figure 1B. The energy of the main  $\pi$ - $\pi^*$  transition deduced from the measurements, and termed L1 in Figure 1, is in good agreement with the position of the bump maximum. A careful analysis and modelling of the data of Gavilan et al. (2017) indicates that the polyaromatic units in the soot samples accounting for the UV bump should have between 20 and 100 C atoms.

Different kinds of materials, including graphite and gas phase PAHs, can contribute to the ubiquitous 217.5 nm bump in astronomical observations, but, at present, a comparison of laboratory and experimental data strongly suggests that the main carriers of this extinction feature should be small (a few nm) particles made of some sort of disordered hydrogenated carbon with a largely polyaromatic structure and a comparatively small hydrogen content. The carriers of the UV bump could be related with other spectroscopic signatures of IS carbonaceous matter. Xiang et al. (2017) have explored possible correlations between the UV bump and diffuse interstellar bands. Correlations with DIBs would indeed be very interesting, since they could help constrain the nature of the unknown DIB carriers, but Xiang et al. did not find any. In contrast, in a recent work, Massa et al. (2022), using UV and IR data from 16 stars, found a strong correlation between the area of the

217.5 nm bump and the strengths of the major emission features of the aromatic infrared bands (to be discussed in Section 2.3). This correlation is not unexpected considering the likely bump carriers discussed above.

## 2.2 The carriers of the infrared absorption bands

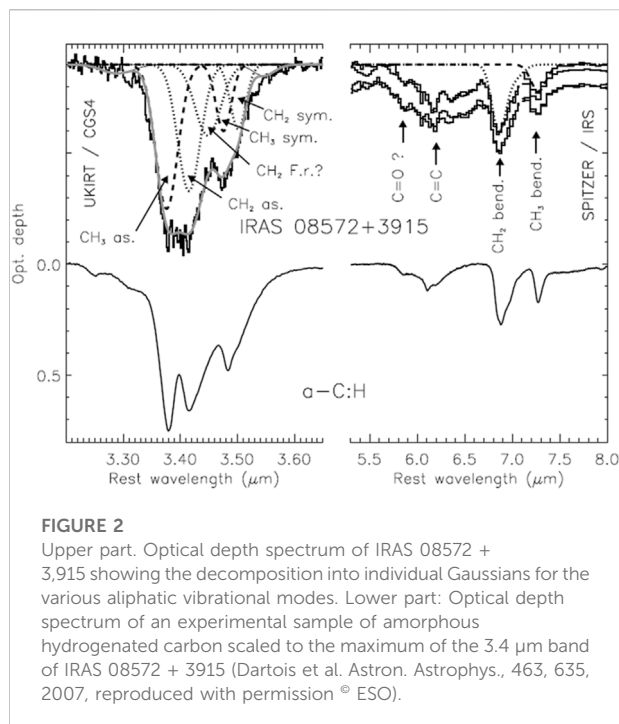
In the IR region, between 3 and 8  $\mu\text{m}$ , there are some extinction features associated with carbonaceous matter. They are much weaker than the pronounced IR silicate bands at 9.7  $\mu\text{m}$  and 18  $\mu\text{m}$  mentioned in the introduction. The most relevant carbonaceous IR band is the 3.4  $\mu\text{m}$  ( $2950\text{ cm}^{-1}$ ) absorption. It was first identified as an IS feature, of uncertain origin, in observations toward the Sgr A IRS 7 Galactic center source (Soifer et al., 1976; Willner et al., 1979a), and it was subsequently attributed to CH stretching vibrations of organic matter by Wickramasinghe and Allen. (1980). Given the intrinsic weakness of the band, high column densities of the carrier are required for its observation. It is present in many lines of sight, against bright IR background sources, in the direction of the Galactic center. Observations towards the heavily obscured supergiant Cyg OB2-12 (Whittet et al., 1997), indicate that the band is not restricted to Galactic center sources, but is common in the local diffuse ISM. The 3.4  $\mu\text{m}$  feature is also found in the ISM of external galaxies (Imanishi, 2000; Dartois and Muñoz-Caro, 2007). Duley and Williams (1983) identified a subband structure at 3.48, 3.41, and 3.38  $\mu\text{m}$ , and noted the similarity in shape with the 3.4  $\mu\text{m}$  IR band of a-C:H produced in a glow discharge of ethylene. Sandford et al. (1991) attributed the subband structure to  $\text{CH}_2$  and  $\text{CH}_3$  groups of saturated aliphatic hydrocarbons, and an approximate  $\text{CH}_2/\text{CH}_3$  ratio of 2–2.5 was estimated for the band carriers (Sandford et al., 1991; Pendleton et al., 1994). The presence of a saturated aliphatic component in the dust was corroborated by weaker absorption bands at 6.85  $\mu\text{m}$  and 7.25  $\mu\text{m}$ , attributed to deformation and bending vibrations of  $\text{CH}_2$  and  $\text{CH}_3$  groups. They were observed towards the Galactic center (Tielens et al., 1996; Chiar et al., 2000), in the local diffuse ISM (Hensley and Draine, 2020), and in extragalactic sources (Dartois et al., 2007). Weak absorptions at 3.3  $\mu\text{m}$  and 6.2  $\mu\text{m}$  attributed to CH and C=C aromatic stretching vibrations have also been reported in the same environments (Chiar et al., 2000; Chiar et al., 2013; Dartois et al., 2007; Hensley and Draine, 2020). In addition, a 7.7  $\mu\text{m}$  feature, possibly from aromatic C-C stretching modes (Allamandola et al., 1989), was observed by Hensley and Draine. (2020) in the diffuse ISM toward Cyg OB2-12. Of all the absorption bands commented on in this paragraph, the 3.4  $\mu\text{m}$  feature is the best known one. It is the most intense and is accessible from ground based telescopes. Data beyond 5  $\mu\text{m}$  are based on observations from space missions (ISO, Spitzer) and are much less abundant. In contrast to silicate

absorption features, the 3.4  $\mu\text{m}$  carbonaceous band is unpolarized (Hensley and Draine, 2021). This points to different populations of carbon and silicate grains and questions the possibility of a significant presence of mixed grains with carbonaceous mantles on top of silicate particles.

The absence of some IR bands in the diffuse ISM is also illustrative. Silicon carbide has been found in presolar grains, and its 11.3  $\mu\text{m}$  Si-C stretch band has been detected in the atmosphere of carbon-rich evolved stars. If it were present in the ISM even as a small fraction (a few per cent) in abundance with respect to the silicates, the 11.3  $\mu\text{m}$  band should be observable, but it has never been found. The reason for the absence of SiC in the ISM is unknown, and is currently a matter of debate (see Chen et al., 2022 for a recent discussion). As mentioned in the previous section, polycrystalline graphite is expected to have a lattice line at 11.53  $\mu\text{m}$  (Draine 2016). The line was not detected by Hensley and Draine. (2020) in observations of the diffuse ISM towards Cyg OB2-12, and they estimated an upper limit of 160 ppm of carbon as graphite.

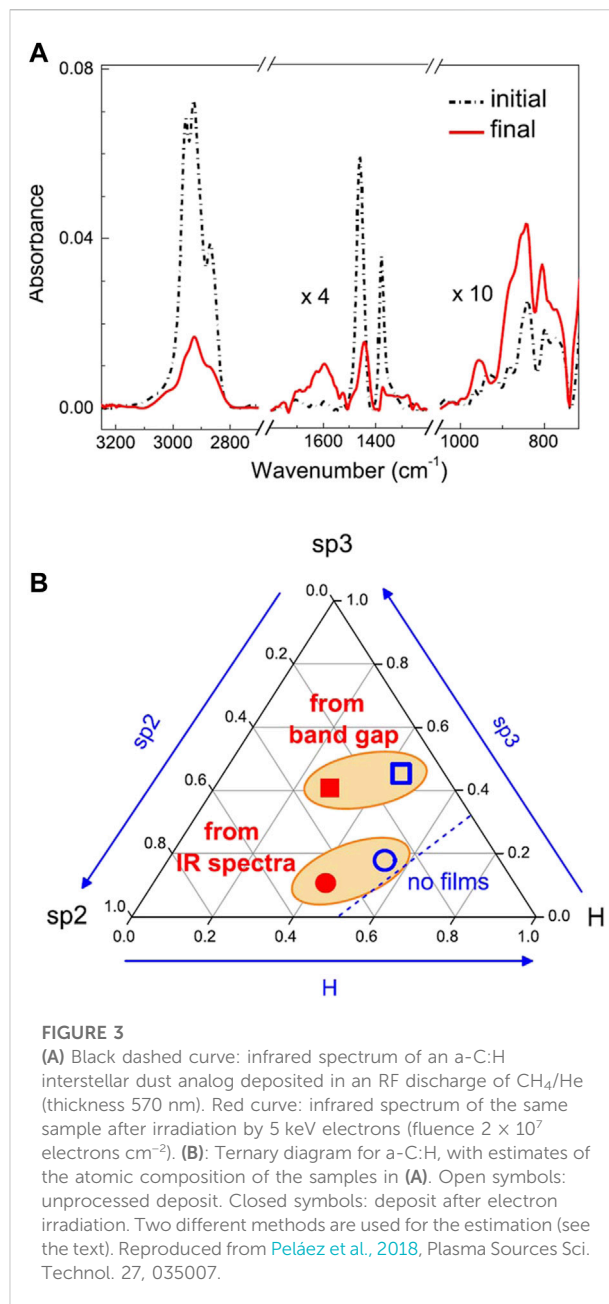
Since the observation of the 3.4  $\mu\text{m}$  band, many different materials were proposed as possible carriers of the hydrocarbon features. Pendleton and Allamandola. (2002) made a critical study of likely candidates based on a series of observational constraints as of 2002. They included various laboratory produced analogs and also material from carbonaceous chondrites and even *E. coli* bacteria, that had also been discussed in the literature as possibly relevant in the diffuse ISM (Hoyle et al., 1982). Pendleton and Allamandola concluded that the organic refractory material responsible for the observed features was predominantly hydrocarbon in nature with little nitrogen or oxygen and with a mixture of aromatic and aliphatic structures. Comparison of laboratory spectra with those of observations showed that the best of their laboratory analogs were the a-C:H deposits produced in hydrocarbon plasmas.

Over the years, different experimental methods have been used for the production of laboratory analogs to the carriers of the IR absorption bands. These techniques include laser ablation of carbon-containing precursors (Scott and Duley, 1996; Mennella et al., 1999; Grishko and Duley, 2000; Llamas Jansa et al., 2007; Jäger et al., 2008, 2009; Duley and Hu, 2012; Gadallah et al., 2012; Fulvio et al., 2017), plasma deposition (Furton et al., 1999; Kovačević et al., 2005; Stefanović et al., 2005; Jäger et al., 2008; Godard and Dartois, 2010; Godard et al., 2011; Contreras and Salama, 2013; Maté et al., 2014; Maté et al., 2016; Molpeceres et al., 2017; Günay et al., 2018; Hodoroba et al., 2018; Peláez et al., 2018; Gavilan Marin et al., 2020; Sciamma-O'Brien and Salama, 2020), combustion flames (Pino et al., 2008; Carpentier et al., 2012), pyrolysis (Herlin et al., 1998; Biennier et al., 2009; Jäger et al., 2009) or low temperature photolysis of hydrocarbons (Dartois et al., 2004; Dartois et al., 2005). Different kinds of solids are obtained in the mentioned experiments. Soot like particles, poor in hydrogen and with a high polyaromatic content, tend to form in experiments using carbon targets. In contrast, solids with



a high proportion of aliphatic material can be obtained in discharges of saturated hydrocarbons. The good agreement that can be attained between the observational and laboratory spectra is illustrated in Figure 2, taken from Dartois et al. (2007), where the IR spectrum of the ISM in the infrared galaxy IRAS 08572 + 3915 is compared to that of an a-C:H sample prepared in the laboratory through the UV photolysis of frozen hexane.

The label “hydrogenated amorphous carbon” includes a wide group of materials with variously hybridized carbon atoms and different C/H ratios. They have three dimensional structures, with a tendency to cluster, made of aromatic islands of variable sizes linked by saturated aliphatic chains with possible olefinic contributions (Robertson, 1986; Schultrich, 2018). a-C:H occupies much of the central part in the ternary diagram shown in the Figure 3B. The diagram describes the C/H ratio and the C hybridization states in a variety of solids containing carbon and hydrogen. The adoption of this diagram implies that all atoms in a-C:H are  $C_{sp^3}$ ,  $C_{sp^2}$ , or hydrogen. The possible contribution of sp carbon atoms is tacitly neglected. Graphite is located at the lower left vertex of the diagram, and diamond at the upper vertex. PAHs are in the horizontal axis, between the  $sp^2$  and H vertices. For historical reasons, in the literature on material science, the term a-C:H is often interchanged with “diamond like amorphous carbon”, a solid with a relatively high proportion of  $sp^3$  carbon (Robertson, 2002). In the astrophysical literature the term is more flexible and includes also aromatic-rich, H-poor material (soot, carbon black), sometimes referred to as amorphous carbon (a-C) (Jones et al., 2013; Jones et al., 2014;



Jones et al., 2017), that would occupy a region close to the graphite vertex.

As indicated above, a-C:H solids are semiconductors, and  $\pi-\pi^*$  transitions in these materials are assumed to be the cause of the 217.5 nm bump. The optical band gap of amorphous semiconductors, also named the Tauc gap (Tauc et al., 1966), can be approximately derived from measurements in the visible spectral range. This band gap,  $E_g$ , determines the wavelength of  $\pi-\pi^*$  transitions (Gavilan et al., 2017) and can be correlated with structural properties. From a detailed study of a large number of different a-C:H solids, correlations of  $E_g$  have been proposed with

the size of the polyaromatic units (Robertson, 1986), with the  $C_{sp^2}$  vs.  $C_{sp^3}$  proportion (Robertson, 2002), and with the H/C ratio (Casiraghi et al., 2005). Correlations of this type are of course only approximate and have limitations (Llamas Jansa et al., 2007). Despite these limitations, the band gap has proven very useful as a key parameter in models of interstellar a-C:H (Jones et al., 2013).

The predominant structure of the a-C:H dust material associated with the IR absorptions in the diffuse ISM is currently a matter of debate between two competing models. The first of these models assumes that the material in the grains is relatively hydrogen rich, composed by small aromatic islands linked by aliphatic chains (Dartois et al., 2005; Kwok and Zhang 2013). The second model assumes that the a-C:H making diffuse ISM grains is much more graphitic, with large polyaromatic sheets terminated by short aliphatic endings (Chiar et al., 2013; Steglich et al., 2013). Estimates of the  $C_{sp^2}/C_{sp^3}$  proportion and of the H/C ratio of IS dust from the observed IR spectra have been attempted through subband profile decompositions like the one shown in Figure 2. However, this procedure should be taken with care. Estimates of the a-C:H composition based just on IR data might be unreliable (Jacob and Möller, 1993), because the band strengths of the individual modes are poorly known for the disordered solid structures in a-C:H. Band strengths based on small organic molecules and PAHs have been often used (Sandford et al., 1991; Pendleton et al., 1994; Dartois et al., 2007). As an example, the value of the band strength of the antisymmetric  $CH_3$  stretching vibration taken by Dartois et al. (2007) is  $A_{as}(CH_3) = 12.5 \times 10^{-18} \text{ cm group}^{-1}$ . A different set of band strengths, based on IR models of a-C:H, was proposed by Chiar et al. (2013). These band strengths are appreciably larger than those based on molecules ( $A_{as}(CH_3) = 24.3 \times 10^{-18} \text{ cm group}^{-1}$ ). On the other hand, estimates of the aliphatic band strengths based directly on measurements performed on a-C:H analogs yield lower values. Duley et al. (1998) reported an experimental value of  $A_{as}(CH_3) = 1.9 \times 10^{-18} \text{ cm group}^{-1}$ . In a recent experiment Günay et al. (2018) obtained a strength,  $A(3.4 \mu\text{m}) = 4.7 \times 10^{-18} \text{ cm group}^{-1}$ , for the whole 3.4  $\mu\text{m}$  absorption band. This experiment combined nuclear magnetic resonance (NMR) and IR measurements for an accurate evaluation of the aliphatic dust content. In addition to these discrepancies, a large uncertainty is attached to the band strength of the weak absorption features of the aromatic C-H and C=C stretching vibrations, that are used to estimate the  $C_{sp^2}$  fraction in the solid network. Density functional theory (DFT) calculations by Molpeceres et al. (2017), performed on models of a-C:H dust analogs, further showed that the procedure of estimating the hydrogen and graphitic content of a-C:H samples through the decomposition of IR features into vibrational modes of individual functional groups is problematic, owing to appreciable mode mixing and to the difficulty of assigning reliable and unique band strengths to the various molecular vibrations. Besides, the calculated band

strengths were found to be strongly dependent on the assumed density.

Figure 3, adapted from Peláez et al. (2018), shows the IR spectra of two dust analogs, and illustrates the uncertainty in the estimation of their structural properties. The first of the two analogs (black dashed trace in upper panel) was deposited from a He/ $CH_4$  mixture in an inductively coupled RF discharge. Its spectrum is dominated by the aliphatic bands of  $CH_3$  and  $CH_2$  groups at  $2,950 \text{ cm}^{-1}$  (3.4  $\mu\text{m}$ ),  $1,460 \text{ cm}^{-1}$  (6.85  $\mu\text{m}$ ) and  $1,379 \text{ cm}^{-1}$  (7.25  $\mu\text{m}$ ). The second dust analog (red trace in the upper panel) was obtained from the bombardment of the first one with 5 keV electrons. This energetic processing causes structural changes that result in a decrease in the aliphatic bands and an enhancement of aromatic bands at about  $1,600 \text{ cm}^{-1}$  (6.25  $\mu\text{m}$ ) and in the region below  $1,000 \text{ cm}^{-1}$  (10  $\mu\text{m}$ ). Tauc gap,  $E_g$ , energies of 2.7 eV (unprocessed sample) and 1.6 eV (processed sample) were obtained from reflectivity spectra. Estimates of the composition of the two samples were derived alternatively from a decomposition of the IR bands, using the band strengths of Chiar et al. (2013), and from literature  $E_g$  correlations (see Peláez et al., 2018 for details). The results are represented in the ternary diagram in the lower part of the figure. Both methods yield a comparable H/C ratio and consistently describe the graphitization and dehydrogenation of the original a-C:H upon electron bombardment, but they differ largely in the  $C_{sp^2}/C_{sp^3}$  hybridization ratio, with IR determinations favoring a much larger  $C_{sp^2}$  network.

The abundance of aliphatic (saturated) hydrocarbon in interstellar dust has been evaluated using observations of the 3.4  $\mu\text{m}$  absorption band (Sandford et al., 1991; Pendleton et al., 1994; Sandford et al., 1995; Duley et al., 1998). The percentage of aliphatic carbon with respect to cosmic carbon derived in these studies ranges from a few per cent to 40 per cent, depending on the band strengths, model, and assumed cosmic carbon abundance. In recent works, Günay et al. (2020); Günay et al. (2022) have used their experimentally measured band strength (Günay et al., 2018) to estimate the amount of aliphatic carbon towards many lines of sight in the Galactic center and in the local diffuse ISM. They found typical abundances [C/H] of several tens of ppm and concluded that the amount of (saturated) aliphatic carbon locked in dust grains amounts to 10–20 per cent of the available cosmic carbon. The scarcity of observations, and the intrinsic weakness of the aromatic bands, hamper a reliable estimate of the aromatic component of dust based on IR absorption measurements.

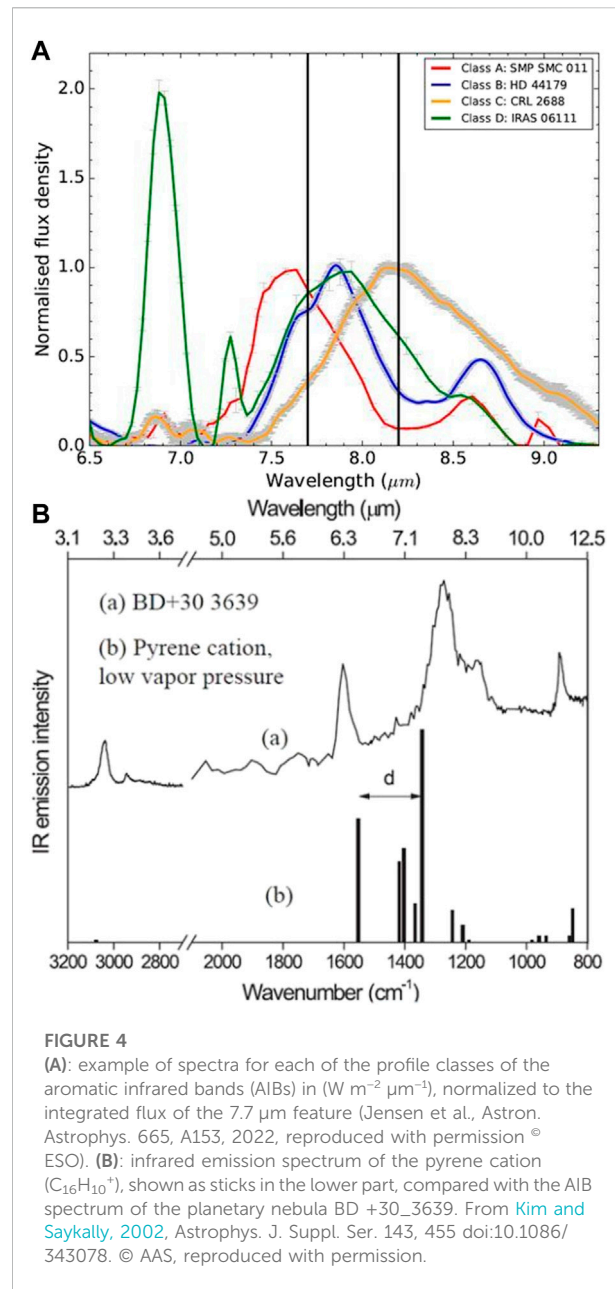
## 2.3 The carriers of the infrared emission bands

A strong IR emission band was first observed at 11.3  $\mu\text{m}$  by Gillett et al. (1973) in the NGC 7027 planetary nebula. It was tentatively attributed to mineral carbonate in dust grains.



Subsequent work led to the rejection of the carbonate hypothesis and to the finding of further strong and broad emission features at 3.3, 6.2, 7.7, and 8.6  $\mu\text{m}$  in the same source. Likely carriers for these bands were not immediately obvious, and they were globally termed unidentified infrared emission (UIE) bands (Willner et al., 1979b). The UIE bands, that were found to occur together, happened to be common in regions illuminated by UV photons: planetary nebulae, reflection nebulae, H<sub>II</sub> regions, and the diffuse ISM of the Milky Way and of external galaxies. Duley and Williams. (1981) noted that the location of the UIE band maxima was characteristic for polycyclic aromatic compounds, and proposed as band carriers polycyclic aromatic surface groups on top of bulk grains. Since then, the polycyclic aromatic origin of the bands has been accepted and they are often called aromatic infrared bands (AIBs). An assignment of these features to vibrational modes can be found in Table 1. A variety of carbonaceous structures have been suggested as possible carriers of all, or some, of the AIBs, including polycyclic aromatic hydrocarbons (Léger and Puget, 1984; Allamandola et al., 1985), amorphous hydrogenated carbon (Duley and Williams, 1983), carbon nanoparticles (Hu and Duley, 2008), kerogen and coal (Papoular et al., 1989), petroleum derivatives (Cataldo et al., 2002; Cataldo et al., 2004), mixtures of aromatic and aliphatic organic nanoparticles (Kwok and Zhang, 2011; Kwok and Zhang, 2013), and quenched nitrogen-included carbonaceous composite, QNCC, (Endo et al., 2021). Among all these possible carriers, polycyclic aromatic hydrocarbons are the most generally accepted. Besides the identification of aromatic bands, the PAH hypothesis relies on work by Sellgren. (1984), who observed that, in reflection nebulae, the IR emission took place at a long distance from the illuminating star, where the radiative temperature of bulk grains should be too low (<100 K) to emit in the IR. Single UV photons from the star could heat the dust grains, but these grains should be very small, of the order of 1 nm, to reach the temperatures of about 1000 K necessary to justify the observed IR continuum emission. Léger and Puget, 1984 and Allamandola et al. (1985) realized that large molecules could also be heated to  $\approx 1000$  K by absorption of a single UV photon, and proposed PAHs (with tens of C atoms) as carriers of the UIE bands. The PAH hypothesis has been refined over the years to account for a growing body of observations and experiments (Tielens, 2008; Peeters et al., 2011; Tielens, 2011; Peeters et al., 2021).

Besides the main AIB bands, aliphatic transitions at 3.4, 6.85, and 7.27  $\mu\text{m}$  and a number of weak features in the 3–20  $\mu\text{m}$  range were also found in emission, and the emission bands are often found on top of broad emission plateaus at about 3.2–3.6, 6–9, 10–15, and 15–20  $\mu\text{m}$ . The relative intensities and profiles of the AIB bands vary from source to source. Band profile modifications are especially prominent in the 6–9  $\mu\text{m}$  region. The sources are classified into A, B, C and D (Peeters et al., 2002; van Diedenhoven et al., 2004; Matsuura et al., 2014; Jensen et al.,



**FIGURE 4**  
 (A): example of spectra for each of the profile classes of the aromatic infrared bands (AIBs) in ( $\text{W m}^{-2} \mu\text{m}^{-1}$ ), normalized to the integrated flux of the 7.7  $\mu\text{m}$  feature (Jensen et al., *Astron. Astrophys.* 665, A153, 2022, reproduced with permission © ESO). (B): infrared emission spectrum of the pyrene cation ( $\text{C}_{16}\text{H}_{10}^+$ ), shown as sticks in the lower part, compared with the AIB spectrum of the planetary nebula BD +30\_3639. From Kim and Saykally, 2002, *Astrophys. J. Suppl. Ser.* 143, 455 doi:10.1086/343078. © AAS, reproduced with permission.

2022). Examples of these classes are shown in Figure 4. Classes A, B, C reflect profiles with increasing central wavelength of the 7.7  $\mu\text{m}$  transition complex (the maximum can vary between 7.6  $\mu\text{m}$  for class A and 8.2  $\mu\text{m}$  for class C). Class D has similar central wavelength as class B, but a similar width as class C. The classes depend on source type and correspond thus to different environments. Class A spectra generally arise from interstellar objects, for example H<sub>II</sub> regions and reflection nebulae, along with a small number of evolved stellar objects. Class B spectra predominantly come from carbon-rich planetary nebulae and the disks around young stellar objects (YSOs). Class C emission arises from a variety of objects, including

Herbig Ae/Be stars, T Tauri stars, carbon-rich objects which have evolved past the asymptotic giant branch, and carbon-rich red giants. Class D spectra are only observed in carbon-rich post-AGB objects. The bands from interstellar sources (class A) are highly aromatic, whereas circumstellar sources, especially those of class D, present a higher aliphatic component (Jensen et al., 2022). Class A emission is ubiquitous and is attributed to the fluorescence mechanism commented on above, which is independent of the photon flux and, thus, of the distance to the photon source. Some of the class C and D emissions may be related to a thermal emission mechanism which could only be active in the vicinity of the photon sources (Dartois, 2019).

In contrast with the IR absorption bands discussed in the previous subsection, it has not been possible to reproduce in the laboratory experimental IR emission spectra that match the AIBs. Emission spectroscopy in the IR is complicated due to the background radiation, and most spectroscopic information on PAHs has been derived from IR absorption measurements (See Oomens, 2011 for an overview on the laboratory IR spectroscopy of PAHs). Gas-phase absorption spectra of PAHs were recorded by Joblin et al. (1995), Oomens et al. (2000) and Cazaux et al. (2019). Matrix isolation techniques have proven especially useful (Vala et al., 1994; Hudgins and Allamandola, 1995; Garkusha et al., 2012). They have allowed the compilation of a large database of spectra of neutral and ionic PAHs that has been enlarged over the years (Hudgins and Allamandola, 2004; Mattioda et al., 2020). In spite of the difficulties, gas phase IR emission spectra of small neutral PAHs excited by UV photons were measured in sophisticated experiments with an extremely sensitive IR detector (Schlemmer et al., 1994; Cook et al., 1996; Cook et al., 1998; Wagner et al., 2000). The results established that small neutral PAHs could not be the main carriers of the AIBs, since their emission spectra are dominated by strong features near 3.3  $\mu\text{m}$  (CH stretching) and beyond 11  $\mu\text{m}$  (CH out of plane bending), and present only weak absorptions in the 6–9  $\mu\text{m}$  range, where the intensities of the AIBs are high. However, as discussed in Allamandola et al. (1999), the band intensity pattern changes dramatically for ionic PAHs where the CC stretching and the CH in plane vibrations, with wavelengths in the 6–9  $\mu\text{m}$  interval, see their intensity enhanced by more than an order of magnitude and become dominant, in qualitative agreement with the observed AIBs. Later experiments with protonated PAHs (see for instance Dopfer 2011; Tsuge et al., 2018) corroborated this agreement. A refinement of the just mentioned gas phase IR fluorescence experiments allowed the measurement of the IR emission from excited pyrene cations and dehydrogenated pyrene cations (Kim et al., 2001; Kim and Saykally 2002) and showed that the dominant bands were indeed in the 6–9  $\mu\text{m}$  range, close to some of the AIBs (see Figure 4B).

Allamandola et al. (1999) suggested that the infrared emission band spectrum associated with many different interstellar objects could be successfully modelled by using combined laboratory

spectra of neutral and positively charged PAHs. This procedure has been applied and refined in later works (Joblin et al., 2008; Rosenberg et al., 2014). To account for the variety of observed AIB profiles, the original PAH model has been modified to incorporate different ionization states, larger molecular sizes, dehydrogenation, superhydrogenation, and small aliphatic side groups or heteroatoms, as well as clusters (see references in Peeters et al., 2021). This is a significant departure from the initial PAH hypothesis, but still the basic ingredients are large polyaromatic structures. Extensive databases of IR spectra of PAHs, both experimental (Mattioda et al., 2020) and theoretical (Bauschlicher et al., 2018), are now available.

The PAH hypothesis has been criticized (Kwok and Zhang, 2011; Kwok and Zhang, 2013; Zhang and Kwok, 2015; Kwok, 2016; Kwok, 2022) because an artificial mixture of PAH structures, sizes and ionization states, with a large number of free parameters, must be used to account for the broad emission features, and because it cannot satisfactorily explain the very small variations in the AIB pattern in regions with widely different UV backgrounds. Besides, individual PAHs have been elusive in space. Only recently, a bicyclic aromatic molecule, indene, formed by two fused rings with six and five atoms respectively, has been detected in the dense cloud TMC-1 (Burkhardt et al., 2021; Cernicharo et al., 2021). As an alternative to PAHs, very small particles of other carbonaceous solids have been suggested as possible AIB carriers. These candidates include various types of hydrogen poor aromatic rich soot, similar to the materials discussed as carriers for the 217.5 nm bump, or substances derived from petroleum fractions (Dischler et al., 1983; Herlin et al., 1998; Cataldo et al., 2002; Cataldo et al., 2004; Cataldo et al., 2021), whose IR absorption spectra have aromatic bands with some resemblance to those in the AIBs. This type of substances would fit into the model of aromatic/aliphatic organic nanoparticles (MAON) advanced by Kwok and Zhang. (2011); Kwok and Zhang. (2013), that assumes carbonaceous compounds containing aromatic rings of various sizes and aliphatic chains of different lengths and orientations arranged in a 3-D amorphous structure, mixed with heteroatoms. This model has also been criticized because it lacks a convincing excitation mechanism (Rosenberg et al., 2014) and because there is no specific assignment of vibrational modes to the observed bands. Although in many aspects the PAH and MAON models are not necessarily contradictory, there is still a vivid controversy between the groups advocating large molecules (including clusters) and those proposing very small grains as the AIB carriers (Candian et al., 2019; Tokunaga and Knacke, 2019). A connection between the carriers of the UV bump and those of the AIBs has always been suspected, and a recent work by Massa et al. (2022) corroborates this connection by showing a strong correlation between the two features. From an experimental point of view, the performance of IR fluorescence experiments on the large-size species likely responsible for the AIBs remains to date a formidable challenge.

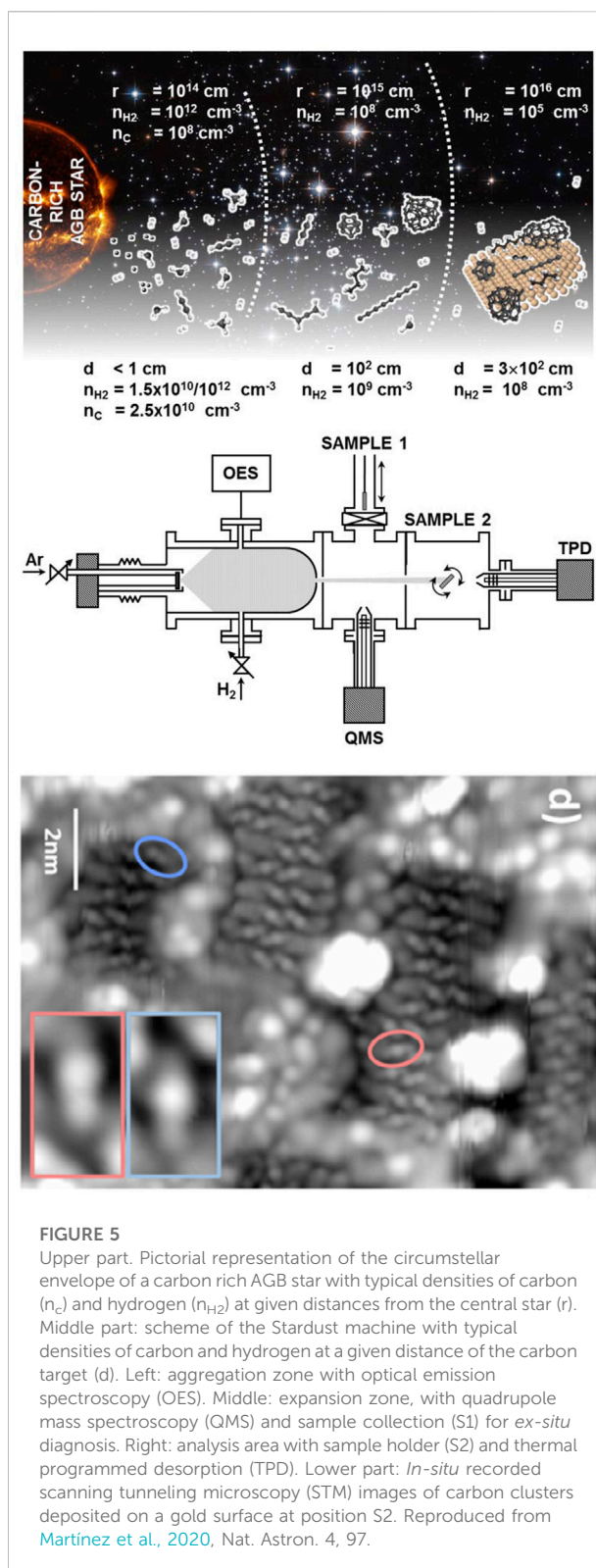
It is estimated that the carriers of the AIBs, usually assumed to be PAHs in the models, represent  $\approx 5$ –10 per cent of the cosmic carbon (Draine and Li, 2007, see also references in Dartois, 2019; Peeters et al., 2021), and are responsible for a 10–15 per cent of the IR power output of galaxies (Smith et al., 2007).

### 3 Origin and evolution of carbonaceous dust

Carbonaceous dust grains are formed in the circumstellar envelopes of carbon rich AGB stars, although other sources, especially core collapse supernovae, can also be significant (Dorschner and Henning, 1995; Sarangi et al., 2018). After their formation, the grains move away from stars and begin a journey through the diffuse ISM where they can be modified through the interaction with H atoms, UV radiation and cosmic rays, and can be destroyed by shock waves from supernova explosions. Surviving grains will eventually enter a dense cloud and participate in the cloud collapse giving rise to a new star, closing thus the cycle. However, it is estimated that the stellar injection rate is much smaller than the shock wave destruction rate (Draine et al., 2009; Jones and Nuth, 2011), and this implies that much of the observable interstellar dust has not been directly produced in stellar outflows, but has been formed or re-formed in the ISM. This is particularly so for carbonaceous grains, that are more labile (Jones and Nuth, 2011). The mechanisms of dust grain re-formation in the ISM are not well known, but it has been suggested that carbonaceous grains can grow significantly, in dense, cold phases of the ISM, by accretion of atoms and molecules on pre-existing particles, and then by coagulation (Jones et al., 2013; Jones et al., 2014; Jones et al., 2017).

#### 3.1 Carbonaceous dust production

In a typical AGB star, dust starts to form in the inner shell region (an equilibrium zone with a low ionization degree, largely devoid of UV photons), and evolves until it is ejected into the ISM. It is estimated that the temperature in the dust formation region is around 1000 K but the physical conditions of the nucleation zone remain uncertain (Fonfría et al., 2008), since direct observation is difficult due to the high opacity. It is thus not clear what kind of carbonaceous solids are formed in the early stages of condensation. It has often been conjectured that PAHs are formed in these stellar envelopes through polymerization of  $C_2H_2$  (Frenklach and Feigelson, 1989; Cherchneff et al., 1992; Cherchneff, 2011; Cherchneff, 2012), and experimental measurements by Jäger et al. (2009) and Biennier et al. (2009) have shown that the pyrolysis of  $C_2H_2$  at 1000–1500 K, leads indeed to dust particles with large polyaromatic planar layers.



Mechanisms of formation and growth of PAHs from organic precursors larger than  $C_2H_2$  have also been experimentally studied at high temperature (Parker et al., 2014; Yang et al.,

2017; Zhao et al., 2019). However, PAHs have not been found in the close vicinity of stellar envelopes. Emissions from AIBs, characteristic of PAHs, are only detected in later stages of stellar evolution like protoplanetary and planetary nebulae (Kwok 2011), in the presence of UV fields. To shed more light on the dust formation chemistry in circumstellar envelopes, dedicated experiments have been performed. We will consider these experiments in some detail. Martínez et al. (2020) investigated the formation of dust seeds using exclusively carbon atoms and molecular hydrogen in a proportion relevant for the conditions expected for the inner shell of C rich AGB stars (Cernicharo, 2004). This simulates the very first stages of condensation. The experimental set-up (“Stardust”) consists of a set of ultrahigh vacuum (UHV) chambers that host a sputtering gas aggregation source and a series of diagnostic techniques. The sputtered C atoms react with H<sub>2</sub> in the first chamber, and the products travel then to the next chambers, where they are either observed in the gas phase or collected on inert surfaces for further analysis. The temperature in the aggregation region was estimated to be <1000 K and possibly close to 500 K. A scheme of this apparatus can be seen in Figure 5, where a pictorial representation of the circumstellar envelope, with an indication of typical carbon and hydrogen densities, is also given. The particles formed were analyzed with atomic force microscopy (AFM) and scanning tunneling microscopy (STM), as well as with ultrasensitive laser desorption/ionization-mass spectroscopy (LDI-MS) (Sabbah et al., 2017). This technique is especially adequate for aromatic compounds. The results of the combined analysis techniques showed that the particles produced in the experiment were small ( $\approx 10$  nm), formed by carbon nanograins and aliphatic HC clusters with a very small ( $\approx 3$  per cent) aromatic content, strongly suggesting that aromatic species or fullerenes do not form effectively in the inner circumstellar envelopes of carbon rich stars.

Further measurements also showed that the particles collected on substrates transformed partly into aromatic compounds upon thermal heating (Martínez et al., 2020). This suggests that IS grain surfaces could catalyze the formation of aromatic species as a result of the substantial rise in dust temperature occurring in UV-irradiated environments, where AIBs are indeed observed. Carbon dimers and C<sub>2</sub>H<sub>2</sub> were also produced in the gas phase. The two species had been found in the envelope of the typical C rich AGB star IRC +10216 (Fonfría et al., 2008), but the amount of C<sub>2</sub>H<sub>2</sub> formed in the experiments was apparently too small to observe possible polymerization products.

Gas phase polymerization of acetylene (C<sub>2</sub>H<sub>2</sub>) is well known to happen in energetic environments like combustion, pyrolysis or plasmas, and it has been used in the astrochemical context for the production of IS dust analogs. As already mentioned, Biennier et al. (2009), and Jäger et al. (2009) obtained polyaromatic rich soot in the pyrolysis of C<sub>2</sub>H<sub>2</sub> at  $\approx 1000$ – $1500$  K, and Kovačević et al. (2005) and Stefanović et al.

(2005) used room temperature C<sub>2</sub>H<sub>2</sub>/Ar RF discharges to generate dust analogs with a mixture of saturated aliphatic and aromatic structures. The polymerization of acetylene proceeds through the formation of polyynes (molecules with alternating single and triple bonds), and can take place in neutral, cationic and anionic routes (Benedikt, 2010). Chemical models of C<sub>2</sub>H<sub>2</sub> polymerization have been reported for different environments (see for instance Frenklach and Feigelson, 1989; Cernicharo, 2004; De Bleeker et al., 2006; Denysenko et al., 2019), and, although some of them include schemes for the formation of benzene rings, the details of the transformation of the large polyyne (C<sub>sp</sub>) chains, observed in the gas-phase (Descheneaux et al., 1999; Jiménez-Redondo et al., 2019, 2022), into dust grains dominated by aromatic (C<sub>sp</sub><sup>2</sup>) and saturated aliphatic (C<sub>sp</sub><sup>3</sup>) structures (Kovačević et al., 2005; Stefanović et al., 2005) are not yet clear. The first molecule in the polyyne series, C<sub>4</sub>H<sub>2</sub>, has been recently detected in the C rich AGB star IRC +10216 (Fonfría et al., 2018), and the first two polyynes, C<sub>4</sub>H<sub>2</sub>, C<sub>6</sub>H<sub>2</sub>, and benzene were found in the protoplanetary nebula CRL 618 (Cernicharo et al., 2001), but the next steps toward the formation of polyaromatic molecules are largely unknown. As mentioned above, the first detection of a polyaromatic molecule, the bicyclic molecule indene, has taken place recently (Burkhardt et al., 2021; Cernicharo et al., 2021) in the molecular cloud TMC-1, an environment with a chemistry quite different from that of AGB and post AGB stars (Guélin and Cernicharo, 2022). To investigate the evolution of acetylene in the reactions with C atoms and C<sub>2</sub> dimers present in the inner shells of AGB stars, Santoro et al. (2020) used the “Stardust” set up (Martínez et al., 2020 and Figure 5), but introduced C<sub>2</sub>H<sub>2</sub>, instead of H<sub>2</sub>, in the sputtering chamber. The analysis of the nanoparticles showed that they were made of a complex mixture of C<sub>sp</sub>, C<sub>sp</sub><sup>2</sup> and C<sub>sp</sub><sup>3</sup> hydrocarbons with amorphous morphology. The polyaromatic content increased appreciably (from 3 per cent to 15 per cent) as compared with the previous experiment with H<sub>2</sub> (Martínez et al., 2020), but still the composition of the particles was dominated by C and HC clusters (which includes polyynes). The result suggests again that the conditions in the inner circumstellar envelope of AGB stars are not ideal for the formation of predominantly polyaromatic dust grains.

In a recent study, Gavilan Marin et al. (2020) have used the COSMIC facility (Contreras and Salama, 2013) to investigate the formation of dust grains from gas-phase polyaromatic hydrocarbon precursors at a low temperature (<200 K), representative of the outer dust condensation zone of circumstellar envelopes. Aromatic hydrocarbons with increasing ring number (one to four) were expanded through a pulsed discharge nozzle, that provides a plasma reactor without walls. The dust samples formed were collected on solid substrates and analyzed *ex situ* with laser desorption/ionization mass spectrometry. The molecular compounds making the grains were found to be mostly aromatic having between 5 and 35 carbon atoms, and many of them were alkylated. Pyrene,

$C_{16}H_{10}$ , and its isomers dominated the distributions irrespective of the initial precursor. The predominant formation of pyrene signals a stable route in the growth of larger PAHs. Using the same experimental set up, Sciamma-O'Brien and Salama (2020) investigated the formation of dust grains of different sizes and morphologies from  $CH_4$  and  $C_2H_2$  precursors. A preliminary transmission electron microscopy (TEM) analysis showed that the grains were made of amorphous carbon, but the detailed chemical composition was not provided. The results of these experiments show that dust growth from molecular precursors is possible in the colder outer region of a circumstellar envelope, but it is not clear that PAHs can form under these conditions from small molecular precursors like  $CH_4$  or  $C_2H_2$ .

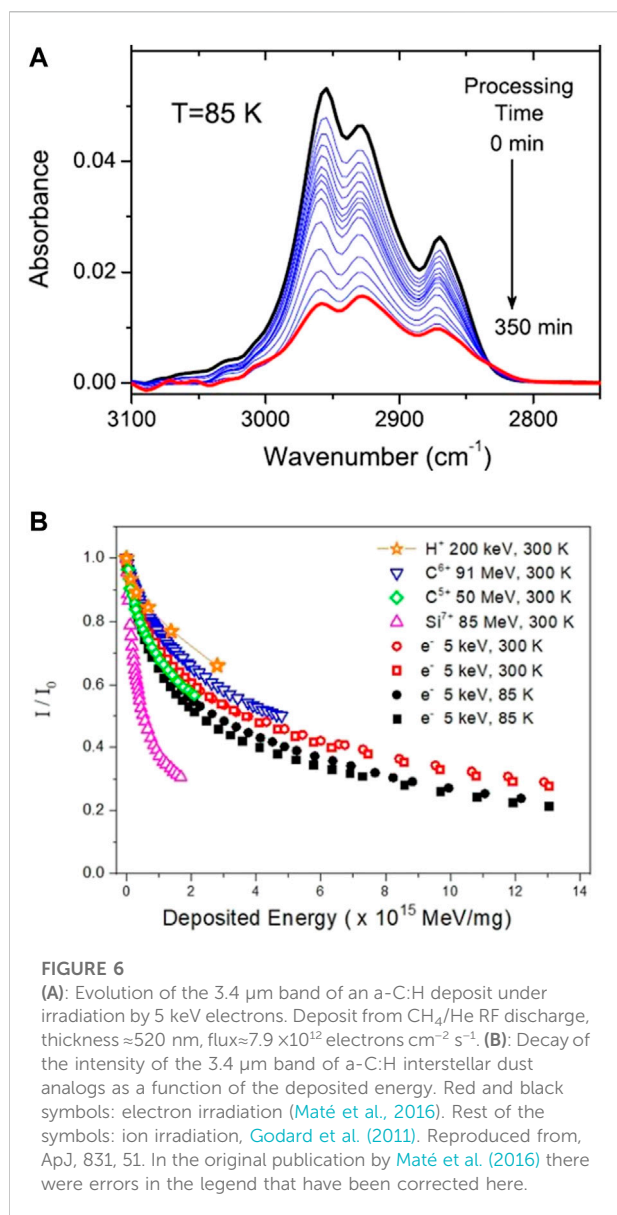
A different grain growth mechanism, that could account for the re-formation of IS carbonaceous grains in cold regions of the ISM, needed to maintain the balance between dust production and destruction (Jones et al., 2013), was experimentally investigated by Fulvio et al. (2017). Gas-phase carbonaceous precursors, created by laser ablation of graphite, were forced to accrete on cold substrates ( $T \approx 10$  K) that represented surviving dust grains. The growth and evolution of the condensing carbonaceous precursors were monitored by IR and UV spectroscopy. The condensation process was found to be governed by carbon chains that first condense into small carbon clusters and finally into more stable carbonaceous materials, with structural characteristics comparable to the material formed in gas-phase condensation experiments at very high temperature. VUV irradiation leads to the formation of more ordered polyaromatic structures. More work along this line has been recently reported by Rouillé et al. (2020) who observed that at these cryogenic temperatures silicate and carbonaceous grains could form simultaneously, but remained chemically separated, in agreement with observations.

### 3.2 Evolution of dust. Energetic processing

Carbonaceous dust leaving the stellar envelopes eventually enters the ISM, where it is subjected to an intense VUV field, to the bombardment by cosmic rays (CRs), to shock waves, and to reaction with hydrogen atoms. The interplay between all these factors will determine the ultimate fate of dust. The largest fraction of carbonaceous dust in the diffuse ISM is probably made of a-C:H (Jones et al., 2013; Jones et al., 2014; Jones et al., 2017) with a significant saturated aliphatic content, as evinced by the ubiquitous  $3.4 \mu\text{m}$  absorption band corresponding to  $CH_2$  and  $CH_3$  groups (see Section 2.2). The aliphatic carriers of this band could be already present in circumstellar material (Chiar et al., 1998; Chiar and Pendleton 2008), and/or could form directly in the ISM where H atoms are prevalent. For a sound appraisal of the different ways of destruction and formation of aliphatic structures in the ISM, laboratory data are again

necessary. Direct formation of  $CH_2$  and  $CH_3$  groups in the diffuse interstellar medium was advocated by Mennella et al. (1999); Mennella et al. (2002), who demonstrated that the  $3.4 \mu\text{m}$  band could be efficiently activated through the interaction of H atoms with carbon nanograins. The C nanograins were generated by laser evaporation of carbon rods in an Ar atmosphere, and were then subjected to an H atom beam produced by dissociation of  $H_2$  in a microwave discharge. In other experiments, Mennella et al. (2001) produced dust grain analogs with an appreciable aliphatic component through evaporation of carbon in a  $H_2$  atmosphere, and irradiated these grains with VUV photons from a hydrogen discharge lamp. Photolysis cross sections were derived from the decay of the  $3.4 \mu\text{m}$  band with time. Later experiments by Alata et al. (2014) yielded similar values for the destruction cross sections of the  $3.4 \mu\text{m}$  band in a different type of dust analog generated from RF discharges of hydrocarbons, which seems to confirm the generality of the measured VUV destruction cross section for the aliphatic component of dust. Destruction cross sections for cosmic rays were also derived from experiments of ion ( $30 \text{ keV He}^+$ ) bombardment (Mennella et al., 2003). Due to the very small cosmic ray flux, their effect was found to be negligible as compared with that of the UV field. Using the experimental cross sections for the formation (Mennella et al., 2002) and the destruction (Mennella et al., 2001, 2003) of the  $3.4 \mu\text{m}$  band carriers, the authors of these works concluded that hydrogenation should clearly dominate over photolysis and cosmic ray destruction in the diffuse interstellar medium (Mennella et al., 2002; Mennella et al., 2003).

A puzzling result of astronomical observations is the absence of the  $3.4 \mu\text{m}$  band in molecular clouds. In these dark, cold environments, dust grains are covered by ice mantles (Boogert et al., 2015) that give rise to an intense water absorption at  $3 \mu\text{m}$ . However, the  $3.4 \mu\text{m}$  band disappears, indicating that at some point the destructive effects of VUV photons or cosmic rays should prevail over hydrogenation. In the interior of dark clouds, where temperatures can go down to 10 K, hydrogenation should be inhibited by the ice layers covering the carbonaceous surface. Even on hypothetical bare grains, the rate of hydrogenation should drop drastically due to the recombination of most gas-phase H atoms to  $H_2$  molecules, and to the (small) activation barrier of the hydrogenation reaction (Mennella, 2006). The interior of dense clouds is largely shrouded from the Galactic UV field, but not so from cosmic rays. Mennella et al. (2003) estimated that inside the cloud, for values of the visual extinction larger than  $A_v \approx 5$  mag, cosmic rays would be the most significant C-H bond destruction mechanism. According to this estimate, cosmic rays would lead to an appreciable decay, but not to the total disappearance of the band over the dense cloud lifetime ( $\approx 3 \times 10^7$  yr). Further measurements of the effects of cosmic rays on the carriers of the  $3.4 \mu\text{m}$  band were carried out by Godard et al. (2011) and by Maté et al. (2016) using multiple ions, mostly in the MeV range, and 5 keV electrons respectively. The energy doses deposited on material samples by keV electrons are similar



to those of MeV ions, and it is generally assumed that electron bombardment provides a good proxy for the effects of cosmic rays. The decay of the 3.4  $\mu\text{m}$  band under ion and electron bombardment is compared in Figure 6.

The new experiments (Godard et al., 2011; Maté et al., 2016) yielded appreciably lower C-H destruction rates than the previous measurements of Mennella et al. (2003), and showed that cosmic ray bombardment cannot justify the absence of the 3.4  $\mu\text{m}$  band in dense clouds. The most likely environment for the destruction of the aliphatic carbon structures is thus the transition region between diffuse and molecular clouds. Chiar et al. (2013) suggested that the aliphatic mantles of dust particles were probably destroyed somewhere in the translucent cloud phase, for extinction values up to  $A_v \approx 3$  mag, which they took as

the approximate start of ice mantle formation. In the region close to  $A_v = 3$  mag, the Galactic UV field is not totally attenuated and can prevail over hydrogenation (Mennella et al., 2002; Chiar et al., 2013). The assumption of an aliphatic mantle at the surface of carbonaceous grains in the diffuse ISM has been contested by Jones et al. (2013).

The model of Jones et al. contemplates different C grain families based on a-C:H, namely a population of small, predominantly aromatic, C-grains and another group of large grains with a high aliphatic content. The model provides a good semiquantitative description of many dust properties, like the 217.5 nm bump and IR emissions associated with the small, aromatic-rich grains, and also of the 3.4  $\mu\text{m}$  absorption caused by the larger, aliphatic-rich particles. Contrary to Chiar et al. (2013), Jones et al. (2013), assume that mostly aliphatic structures can be formed at an early stage of grain evolution, still in the stellar outflows. In stark contrast to Chiar et al. (2013), they propose that photoprocessing prevails over hydrogenation in the diffuse ISM, and leads to the formation of an aromatic mantle on an aliphatic core that would become shielded from UV radiation in large grains. Present data from observations and experiment cannot decide whether the aliphatic structures, responsible for the 3.4  $\mu\text{m}$  absorption, are in the core Jones et al. (2013) or in the mantle (Chiar et al., 2013) of the grains. The model of Jones et al. does not provide a destruction mechanism for the aliphatic CH bonds in dense clouds, and cannot explain the disappearance of the 3.4  $\mu\text{m}$  absorption band.

As indicated above and illustrated in Figures 3, 6 the energetic processing of a-C:H, either by UV photons or by high energy charged particles, leads to a dehydrogenation and graphitization of a-C:H (Mennella et al., 1996; Gadallah et al., 2012; Peláez et al., 2018), but it also leads to the production of other molecular fragments like  $\text{CH}_4$  and other small hydrocarbon, as observed in the UV photolysis experiments of Alata et al. (2014); Alata et al. (2015) and Duley et al. (2015). Photolysis of a-C:H grains could explain the presence of small hydrocarbons in the diffuse ISM, where they are often observed. In this respect, sharp molecular cloud edges subjected to an intense field of UV photons, are particularly interesting. One of these photon dominated regions (PDRs), the Horsehead nebula, is currently receiving much attention. Gas phase chemical models cannot account for the high concentration of some of the molecular species observed in this environment, and it is conjectured that they must come from the fragmentation of large carbonaceous material (Guzmán et al., 2015). Model estimates of this PDR by Alata et al. (2015) show that the photolysis of a-C:H grains could enhance the concentration of carbonaceous molecules by orders of magnitude at intermediate visual extinctions. Besides photolysis, cosmic rays can lead to significant grain fragmentation. Recent experiments by Pino et al. (2019) have demonstrated that many PAHs and fullerenes are produced in the swift heavy ion bombardment of aromatic rich soot. Although the global effects of cosmic rays on grains in the

diffuse ISM are expected to be small as compared with those of the VUV field, they can induce a more massive fragmentation leading to the production of larger molecular species. Sputtering yields of large carbonaceous molecules from solids subjected to ion bombardment have been recently reported by [Dartois et al., 2022](#). The fragmentation of carbonaceous grains under energetic processing can provide a general top down route for the formation of many of the molecules being found in the diffuse ISM. Astrochemical models including this top down chemistry are now being developed ([Awad and Viti, 2022](#)), but there is still a lack of experimental data on the details of the fragmentation processes and on the injection of the fragmented molecules to the ISM.

## 4 Summary and conclusion

The presence of dust in the interstellar medium was discovered almost a century ago. It has long been known that dust grains are mostly made of silicates and carbonaceous matter. Except for presolar grains found in some meteorites, information about interstellar dust has been derived from remote observations of light extinction and emission. The most relevant spectral features of carbonaceous dust are a prominent extinction bump in the UV region, at 217.5 nm, and a series of absorption and emission bands in the infrared. At present, a combination of observations, models, and experiments has provided the following picture: carbonaceous dust is mostly made of different sorts of hydrogenated amorphous carbon. Dust grains have different sizes, different hydrogen content, and a variable proportion of aliphatic and aromatic structures. Other carbon forms, like nanodiamonds and fullerenes, have also been found, but make only a small contribution to the carbon budget. SiC is observed in circumstellar envelopes, but not in the interstellar medium. Graphite is known to be there, because it appears in presolar grains, but without the detection of a specific spectral feature it is difficult to quantify.

Grains of a few nanometers, with a largely polyaromatic structure and a small hydrogen proportion, are believed to cause the UV bump, with the possible contribution of polycyclic aromatic hydrocarbons. Larger grains ( $\approx 100$  nm), with a higher saturated aliphatic content, are the generally accepted carriers of the IR absorptions and, especially, of the widely observed  $3.4 \mu\text{m}$  feature. The proportion of aliphatic and aromatic structures is currently debated. Quantitative estimates are difficult due to large uncertainties in the IR band strengths of these disordered materials. The main IR emission features correspond to aromatic vibrational transitions and are termed aromatic infrared bands. They are usually associated with mixtures of large polycyclic aromatic hydrocarbons, but mixed aromatic/aliphatic nanoparticles have also been suggested. Recent observations indicate a strong

correlation between the carriers of the aromatic infrared emission bands and those of the UV bump.

The UV bump and the IR absorption features have been reproduced with laboratory dust analogs, but the simulation of the gas phase IR fluorescence giving rise to the aromatic infrared bands remains a great experimental challenge. A considerable proportion of interstellar carbon  $\approx 40$  per cent (with a large uncertainty) is locked up in dust, and the fraction of carbon in the bigger, more aliphatic grains is probably higher than that in the small, more aromatic particles.

Carbonaceous grains are initially formed in the inner envelopes of carbon rich AGB stars. Recent experiments show that these environments might not favor the formation of large polyaromatic structures, as often assumed, but would rather lead to the production of amorphous carbon clusters. The further heating or UV processing of that carbonaceous material could induce graphitization at a later stage of stellar evolution. Recent experiments have also demonstrated the possibility of carbonaceous grain growth in very cold environments of the interstellar medium. This source of grain growth could counter the high destruction rate of dust grains by shock waves, and could help solve the present dilemma between the estimated rates of dust formation and destruction.

The interaction of carbonaceous grains with H atoms, VUV photons, and cosmic rays has also been studied in the laboratory. For the conditions of the diffuse medium, hydrogenation was found to prevail over destruction by VUV photons and cosmic rays, giving rise to an aliphatic mantle, responsible for the  $3.4 \mu\text{m}$  band, on top of the grain. This band is not found in the interior of dense clouds. Laboratory measurements show that neither UV photons nor cosmic rays would be enough to destroy the aliphatic structures inside the cloud. The aliphatic mantle is probably destroyed in the transition region from the diffuse to the dense medium, but the details are not known. A recent model contests this picture, suggesting that UV prevails over hydrogenation in the diffuse medium, and proposes a grain structure with an aliphatic core and an aromatic mantle. Present data from observation and experiments cannot decide whether the aliphatic component is in the core or in the mantle of the grains.

Recent laboratory experiments show that VUV photons and cosmic rays can lead to the release of small molecules, and even of comparatively large polycyclic aromatic hydrocarbons or fullerenes, from dust grains. This would induce an interesting top down chemistry that could explain the comparatively rich molecular inventory sometimes found in the diffuse medium, especially in photon dominated regions at the edge of dense clouds.

The previous paragraphs point to unresolved issues and open questions that prompt more experimental work. The validity of experimental data for the interpretation of astrophysical observations is sometimes questioned, due to the large differences between the conditions in the laboratory and those

in astronomical environments. It is true that, contrary to some daring statements, the interstellar medium, or circumstellar envelopes, cannot be recreated in the laboratory, not even approximately, but physicochemical conditions relevant for these environments can indeed be simulated and can provide most useful information.

## Author contributions

All authors listed have made a substantial and direct contribution to the work and approved it for publication. VH wrote most of the text.

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## References

- Alata, I., Cruz-Díaz, G. A., Muñoz Caro, G. M., and Dartois, E. (2014). Vacuum ultraviolet photolysis of hydrogenated amorphous carbons I. Interstellar H-2 and CH<sub>4</sub> formation rates. *Astron. Astrophys.* 569, A119. doi:10.1051/0004-6361/201323118
- Alata, I., Jallat, A., Gavilan, L., Chabot, M., Cruz-Díaz, G. A., Muñoz Caro, G. M., et al. (2015). Vacuum ultraviolet of hydrogenated amorphous carbons. *Astron. Astrophys.* 584, A123. doi:10.1051/0004-6361/201526368
- Allamandola, L. J., Hudgins, D. M., and Sandford, S. A. (1999). Modeling the unidentified infrared emission with combinations of polycyclic aromatic hydrocarbons. *Astrophys. J.* 511, L115–L119. doi:10.1086/311843
- Allamandola, L. J., Tielens, A. G. G. M., and Barker, J. R. (1989). Interstellar polycyclic aromatic-hydrocarbons - the infrared-emission bands, the excitation emission mechanism, and the astrophysical implications. *Astrophys. J. Suppl. Ser.* 71, 733. doi:10.1086/191396
- Allamandola, L. J., Tielens, A. G. G. M., and Barker, J. R. (1985). Polycyclic aromatic-hydrocarbons and the unidentified infrared-emission bands - auto exhaust along the milky-way. *Astrophys. J.* 290, L25. doi:10.1086/184435
- Awad, Z., and Viti, S. (2022). Interstellar hydrocarbons: Degradation chemistry in diffuse clouds. *Mon. Not. R. Astron. Soc.* 511, 3832–3843. doi:10.1093/mnras/stac297
- Bauschlicher, C. W., Jr., Ricca, A., Boersma, C., and Allamandola, L. J. (2018). The NASA ames PAH IR spectroscopic database: Computational version 3.00 with updated content and the introduction of multiple scaling factors. *Astrophys. J. Suppl. Ser.* 234, 32. doi:10.3847/1538-4365/aaa019
- Benedikt, J. (2010). Plasma-chemical reactions: Low pressure acetylene plasmas. *J. Phys. D. Appl. Phys.* 43, 043001. doi:10.1088/0022-3727/43/4/043001
- Berné, O., Cox, N. L. J., Mulas, G., and Joblin, C. (2017). Detection of buckminsterfullerene emission in the diffuse interstellar medium. *Astron. Astrophys.* 605, L1. doi:10.1051/0004-6361/201630325
- Biennier, L., Georges, R., Chandrasekaran, V., Rowe, B., Bataille, T., Jayaram, V., et al. (2009). Characterization of circumstellar carbonaceous dust analogues produced by pyrolysis of acetylene in a porous graphite reactor. *Carbon* 47, 3295–3305. doi:10.1016/j.carbon.2009.07.050
- Boogert, A. C. A., Gerakines, P. A., Whittet, D. C. B., and Douglas, C. B. (2015). Observations of the icy universe. *Annu. Rev. Astron. Astrophys.* 53, 541–581. doi:10.1146/annurev-astro-082214-122348
- Burkhardt, A. M., Lee, K. L. K., Changala, B., Shingledecker, C. N., Cooke, I. R., Loomis, R. A., et al. (2021). Discovery of the pure polycyclic aromatic hydrocarbon

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## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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- indene (c-C<sub>9</sub>H<sub>8</sub>) with GOTHAM observations of TMC-1. *Astrophys. J. Lett.* 913, L18. doi:10.3847/2041-8213/abfd3a
- Cami, J., Bernard-Salas, J., Peeters, E., and Malek, S. E. (2010). Detection of C<sub>60</sub> and C<sub>70</sub> in a young planetary nebula. *Science* 329, 1180–1182. doi:10.1126/science.1192035
- Campbell, E. K., Holz, M., Gerlich, D., and Maier, J. P. (2015). Laboratory confirmation of C<sub>60</sub>+ as the carrier of two diffuse interstellar bands. *Nature* 523, 322–323. doi:10.1038/nature14566
- Candian, A., Tielens, X., and Zhen, J. F. (2019). More whiffs of the aromatic universe. *Phys. Today* 72, 13–14. doi:10.1063/PT.3.4285
- Carpentier, Y., Féraud, G., Dartois, E., Brunetto, R., Charon, E., Cao, A. T., et al. (2012). Nanostructuring of carbonaceous dust as seen through the positions of the 6.2 and 7.7 μm AIBs. *Astron. Astrophys.* 548, A40. doi:10.1051/0004-6361/201118700
- Casiraghi, C., Ferrari, A. C., and Robertson, J. (2005). Raman spectroscopy of hydrogenated amorphous carbons. *Phys. Rev. B* 72, 085401. doi:10.1103/PhysRevB.72.085401
- Cataldo, F., Keheyan, Y., and Heymann, D. (2002). A new model for the interpretation of the unidentified infrared bands (UIBS) of the diffuse interstellar medium and of the protoplanetary nebulae. *Int. J. Astrobiol.* 1, 79–86. doi:10.1017/S1473550402001131
- Cataldo, F., Garcia-Hernandez, D. A., and Machado, A. (2021). Asphaltene as model compounds of the UIBS/AIBs detected in various astrophysical objects. Part 1-Petroleum asphaltene carbonization. *Fullerenes Nanotub. Carbon Nanostructures* 30, 571–583. doi:10.1080/1536383X.2021.1967325
- Cataldo, F., Keheyan, Y., and Heymann, D. (2004). Complex organic matter in space: About the chemical composition of carriers of the unidentified infrared bands (UIBS) and protoplanetary emission spectra recorded from certain astrophysical objects. *Orig. Life Evol. Biosph.* 34, 13–24. doi:10.1023/B:ORIG.0000009825.76147.c7
- Cazaux, S., Arribard, Y., Egorov, D., Palotas, J., Hoekstra, R., Berden, G., et al. (2019). The sequence of coronene hydrogenation revealed by gas-phase IR spectroscopy. *Astrophys. J.* 875, 27. doi:10.3847/1538-4357/ab0e01
- Cernicharo, J., Agúndez, M., Cabezas, C., Tercero, B., Marcelino, N., Pardo, J. R., et al. (2021). Pure hydrocarbon cycles in TMC-1: Discovery of ethynyl cyclopropenylidene, cyclopentadiene, and indene. *Astron. Astrophys.* 649, L15. doi:10.1051/0004-6361/202141156
- Cernicharo, J., Heras, A. M., Tielens, A. G. G. M., Pardo, J. R., Herpin, F., Guélin, M., et al. (2001). Infrared space observatory's discovery of C<sub>4</sub>H<sub>2</sub>, C<sub>6</sub>H<sub>2</sub>, and benzene in CRL 618. *Astrophys. J.* 546, L123–L126. doi:10.1086/318871



- Cernicharo, J. (2004). The polymerization of acetylene, hydrogen cyanide, and carbon chains in the neutral layers of carbon-rich proto-planetary nebulae. *Astrophys. J.* 608, L41–L44. doi:10.1086/422170
- Chen, T., Xiao, C. Y., Li, A. G., and Zhou, C. T. (2022). Where have all the interstellar silicon carbides gone? *Mon. Not. R. Astron. Soc.* 509, 5231–5236. doi:10.1093/mnras/stab3175
- Cherchneff, I., Barker, J. R., and Tielens, A. G. G. M. (1992). Polycyclic aromatic hydrocarbon formation in carbon-rich stellar envelopes. *Astrophys. J.* 401, 269. doi:10.1086/172059
- Cherchneff, I. (2011). “The Formation of polycyclic aromatic hydrocarbons in evolved circumstellar environments,” in *PAHs and the Universe*, *EAS Pub. Ser.* Editors C. Joblin and A. G. G. M. Tielens (Les Ulis, France: EDP Sciences) 46, 177. doi:10.1051/eas/1146019
- Cherchneff, I. (2012). The inner wind of IRC+10216 revisited: New exotic chemistry and diagnostic for dust condensation in carbon stars. *Astron. Astrophys.* 545, A12. doi:10.1051/0004-6361/201118542
- Chiar, J. E., Pendleton, Y. J., Geballe, T. R., and Tielens, A. G. G. M. (1998). Near-infrared spectroscopy of the proto-planetary nebula CRL 618 and the origin of the hydrocarbon dust component in the interstellar medium. *Astrophys. J.* 507, 281–286. doi:10.1086/306318
- Chiar, J. E., and Pendleton, Y. J. (2008). The origin and evolution of interstellar organics. *Proc. Int. Astron. Union* 251, 35–44. doi:10.1017/S1743921308021133
- Chiar, J. E., Tielens, A. G. G. M., Adamson, A. J., and Ricca, A. (2013). The structure, origin, and evolution of interstellar hydrocarbon grains. *Astrophys. J.* 770, 78. doi:10.1088/0004-637X/770/1/78
- Chiar, J. E., Tielens, A. G. G. M., Whittet, D. C. B., Schutte, W. A., Boogert, A. C. A., Lutz, D., et al. (2000). The composition and distribution of dust along the line of sight toward the Galactic center. *Astrophys. J.* 537, 749–762. doi:10.1086/309047
- Contreras, C. S., and Salama, F. (2013). Laboratory investigations of polycyclic aromatic hydrocarbon formation and destruction in the circumstellar outflows of carbon stars. *Astrophys. J. Suppl. Ser.* 208, 6. doi:10.1088/0067-0049/208/1/6
- Cook, D. J., Schlemmer, S., Balucani, N., Wagner, D. R., Harrison, J. A., Steiner, B., et al. (1998). Single photon infrared emission spectroscopy: A study of IR emission from UV laser excited PAHs between 3 and 15  $\mu\text{m}$ . *J. Phys. Chem. A* 102, 1465–1481. doi:10.1021/jp9724434
- Cook, D. J., Schlemmer, S., Balucani, N., Wagner, D. R., Steiner, B., and Saykally, R. J. (1996). Infrared emission spectra of candidate interstellar aromatic molecules. *Nature* 380, 227–229. doi:10.1038/380227a0
- Dartois, E., Caro, G. M., Deboffle, D., Montagnac, G., and d’Hendecourt, L. (2005). Ultraviolet photoproduction of ISM dust - laboratory characterisation and astrophysical relevance. *Astron. Astrophys.* 432, 895–908. doi:10.1051/0004-6361:20042094
- Dartois, E., Chabot, M., Koch, F., Bachelet, C., Bender, M., Bourçois, J., et al. (2022). Desorption of polycyclic aromatic hydrocarbons by cosmic rays. Implications for PAH inventories under TMC-1 dense cloud conditions. *Astron. Astrophys.* 663, A25. doi:10.1051/0004-6361/202243274
- Dartois, E., Geballe, T. R., Pino, T., Cao, A. T., Jones, A., Deboffle, D., et al. (2007). Iras 08572+3915: Constraining the aromatic versus aliphatic content of interstellar HACs. *Astron. Astrophys.* 463, 635–640. doi:10.1051/0004-6361:20066572
- Dartois, E. (2019). Interstellar carbon dust. *C J. Carbon Res.* 5, 80. doi:10.3390/c5040080
- Dartois, E., Muñoz Caro, G. M., Deboffle, D., and d’Hendecourt, L. (2004). Diffuse interstellar medium organic polymers. *Astron. Astrophys.* 423, L33–L36. doi:10.1051/0004-6361:200400032
- Dartois, E., and Muñoz-Caro, G. M. (2007). Carbonaceous dust grains in luminous infrared galaxies. Spitzer/IRS reveals a-C:H as an abundant and ubiquitous ISM component. *Astron. Astrophys.* 476, 1235–1242. doi:10.1051/0004-6361:20077798
- Davies, A. M. (2011). Stardust in meteorites. *Proc. Natl. Acad. Sci. U. S. A.* 108, 19142–19146. doi:10.1073/pnas.1013483108
- De Bleecker, K., Bogaerts, A., and Goedheer, W. (2006). Detailed modeling of hydrocarbon nanoparticle nucleation in acetylene discharges. *Phys. Rev. E* 73, 026405. doi:10.1103/PhysRevE.73.026405
- Denysenko, I. B., von Wahl, E., Labidi, S., Mikikian, M., Kersten, H., Gibert, T., et al. (2019). Modeling of argon acetylene dusty plasma. *Plasma Phys. Control. Fusion* 61, 014014. doi:10.1088/1361-6587/aae2d
- Deschenaux, C., Affolter, A., Magni, D., Hollenstein, C., and Fayet, P. (1999). Investigations of CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> dusty RF plasmas by means of FTIR absorption spectroscopy and mass spectrometry. *J. Phys. D. Appl. Phys.* 32, 1876–1886. doi:10.1088/0022-3727/32/15/316
- Dischler, B., Bubenzer, A., and Koidl, P. (1983). Hard carbon coatings with low optical-absorption. *Appl. Phys. Lett.* 42, 636–638. doi:10.1063/1.94056
- Dopfer, O. (2011). “Laboratory spectroscopy of protonated PAH molecules relevant for the interstellar chemistry,” in *PAHs and the Universe*, *EAS Pub. Ser.* Editors C. Joblin and A. G. G. M. Tielens (Les Ulis, France: EDP Sciences) 46, 103. doi:10.1051/eas/1146010
- Dorschner, J., and Henning, T. (1995). Dust metamorphosis in the galaxy. *Astron. Astrophys. Rev.* 6, 271–333. doi:10.1007/BF00873686
- Douglas, A. E., and Herzberg, G. (1941). Note on CH<sub>3</sub><sup>+</sup> in interstellar space and in the laboratory. *Astrophys. J.* 94, 381. doi:10.1086/144342
- Draine, B. T. (2016). Graphite revisited. *Astrophys. J.* 831, 109. doi:10.3847/0004-637X/831/1/109
- Draine, B. T., Henning, T., Grün, E., and Steinacker, J. (2009). “Interstellar dust models and evolutionary implications,” in *Cosmic Dust—Near and Far*. *ASP Conf. Ser.* Editors T. Henning, E. Grün, and J. Steinacker (San Francisco, California: Astronomical Soc. Pacific) 414, 453. doi:10.48550/arXiv.0903.1658
- Draine, B. T. (1989). “Interstellar dust,” in *Pro. Of IAU symp.* 135. Editors L. J. Allamandola and A. G. G. M. Tielens (Dordrecht: Kluwer), 313. doi:10.1007/978-94-009-2462-8\_27
- Draine, B. T. (2003). Interstellar dust grains. *Annu. Rev. Astron. Astrophys.* 41, 241–289. doi:10.1146/annurev.astro.41.011802.094840
- Draine, B. T., and Lee, H. M. (1984). Optical properties of interstellar graphite and silicate grains. *Astrophys. J.* 285, 89. doi:10.1086/162480
- Draine, B. T., and Li, A. (2007). Infrared emission from interstellar dust. IV. The silicate-graphite-PAH model in the post-Spitzer era. *Astrophys. J.* 657, 810–837. doi:10.1086/511055
- Duley, W. W., and Hu, A. (2012). The 217.5 nm band, infrared absorption, and infrared emission features in hydrogenated amorphous carbon nanoparticles. *Astrophys. J.* 761, 115. doi:10.1088/0004-637X/761/2/115
- Duley, W. W., and Williams, D. A. (1981). The infrared-spectrum of inter-stellar dust - surface functional-groups on carbon. *Mon. Not. R. Astron. Soc.* 196, 269–274. doi:10.1093/mnras/196.2.269
- Duley, W. W., Scott, A. D., Seahra, S., and Dadswell, G. (1998). Integrated Absorbances in the 3.4  $\mu\text{m}$  CHn Band in Hydrogenated Amorphous Carbon. *Astrophys. J.* 503, L183–L185. doi:10.1086/311548
- Duley, W. W., and Williams, D. A. (1983). A 3.4  $\mu\text{m}$  absorption band in amorphous carbon: Implications for interstellar dust. *Mon. Not. R. Astron. Soc.* 205, 67–70P. doi:10.1093/mnras/205.1.67P
- Duley, W. W., Zaidi, A., Wesolowski, M. J., and Kuzmin, S. (2015). Small molecules from the decomposition of interstellar carbons. *Mon. Not. R. Astron. Soc.* 447, 1242–1246. doi:10.1093/mnras/stu2508
- Endo, I., Sakon, I., Onaka, T., Kimura, Y., Kimura, S., Wada, S., et al. (2021). On the nature of organic dust in novae. *Astrophys. J.* 917, 103. doi:10.3847/1538-4357/ac0cfl
- Fitzpatrick, E. L., and Massa, D. (2007). An analysis of the shapes of interstellar extinction curves. V. The IR-through-UV curve morphology. *Astrophys. J.* 663, 320–341. doi:10.1086/518158
- Fonfría, J. P., Agúndez, M., Cernicharo, J., Richter, M. J., and Lacy, J. H. (2018). Carbon chemistry in IRC+10216: Infrared detection of diacetylene. *Astrophys. J.* 852, 80. doi:10.3847/1538-4357/aa9ee0
- Fonfría, J. P., Cernicharo, J., Richter, M. J., and Lacy, J. H. (2008). A detailed analysis of the dust formation zone of IRC+10216 derived from mid-infrared bands of C<sub>2</sub>H<sub>2</sub> and HCN. *Astrophys. J.* 673, 445–469. doi:10.1086/523882
- Forrest, W. J., McCarthy, J. F., and Houck, J. R. (1979). 16–39 micron spectroscopy of oxygen-rich stars. *Astrophys. J.* 233, 611. doi:10.1086/157422
- Frenklach, M., and Feigelson, E. (1989). Formation of polycyclic aromatic hydrocarbons in circumstellar envelopes. *Astrophys. J.* 341, 372. doi:10.1086/167501
- Fulvio, D., Sandor, G., Jäger, C., Akos, K., and Henning, T. (2017). Laboratory experiments on the low-temperature formation of carbonaceous grains in the ISM. *Astrophys. J. Suppl. Ser.* 233, 14. doi:10.3847/1538-4365/aa9224
- Furton, D. G., Lahio, J. W., and Witt, A. N. (1999). The amount of interstellar carbon locked in solid hydrogenated amorphous carbon. *Astrophys. J.* 526, 752–763. doi:10.1086/308016
- Gadallah, K. A. K. (2015). Hydrocarbon analogs of cosmic dust to trace the solid carbon abundance in the interstellar medium. *Adv. Space Res.* 55, 705–715. doi:10.1016/j.asr.2014.10.022
- Gadallah, K. A. K., Mutschke, H., and Jäger, C. (2012). Mid-infrared spectroscopy of UV irradiated hydrogenated amorphous carbon materials. *Astron. Astrophys.* 544, A107. doi:10.1051/0004-6361/201219248

- Gadallah, K. A. K., Mutschke, H., and Jäger, C. (2011). UV irradiated hydrogenated amorphous carbon (HAC) materials as a carrier candidate of the interstellar UV bump at 217.5 nm. *Astron. Astrophys.* 528, A56. doi:10.1051/0004-6361/201015542
- Garkusha, I., Fulara, J., and Maier, J. P. (2012). Fluorescence of protonated pyrene and coronene in neon matrices. *J. Mol. Struct.* 1025, 147–150. doi:10.1016/j.molstruc.2012.02.056
- Gavilan, L., Alata, T., Le, K. C., Pino, T., Giuliani, A., and Dartois, E. (2016). VUV spectroscopy of carbon dust analogs: Contribution to interstellar extinction. *Astron. Astrophys.* 586, A106. doi:10.1051/0004-6361/201527098
- Gavilan, L., Le, K. C., Pino, T., Alata, I., Giuliani, A., and Dartois, E. (2017). Polyaromatic disordered carbon grains as carriers of the UV bump: Far-UV to mid-IR spectroscopy of laboratory analogs. *Astron. Astrophys.* 607, A73. doi:10.1051/0004-6361/201730712
- Gavilan Marin, L., Bejaoui, S., Haggmark, M., Svadlenak, N., de Vries, M., Sciamma-O'Brien, E., et al. (2020). Low-temperature formation of carbonaceous dust grains from PAHs. *Astrophys. J.* 889, 101. doi:10.3847/1538-4357/ab62b7
- Gillett, F. C., Forrest, W. J., and Merrill, K. M. (1973). 8–13 micron spectra of NGC 7027, BD +30 3639 and NGC 6572. *Astrophys. J.* 183, 87. doi:10.1086/152211
- Godard, M., and Dartois, E. (2010). Photoluminescence of hydrogenated amorphous carbons. Wavelength-dependent yield and implications for the extended red emission. *Astron. Astrophys.* 519, A39. doi:10.1051/0004-6361/200913906
- Godard, M., Féraud, G., Chabot, M., Carpentier, Y., Pino, T., Brunetto, R., et al. (2011). Ion irradiation of carbonaceous interstellar analogues. *Astron. Astrophys.* 529, A146. doi:10.1051/0004-6361/201016228
- Grishko, V. I., and Duley, W. W. (2000). Detection of new infrared spectral features in hydrogenated amorphous carbon. *Astrophys. J.* 543, L85–L88. doi:10.1086/318165
- Guélin, M., and Cernicharo, J. (2022). Organic molecules in interstellar space: Latest advances. *Front. Astron. Space Sci.* 9, 787567. doi:10.3389/fspas.2022.787567
- Guillois, O., Ledoux, G., and Reynaud, C. (1999). Diamond infrared emission bands in circumstellar media. *Astrophys. J.* 521, L133–L136. doi:10.1086/312199
- Günay, B., Buron, M. G., Afsar, M., and Schmidt, T. W. (2020). A method for mapping the aliphatic hydrocarbon content of interstellar dust towards the Galactic Centre. *Mon. Not. R. Astron. Soc.* 493, 1109–1119. doi:10.1093/mnras/staa288
- Günay, B., Buron, M. G., Afsar, M., and Schmidt, T. W. (2022). Mapping the aliphatic hydrocarbon content of interstellar dust in the Galactic plane. *Mon. Not. R. Astron. Soc.* 515, 4201–4216. doi:10.1093/mnras/stac1482
- Günay, B., Schmidt, T. W., Burton, M. G., Afsar, M., Krechkivska, O., Nauta, K., et al. (2018). Aliphatic hydrocarbon content of interstellar dust. *Mon. Not. R. Astron. Soc.* 479, 4336–4344. doi:10.1093/mnras/sty1582
- Guzmán, V. V., Pety, J., Goicoechea, J. R., Gerin, M., Roueff, E., Gratier, P., et al. (2015). Spatially resolved L-C3H<sup>+</sup> emission in the Horsehead photodissociation region: Further evidence for a top-down hydrocarbon chemistry. *Astrophys. J.* 800, L33. doi:10.1088/2041-8205/800/2/L33
- Hansen, C. S., Peeters, E., Cami, J., and Schmidt, T. W. (2022). Open questions on carbon-based molecules in space. *Commun. Chem.* 5, 94. doi:10.1038/s42004-022-00714-3
- Henning, T., and Salama, F. (1998). Carbon in the universe. *Science* 282, 2204–2210. doi:10.1126/science.282.5397.2204
- Hensley, B. S., and Draine, B. T. (2020). Detection of PAH absorption and determination of the mid-infrared diffuse interstellar extinction curve from the sight line toward Cyg OB2-12. *Astrophys. J.* 895, 38. doi:10.3847/1538-4357/ab8cc3
- Hensley, B. S., and Draine, B. T. (2021). Observational constraints on the physical properties of interstellar dust in the post planck ERA. *Astrophys. J.* 906, 73. doi:10.3847/1538-4357/abc8f1
- Herlin, N., Bohn, I., Reynaud, C., Cauchetier, M., Galvez, A., and Rouzaud, J.-N. (1998). Nanoparticles produced by laser pyrolysis of hydrocarbons: Analogy with carbon cosmic dust. *Astron. Astrophys.* 330, 1127.
- Herrero, V. J., Maté, B., Molpeceres, G., Jiménez-Redondo, M., and Tanarro, I. (2018). "Spectroscopy of interstellar carbonaceous dust," in *Laboratory Astrophysics. Astrophys. Space Sci.* Editors G. M. Muñoz Caro and R. Escribano (Cham, Switzerland: Springer International Publishing) 451, 159. doi:10.1007/978-3-319-90020-9\_11
- Hodoroaba, B., Gerber, I. C., Ciobotaru, D., Mihaila, I., Dobromir, M., Pohoata, V., et al. (2018). Carbon 'fluffy' aggregates produced by helium-hydrocarbon high-pressure plasmas as analogues to interstellar dust. *Mon. Not. R. Astron. Soc.* 481, 2841–2850. doi:10.1093/mnras/sty2497
- Hoyle, F., Wickramasinghe, N. C., Almufti, S., and Olavesen, A. H. (1982). Infrared-spectroscopy of microorganisms near 3, 4- $\mu$ m in relation to geology and astronomy. *Astrophys. Space Sci.* 81, 489–492. doi:10.1007/BF00676170
- Hoyle, F., and Wickramasinghe, N. C. (1969). Interstellar grains. *Nature* 223, 459–462. doi:10.1038/223459a0
- Hu, A., and Duley, W. W. (2008). Spectra of carbon nanoparticles: Laboratory simulation of the aromatic CH emission feature at 3.29  $\mu$ m. *Astrophys. J.* 677, L153–L156. doi:10.1086/587983
- Hudgins, D., and Allamandola, L. J. (2004). "Polycyclic aromatic hydrocarbons and infrared astrophysics: The state of the PAH model and a possible tracer of nitrogen in carbon-rich dust," in *Astrophysics of Dust, ASP Conf. Ser.* Editors A. N. Witt, G. C. Clayton, and B. T. Draine (San Francisco, California 309–665.
- Hudgins, D. M., and Allamandola, L. J. (1995). Infrared-spectroscopy of matrix-isolated polycyclic aromatic hydrocarbon cations .2. The members of the thermodynamically most favorable series through coronene. *J. Phys. Chem.* 99, 3033–3046. doi:10.1021/j100010a011
- Hudgins, D. M., and Allamandola, L. J. (1999). Interstellar PAH emission in the 11–14 micron region: new insights from laboratory data and a tracer of ionized PAHs. *Astrophys. J.* 516, L41–L44. doi:10.1086/311989
- Imanishi, M. (2000). The 3.4  $\mu$ m absorption feature towards three obscured active galactic nuclei. *MNRAS* 319, 331. doi:10.1046/j.1365-8711.2000.03873.x
- Jacob, W., and Möller, W. (1993). On the structure of thin hydrocarbon films. *Appl. Phys. Lett.* 63, 1771–1773. doi:10.1063/1.110683
- Jäger, C., Huisken, F., Mutschke, H., Jansa, I. L., and Henning, T. (2009). Formation of polycyclic aromatic hydrocarbons and carbonaceous solids in gas-phase condensation experiments. *Astrophys. J.* 696, 706–712. doi:10.1088/0004-637X/696/1/706
- Jäger, C., Mutschke, H., Henning, T., and Huisken, F. (2008). Spectral properties of gas-phase condensed fullerene-like carbon nanoparticles from far-ultraviolet to infrared wavelengths. *Astrophys. J.* 689, 249–259. doi:10.1086/592729
- Jensen, P. A., Shannon, M. J., Peeters, E., Sloan, G. C., and Stock, D. J. (2022). The mid-infrared aliphatic bands associated with complex hydrocarbons. *Astron. Astrophys.* 665, A153. doi:10.1051/0004-6361/202141511
- Jiménez-Redondo, M., Tanarro, I., and Herrero, V. J. (2022). Time evolution of neutral and charged species in Ar/C2H2 capacitively-coupled RF discharges. *Plasma Sources Sci. Technol.* 31, 065003. doi:10.1088/1361-6595/ac70f8
- Jiménez-Redondo, M., Tanarro, I., Peláez, R. J., Díaz-Pérez, L., and Herrero, V. J. (2019). Ionic polymerization in cold plasmas of acetylene with Ar and He. *J. Phys. Chem. A* 123, 8135–8147. doi:10.1021/acs.jpca.9b06399
- Joblin, C., Boissel, P., Leger, A., D'Hendecourt, L., and Defourneau, D. (1995). Infrared-spectroscopy of gas-phase PAH molecules .2. Role of the temperature. *Astron. Astrophys.* 299, 835.
- Joblin, C., Leger, A., and Martin, P. (1992). Contribution of polycyclic aromatic hydrocarbon molecules to the interstellar extinction curve. *Astrophys. J.* 393, L79. doi:10.1086/186456
- Joblin, C., Szczerba, R., Berne, O., and Szyszka, C. (2008). Carriers of the mid-IR emission bands in PNe reanalysed Evidence of a link between circumstellar and interstellar aromatic dust. *Astron. Astrophys.* 490, 189–196. doi:10.1051/0004-6361/20079061
- Jones, A. P., Fanciullo, L., Koehler, M., Verstraete, L., Guillet, V., Bocchio, M., et al. (2013). The evolution of amorphous hydrocarbons in the ISM: Dust modelling from a new vantage point. *Astron. Astrophys.* 558, A62. doi:10.1051/0004-6361/201321686
- Jones, A. P., Köhler, M., Ysard, N., Bocchio, M., and Verstraete, L. (2017). The global dust modelling framework THEMIS. *Astron. Astrophys.* 602, A46. doi:10.1051/0004-6361/201630225
- Jones, A. P., and Nuth, J. A. (2011). Dust destruction in the ISM: A re-evaluation of dust lifetimes. *Astron. Astrophys.* 530, A44. doi:10.1051/0004-6361/201014440
- Jones, A. P., Ysard, N., Koehler, M., Fanciullo, L., Bocchio, M., Micelotta, E., et al. (2014). The cycling of carbon into and out of dust. *Faraday Discuss.* 168, 313–326. doi:10.1039/c3fd00128h
- Kim, H. S., and Saykally, R. J. (2002). Single-photon infrared emission spectroscopy of gaseous polycyclic aromatic hydrocarbon cations: A direct test for proposed carriers of the unidentified infrared emission bands. *Astrophys. J. Suppl. Ser.* 143, 455–467. doi:10.1086/343078
- Kim, H. S., Wagner, D. R., and Saykally, R. J. (2001). Single photon infrared emission spectroscopy of the gas phase pyrene cation: Support for a polycyclic aromatic hydrocarbon origin of the unidentified infrared emission bands. *Phys. Rev. Lett.* 86, 5691–5694. doi:10.1103/PhysRevLett.86.5691
- Kovačević, E., Stefanović, I., Berndt, J., Pendleton, Y. J., and Winter, J. (2005). A candidate analog for carbonaceous interstellar dust: Formation by reactive plasma polymerization. *Astrophys. J.* 623, 242–251. doi:10.1086/428392

- Kwok, S. (2016). Complex organics in space from solar system to distant galaxies. *Astron. Astrophys. Rev.* 24, 8. doi:10.1007/s00159-016-0093-y
- Kwok, S. (2011). "Molecular evolution from AGB stars to planetary nebulae," in *Proceedings IAU Symposium 280 the Molecular Universe*. Editors J. Cericharo and R. Bachiller (Cambridge: Cambridge University Press, 203). doi:10.1017/S1743921311024987
- Kwok, S. (2022). The mystery of unidentified infrared emission bands. *Astrophys. Space Sci.* 367, 16. doi:10.1007/s10509-022-04045-6
- Kwok, S., and Zhang, Y. (2011). Mixed aromatic-aliphatic organic nanoparticles as carriers of unidentified infrared emission features. *Nature* 479, 80–83. doi:10.1038/nature10542
- Kwok, S., and Zhang, Y. (2013). Unidentified infrared emission bands: PAHs or MAONs? *Astrophys. J.* 771, 5. doi:10.1088/0004-637X/771/1/5
- Léger, A., and Puget, J. L. (1984). Identification of the unidentified IR emission features of interstellar dust. *Astron. Astrophys.* 137, L5.
- Li, Q., Li, A. G., and Jiang, B. W. (2009). How much graphene in space? *MNRAS* 400, 3875. doi:10.1093/mnras/stz2740
- Llamas Jansa, I., Jäger, C., Mutschke, H., and Henning, T. (2007). Far-ultraviolet to near-infrared optical properties of carbon nanoparticles produced by pulsed-laser pyrolysis of hydrocarbons and their relation with structural variations. *Carbon* 45, 1542–1557. doi:10.1016/j.carbon.2007.02.032
- Martínez, L., Santoro, G., Merino, P., Accolla, M., Lauwaet, K., Sobrado, J., et al. (2020). Prevalence of non-aromatic carbonaceous molecules in the inner regions of circumstellar envelopes. *Nat. Astron.* 4, 97–105. doi:10.1038/s41550-019-0899-4
- Massa, D., Gordon, K. D., and Fitzpatrick, E. L. (2022). Relations between mid-infrared dust emission and UV extinction. *Astrophys. J.* 925, 19. doi:10.3847/1538-4357/ac3825
- Maté, B., Molpeceres, G., Jimenez-Redondo, M., Tanarro, I., and Herrero, V. J. (2016). High-energy electron irradiation of interstellar carbonaceous dust analogs: Cosmic-ray effects on the carriers of the 3.4  $\mu\text{m}$  absorption band. *Astrophys. J.* 831, 51. doi:10.3847/0004-637X/831/1/51
- Maté, B., Tanarro, I., Moreno, M. A., Jimenez-Redondo, M., Escribano, R., and Herrero, V. J. (2014). Stability of carbonaceous dust analogues and glycine under UV irradiation and electron bombardment. *Faraday Discuss.* 168, 267–285. doi:10.1039/c3fd00132f
- Mathis, J. (1994). Dusting off the calculations. *Nature* 372, 225–226. doi:10.1038/372225a0
- Mathis, J. S., Rumpl, W., and Nordsieck, K. H. (1977). The size distribution of interstellar grains. *Astrophys. J.* 217, 425. doi:10.1086/155591
- Matsuura, M., Bernard-Salas, J., Evans, T. L., Volk, K. M., Hrivnak, B. J., Sloan, G. C., et al. (2014). Spitzer Space Telescope spectra of post-AGB stars in the Large Magellanic Cloud - polycyclic aromatic hydrocarbons at low metallicities. *Mon. Not. R. Astron. Soc.* 439, 1472–1493. doi:10.1093/mnras/stt2495
- Mattioda, A. L., Hudgins, D. M., Boersma, C., Bauschlicher, C. W., Ricca, A., Cami, J., et al. (2020). The NASA ames PAH IR spectroscopic database: The laboratory spectra. *Astrophys. J. Suppl. Ser.* 251, 22. doi:10.3847/1538-4365/abc2c8
- McGuire, B. A. (2022). 2021 census of interstellar, circumstellar, extragalactic, protoplanetary disk, and exoplanetary molecules. *Astrophys. J. Suppl. Ser.* 259, 30. doi:10.3847/1538-4365/ac2a48
- McKellar, A. (1940). Evidence for the molecular origin of some HithertoUnidentified interstellar lines. *Publ. Astron. Soc. Pac.* 52, 187. doi:10.1086/125159
- Mennella, V. (2006). Activation energy of C-H bond formation in carbon grains irradiated with hydrogen atoms. *Astrophys. J.* 647, L49–L52. doi:10.1086/507296
- Mennella, V., Baratta, G. A., Esposito, A., Ferini, G., and Pendleton, Y. J. (2003). The effects of ion irradiation on the evolution of the carrier of the 3.4 micron interstellar absorption band. *Astrophys. J.* 587, 727–738. doi:10.1086/368342
- Mennella, V., Brucato, J. R., Colangeli, L., and Palumbo, P. (1999). Activation of the 3.4 micron band in carbon grains by exposure to atomic hydrogen. *Astrophys. J.* 524, L71–L74. doi:10.1086/312302
- Mennella, V., Brucato, J. R., Colangeli, L., and Palumbo, P. (2002). C - H bond formation in carbon grains by exposure to atomic hydrogen: The evolution of the carrier of the interstellar 3.4 micron band. *Astrophys. J.* 569, 531–540. doi:10.1086/339229
- Mennella, V., Colangeli, L., Palumbo, P., Rotundi, A., Schutte, W., and Bussoletti, E. (1996). Activation of an ultraviolet resonance in hydrogenated amorphous carbon grains by exposure to ultraviolet radiation. *Astrophys. J.* 464, L191–L194. doi:10.1086/310116
- Mennella, V., Muñoz Caro, G. M., Ruitkamp, R., Schutte, W. A., Greenberg, J. M., Brucato, J. R., et al. (2001). UV photodestruction of CH bonds and the evolution of the 3.4  $\mu\text{m}$  feature carrier. *Astron. Astrophys.* 367, 355–361. doi:10.1051/0004-6361/20000340
- Merrill, P. W. (1936). Stationary lines in the spectrum of the binary star boss 6142. *Astrophys. J.* 83, 126. doi:10.1086/143707
- Molpeceres, G., Timón, V., Jimenez-Redondo, M., Escribano, R., Maté, B., Tanarro, I., et al. (2017). Structure and infrared spectra of hydrocarbon interstellar dust analogs. *Phys. Chem. Chem. Phys.* 19, 1352–1360. doi:10.1039/c6cp06043a
- Oomens, J. (2011). "Laboratory infrared spectroscopy of PAHs," in *PAHs and the Universe, EAS Pub. Ser.* Editors C. Joblin and A. G. G. M. Tielens (Les Ulis, France: EDP Sciences) 46, 61. doi:10.1051/eas/1146007
- Oomens, J., van Rooij, A. J. A., Meijer, G., and von Helden, G. (2000). Gas-phase infrared photodissociation spectroscopy of cationic polyaromatic hydrocarbons. *Astrophys. J.* 542, 404–410. doi:10.1086/309545
- Oort, J. H., and van de Hulst, H. C. (1946). Gas and smoke in interstellar space. *Bull. Ast. Inst. Neth.* 10, 187.
- Papoular, R., Conrad, J., Giuliano, M., Kister, J., and Mille, G. (1989). A coal model for the carriers of the unidentified IR bands. *Astron. Astrophys.* 217, 204.
- Parker, D. S. N., Kaiser, R. I., Troy, T. P., and Ahmed, M. (2014). Hydrogen abstraction/acetylene addition revealed. *Angew. Chem. Int. Ed.* 53, 7740. doi:10.1002/anie.201404537
- Peeters, E. (2011). "The PAH Hypothesis after 25 Years," in *Proceedings IAU symposium 280 the molecular universe*. Editors J. Cernicharo and R. Bachiller (Cambridge: Cambridge University Press), 149. doi:10.1017/S174392131102494X
- Peeters, E., Hony, S., Van, K., Tielens, A. G. G. M., Allamandola, L. J., Hudgins, D. M., et al. (2002). The rich 6 to 9  $\mu\text{m}$  spectrum of interstellar PAHs\*. *Astron. Astrophys.* 390, 1089–1113. doi:10.1051/0004-6361/20020773
- Peeters, E., Mackie, C., Candian, A., and Tielens, A. G. G. M. (2021). A spectroscopic view on cosmic PAH emission. *Acc. Chem. Res.* 54, 1921–1933. doi:10.1021/acs.accounts.0c00747
- Peláez, R. J., Maté, B., Tanarro, I., Molpeceres, G., Jiménez-Redondo, M., Timón, V., et al. (2018). Plasma generation and processing of interstellar carbonaceous dust analogs. *Plasma Sources Sci. Technol.* 27, 035007. doi:10.1088/1361-6595/aab185
- Pendleton, Y. J., and Allamandola, L. J. (2002). The organic refractory material in the diffuse interstellar medium: Mid-infrared spectroscopic constraints. *Astrophys. J. Suppl. Ser.* 138, 75–98. doi:10.1086/322999
- Pendleton, Y. J., Sandford, S. A., Allamandola, L. J., Tielens, A. G. G. M., and Sellgren, K. (1994). Near-infrared absorption spectroscopy of interstellar hydrocarbon grains. *Astrophys. J.* 437, 683. doi:10.1086/175031
- Pino, T., Chabot, M., Béroff, K., Godard, M., Fernandez-Villoria, F., Lei, K. C., et al. (2019). Release of large polycyclic aromatic hydrocarbons and fullerenes by cosmic rays from interstellar dust. Swift heavy ion irradiations of interstellar carbonaceous dust analogue. *Astron. Astrophys.* 623, A134. doi:10.1051/0004-6361/201834855
- Pino, T., Dartois, E., Cao, A. T., Carpentier, Y., Chamaille, T., Vasquez, R., et al. (2008). The 6.2  $\mu\text{m}$  band position in laboratory and astrophysical spectra: A tracer of the aliphatic to aromatic evolution of interstellar carbonaceous dust. *Astron. Astrophys.* 490, 665–672. doi:10.1051/0004-6361/200809927
- Potapov, A., and McCoustra, M. (2021). Physics and chemistry on the surface of cosmic dust grains: A laboratory view. *Int. Rev. Phys. Chem.* 40, 299–364. doi:10.1080/0144235X.2021.1918498
- Robertson, J. (1986). Amorphous-carbon. *Adv. Phys. X.* 35, 317–374. doi:10.1080/00018738600101911
- Robertson, J. (2002). Diamond-like amorphous carbon. *Mat. Sci. Eng.* 37, 129–281. doi:10.1016/S0927-796X(02)00005-0
- Rosenberg, M. J. F., Berne, O., and Boersma, C. (2014). Random mixtures of polycyclic aromatic hydrocarbon spectra match interstellar infrared emission. *Astron. Astrophys.* 566, L4. doi:10.1051/0004-6361/201423953
- Rouillé, G., Jäger, C., and Henning, T. (2020). Separate silicate and carbonaceous solids formed from mixed atomic and molecular species diffusing in neon ice. *Astrophys. J.* 892, 96. doi:10.3847/1538-4357/ab7a11
- Sabbah, H., Bonnamy, A., Papanastasiou, D., Cernicharo, J., Martín-Gago, J. A., and Joblin, C. (2017). Identification of PAH isomeric structure in cosmic dust analogs: The AROMA setup. *Astrophys. J.* 843, 34. doi:10.3847/1538-4357/aa73dd
- Sakata, A., Wada, S., Okutsu, Y., Shintani, H., and Nakada, Y. (1983). Does a 2200 Å hump observed in an artificial carbonaceous composite account for UV interstellar extinction? *Nature* 301, 493–494. doi:10.1038/301493a0
- Sakata, A., Wada, S., Tokunaga, A. T., Narisawa, T., Nakagawa, H., and Ono, H. (1994). Ultraviolet spectra of quenched carbonaceous composite derivatives: Comparison to the "217 nanometer" interstellar absorption feature. *Astrophys. J.* 430, 311. doi:10.1086/174405

- Sandford, S. A., Allamandola, L. J., Tielens, A. G. G. M., Sellgren, K., Tapia, M., and Pendleton, Y. (1991). The interstellar C-H stretching band near 3.4 microns: Constraints on the composition of organic material in the diffuse interstellar medium. *Astrophys. J.* 371, 607. doi:10.1086/169925
- Sandford, S. A., Pendleton, Y. J., and Allamandola, L. J. (1995). The galactic distribution of aliphatic hydrocarbons in the diffuse interstellar medium. *Astrophys. J.* 440, 697. doi:10.1086/175307
- Santoro, G., Martínez, L., Lauwaet, K., Accolla, M., Tajuelo-Castilla, G., Merino, P., et al. (2020). The chemistry of cosmic dust analogs from C, C-2, and C(2)H(2) in C-rich circumstellar envelopes. *Astrophys. J.* 895, 97. doi:10.3847/1538-4357/ab9086
- Sarangi, A., Matsuura, M., and Micelotta, E. R. (2018). Dust in supernovae and supernova remnants I: Formation scenarios. *Space Sci. Rev.* 214, 63. doi:10.1007/s11214-018-0492-7
- Schalén, C. (1940). Die dunkle Materie im Sternsystem. *Naturwiss* 28, 81. doi:10.1007/BF01481747
- Schalén, C. (1949). Neuere Untersuchungen über die interstellare Materie. *Naturwiss* 36, 33. doi:10.1007/BF00590445
- Schalén, C. (1929). Zur Frage einer allgemeinen Absorption des Lichtes im Weltraum. *Astr. Nachr.* 236, 249–258. doi:10.1002/asna.19292361602
- Schlemmer, S., Cook, D. J., Harrison, J. A., Wurfel, B., Chapman, W., and Saykally, R. J. (1994). The unidentified interstellar infrared bands: PAHs as carriers? *Science* 265, 1686–1689. doi:10.1126/science.11539830
- Schmidt, G. D., Cohen, M., and Margon, B. (1980). Discovery of optical molecular emission from the bipolar nebula surrounding HD 44179. *Astrophys. J.* 239, 133. doi:10.1086/183309
- Schnaiter, M., Mutschke, H., Dorschner, J., Henning, T., and Salama, F. (1998). Matrix-isolated nano-sized carbon grains as an analog for the 217.5 nanometer feature carrier. *Astrophys. J.* 498, 486–496. doi:10.1086/305543
- Schultrich, B. (2018). Tetrahedrally bonded amorphous carbon films I: Basics, structure and preparation. *Springer Ser. Mat. Sci.* 263, 5525012.
- Sciamma-O'Brien, E., and Salama, F. (2020). Characterization of cosmic grain analogs formed at low temperature from small hydrocarbon precursors in the NASA ames COSMIC facility. *Astrophys. J.* 905, 45. doi:10.3847/1538-4357/abc00d
- Scott, A., and Duley, W. W. (1996). The decomposition of hydrogenated amorphous carbon: A connection with polycyclic aromatic hydrocarbon molecules. *Astrophys. J.* 472, L123–L125. doi:10.1086/310365
- Sellgren, K. (1984). The near-infrared continuum emission of visual reflection nebulae. *Astrophys. J.* 277, 623. doi:10.1086/161733
- Sellgren, K., Werner, M. W., Ingalls, J. G., Smith, J. D. T., Carleton, T. M., and Joblin, C. (2010). C60 in reflection nebulae. *Astrophys. J.* 722, L54–L57. doi:10.1088/2041-8205/722/1/L54
- Smith, J. D., Draine, B. T., Dale, D. A., Moustakas, J., Kennicutt, R. C., Helou, G., et al. (2007). The mid-infrared spectrum of star-forming galaxies: Global properties of polycyclic aromatic hydrocarbon emission. *Astrophys. J.* 656, 770–791. doi:10.1086/510549
- Soifer, B. T., Russell, R. W., and Merrill, K. M. (1976). 2 - 4 micron spectrophotometric observations of the galactic center. *Astrophys. J.* 207, L83. doi:10.1086/182185
- Stecher, T. P., and Donn, B. (1965). On graphite and interstellar extinction. *Astrophys. J.* 142, 1681. doi:10.1086/148461
- Stecher, T. P. (1965). Interstellar extinction in the ultraviolet. *Astrophys. J.* 142, 1683. doi:10.1086/148462
- Stefanović, I., Kovačević, E., Berndt, J., Pendleton, Y., and Winter, J. (2005). Hydrocarbon nanoparticles as a diffuse ISM analogue: Morphology and infrared absorption in the 2000–500 cm<sup>-1</sup> region. *Plasma Phys. Control. Fusion* 47, A179–A189. doi:10.1088/0741-3335/47/5A/013
- Steglich, M., Jäger, C., Huisken, F., Friedrich, M., Plass, W., Raeder, H. J., et al. (2013). The abundances of hydrocarbon functional groups in the interstellar medium inferred from laboratory spectra of hydrogenated and methylated polycyclic aromatic hydrocarbons. *Astrophys. J. Suppl. Ser.* 208, 26. doi:10.1088/0067-0049/208/2/26
- Steglich, M., Jäger, C., Rouillé, G., Huisken, F., Mutschke, H., and Henning, T. (2010). Electronic spectroscopy of medium-sized polycyclic aromatic hydrocarbons: Implications for the carriers of the 2175 Å UV bump. *Astrophys. J.* 712, L16–L20. doi:10.1088/2041-8205/712/1/L16
- Suhasaria, T., and Mennella, V. (2021). Catalytic role of refractory interstellar grain analogs on H-2 formation. *Front. Astron. Space Sci.* 8, 655883. doi:10.3389/fspas.2021.655883
- Swings, P., and Rosenfeld, L. (1937). Considerations regarding interstellar molecules. *Astrophys. J.* 86, 483. doi:10.1086/143880
- Tauc, J., Grigorovici, R., and Vancu, A. (1966). Optical properties and electronic structure of amorphous germanium. *Phys. Stat. Sol.* 15, 627–637. doi:10.1002/pssb.19660150224
- Tielens, A. G. G. M. (2022). Dust Formation in astrophysical environments: The importance of kinetics. *Front. Astron. Space Sci.* 9, 908217. doi:10.3389/fspas.2022.908217
- Tielens, A. G. G. M. (2008). Interstellar polycyclic aromatic hydrocarbon molecules. *Annu. Rev. Astron. Astrophys.* 46, 289–337. doi:10.1146/annurev.astro.46.060407.145211
- Tielens, A. G. G. M. (2011). “25 Years of PAH hypothesis,” in *PAHs and the Universe*, EAS Pub. Ser. Editors C. Joblin and A. G. G. M. Tielens (Les Ulis, France: EDP Sciences) 46, 3. doi:10.1051/eas/1146001
- Tielens, A. G. G. M., Wooden, D. H., Allamandola, L. J., Bregman, J., and Witteborn, F. C. (1996). The infrared spectrum of the Galactic center and the composition of interstellar dust. *Astrophys. J.* 461, 210. doi:10.1086/422404
- Tokunaga, A. T., and Knacke, R. F. (2019). More whiffs of the aromatic universe. *Phys. Today* 72, 12–13. doi:10.1063/PT.3.4284
- Tsuge, M., Tseng, C. Y., and Lee, Y. P. (2018). Spectroscopy of prospective interstellar ions and radicals isolated in para-hydrogen matrices. *Phys. Chem. Chem. Phys.* 20, 5344–5358. doi:10.1039/c7cp05680j
- Tumpler, R. J. (1930). Absorption of light in the galactic system. *Publ. Astron. Soc. Pac.* 42, 214. doi:10.1086/124039
- Vala, M., Szczepanski, J., Pauzat, F., Parisel, O., Talbi, D., and Ellinger, Y. (1994). Electronic and vibrational-spectra of matrix-isolated pyrene radical cations - theoretical and experimental aspects. *J. Phys. Chem.* 98, 9187–9196. doi:10.1021/j100088a017
- van Diedenhoven, B., Peeters, E., Van Kerckhoven, C., Hony, S., Hudgins, D. M., Allamandola, L. J., et al. (2004). The profiles of the 3–12 micron polycyclic aromatic hydrocarbon features. *Astrophys. J.* 611, 928–939. doi:10.1086/422404
- van Dishoeck, E. F. (2014). Astrochemistry of dust, ice and gas: Introduction and overview. *Faraday Discuss.* 168, 9–47. doi:10.1039/C4FD00140K
- Wagner, D. R., Kim, H. S., and Saykally, R. J. (2000). Peripherally hydrogenated neutral polycyclic aromatic hydrocarbons as carriers of the 3 micron interstellar infrared emission complex: Results from single-photon infrared emission spectroscopy. *Astrophys. J.* 545, 854–860. doi:10.1086/317868
- Whittett, D. C. B., Boogert, A. C. A., Gerakines, P. A., Schutte, W., Tielens, A. G. G. M., de Graauw, Th., et al. (1997). Infrared spectroscopy of dust in the diffuse interstellar medium toward Cygnus OB2 No. 12. *Astrophys. J.* 490, 729–734. doi:10.1086/304914
- Wickramasinghe, D. T., and Allen, D. A. (1980). The 3.4- $\mu$ m interstellar absorption feature. *Nature* 287, 518–519. doi:10.1038/287518a0
- Willner, S. P., Puetter, R. C., Russell, R. W., and Soifer, B. T. (1979a). Unidentified infrared spectral features. *Astrophys. Space Sci.* 65, 95–101. doi:10.1007/BF00643492
- Willner, S. P., Russell, R. W., Puetter, R. C., Soifer, B. T., and Harvey, P. M. (1979b). The 4 to 8 micron spectrum of the Galactic center. *Astrophys. J.* 229, L65. doi:10.1086/182931
- Witt, A. N., and Lai, T. S.-Y. (2020). Extended red emission: Observational constraints for models. *Astrophys. Space Sci.* 365, 58. doi:10.1007/s10509-020-03766-w
- Woolf, N. J., and Ney, E. P. (1969). Circumstellar infrared emission from cool stars. *Astrophys. J.* 155, L181. doi:10.1086/180331
- Xiang, F. Y., Li, A., and Zhong, J. X. (2017). Diffuse interstellar bands and the ultraviolet extinction curves: The missing link revisited. *Astrophys. J.* 835, 107. doi:10.3847/1538-4357/835/1/107
- Yang, T., Kaiser, R. I., Troy, T. P., Xu, B., Kostko, O., Ahmed, M., et al. (2017). HACA's heritage: A free-radical pathway to phenanthrene in circumstellar envelopes of asymptotic giant branch stars. *Angew. Chem. Int. Ed.* 56, 4515–4519. doi:10.1002/anie.201701259
- Zhang, Y., and Kwok, S. (2015). On the viability of the PAH model as an explanation of the unidentified infrared emission features. *Astrophys. J.* 798, 37. doi:10.1088/0004-637X/798/1/37
- Zhao, L., Kaiser, R. I., Lu, W., Xu, B., Ahmed, M., Morozov, A. N., et al. (2019). Molecular mass growth through ring expansion in polycyclic aromatic hydrocarbons via radical-radical reactions. *Nat. Commun.* 10, 3689. doi:10.1038/s41467-019-11652-5
- Zubko, V., Dwek, E., and Arendt, R. G. (2004). Interstellar dust models consistent with extinction, emission, and abundance constraints. *Astrophys. J. Suppl. Ser.* 152, 211–249. doi:10.1086/382351
- Zuo, W., Li, A., and Zhao, G. (2021). Interstellar extinction and elemental abundances. *Astrophys. J. Suppl. Ser.* 252, 22. doi:10.3847/1538-4365/abc6cd