NANOSTRUCTURATION OF POLYAROMATIC ANALOGUES OF THE CARBONACEOUS DUST

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Abstract. Carbonaceous cosmic dust is mainly observed through infrared spectroscopy either in absorption or in emission. Laboratory soot analogues of this interstellar or circumstellar dust were produced in fuel-rich, low-pressure, premixed and flat, flames. The particles were investigated by infrared absorption spectroscopy in the 2–15 μm spectral region. The details of the spectral features shed some light on the structure of the material and enable the study of its life cycle. In particular, the 8 μm band position is tentatively attributed to defects at the edge or in the polyaromatic units of the materials, revealing these structural changes in astrophysical dust.

1 Introduction

Carbonaceous materials, from molecules to solid grains, are observed in many regions in space (Ehrenfreund & Charnley 2000; Henning & Salama 1998). Although carbonaceous materials carry spectral features observed in the visible to UV range (Désert *et al.* 1990; Draine 2003; Zubko *et al.* 2004), most of the spectral information is obtained in the infrared domain. In particular the mid-infrared emission features observed in many astronomical objects (Gillett *et al.* 1973), the Aromatic

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Infrared Bands (AIBs), are tracing carbonaceous particles whose inferred size vary from large molecules, the Polycyclic Aromatic Hydrocarbons - PAHs, to nanoparticles of a few nanometers (Crawford *et al.* 1985; Léger & Puget 1984; Tielens 2008). These carbonaceous species, heated by UV/visible starlight, emit through their vibrational bands thanks to the transient heating mechanism (Allamandola *et al.* 1989; Draine & Li 2001; Puget & Léger 1989). Three main classes A, B and C of astrophysical spectra have been proposed based on the observed spectral characteristics in the 6 to 9 μm wavelength region (Peeters *et al.* 2002). The band positions, in most sources, are characteristic of aromatic materials (Goto *et al.* 2007), however, the exact nature of the emitters is still debated. The presence of polymeric hydrogenated amorphous carbon (a-C:H) is also given by the 3.4 μm feature observed in absorption in the diffuse interstellar medium (ISM), and in emission in class C objects. Related bands at 6.85 and 7.25 μm are observed as well (Dartois *et al.* 2007; Dartois & Muñoz-Caro 2007; Dartois *et al.* 2004, 2005; Pendleton & Allamandola 2002). A link between these two components, amorphous and more organised materials, is also expected and different scenarios have been proposed.

In order to study these materials, many studies in laboratory astrophysics are ongoing involving various analogues. At Orsay (France), our gas-phase chemical reactor is a low-pressure flame, flat and premixed. It is a model reactor for combustion studies as it provides a one-dimensional time-resolved burning medium. In this study, we show that our reactor is capable of producing a structural/chemical variety of materials under controlled conditions. We focus here on the use of Fourier Transform Infrared absorption spectra. The laboratory and astronomical IR spectral features are tentatively interpreted in the light of the soot structures.

2   Laboratory astrophysics: On the spectroscopic parameters for soot

The production of laboratory analogues of the interstellar and circumstellar matter opens the way to detailed spectroscopic and structural characterisations. It enables the connection between the nanostructure of the soot grain and the spectral features. Soot grains consist of agglomerated primary particles with diameters of the order of 5–30 nm. We list in Table 1 most of the soot that were produced using different gas phase reactors together with the analytical tools that were used.

The techniques that are used can provide some information on the nature of the chemical bonds (IR – infrared absorption, EELS – Electron Energy Loss Spectroscopy, Raman spectroscopy, C13 NMR – Nuclear Magnetic Resonance, GCMS – Gas Chromatography Mass Spectrometry), the structural organisation of the polyaromatic domain (HRTEM – High Resolution Transmission Electron Microscopy, XRD – X-ray Diffraction, Raman spectroscopy) and the graphitization index (HRTEM, XRD, Raman, EELS, UV-vis absorption) through different spectroscopic parameters. The graphitization index is related to the size distribution of the polyaromatic units and is a major parameter to characterize a polyaromatic material. The polyaromatic unit sizes are equal to about 1–2 nanometers maximum in soot (measurements by Alfè *et al.* 2009; Vander Wal *et al.* 2007) whereas

Table 1. Principal laboratory studies using gas phase reactors to produce the polyaromatic analogues of the interstellar and circumstellar grains. The main diagnostics that were used are also indicated.

Chemical Reactor	Diagnostics
Laser pyrolysis	IR spectroscopy IR and HRTEM (Galvez *et al.* 2002; Herlin *et al.* 1998; Reynaud *et al.* 2001)
Laser pyrolysis	IR spectroscopy, mass spectometry, EELS, HRTEM (Schnaiter *et al.* 1999)
Laser pyrolysis	HRTEM, IR, UV-Vis, GCMS (Jäger *et al.* 2006)
Condensation at high temperature	HRTEM, EELS, C13 NMR, IR-UV (Jäger *et al.* 2009)
Condensation at high temperature	IR, XRD (Biennier *et al.* 2009)
Laser pyrolysis	HRTEM, IR, UV-Vis, GCMS (Jäger *et al.* 2006)
Premix Flame at atmospheric pressure	UV Absorption (Schnaiter *et al.* 1996)
Benzene flame at atmospheric pressure	UV Absorption (Colangeli *et al.* 1995)
Premix and low pressure flame	IR Spectroscopy (Pino *et al.* 2008), Raman Spectroscopy Brunetto *et al.* (2009)

most spectral parameters are built for units longer than 2–3 nm, so that all these techniques can not be conclusive. Other concepts may be used, the main one concerns the organisation of these polyaromatic units: the organised domains range from two to, typically, four stacked polyaromatic layers (Alfè *et al.* 2009; Bockhorn 1994; Dippel *et al.* 1999; Homann 1998; Sadezky *et al.* 2005). These stacked polyaromatic units are forming the basic structural units, the BSUs. This concept of BSU is at the core of the analysis of all polyaromatic materials. The global arrangement of these subunits (orientation) and their proportion depend strongly on the soot itself and therefore on the burning conditions (Alfè *et al.* 2009).

3 Spectral variations and grain nanostructures, astrophysical implications

Infrared astronomical spectra are the sole information that can be used to decipher the intimate structure of the AIB carriers. Therefore only spectroscopic parameters extracted from the infrared bands can be used. We are thus exploring the details of the variations of the infrared bands within different soot samples using complementary Raman spectroscopy and HRTEM imagery (not shown here) in order to link the spectral features to specific structural properties of the polyaromatic

units within the soot. The detailed analysis is reported elsewhere (Carpentier *et al.* 2012). In Figure 1, infrared absorption spectra of three soot samples (1 to 3) produced in different conditions are shown. We found that the evolution observed in this sample (from soot 1 to 3) is in fact rather similar to the evolution of spectral properties from the class A to C of the AIBs.
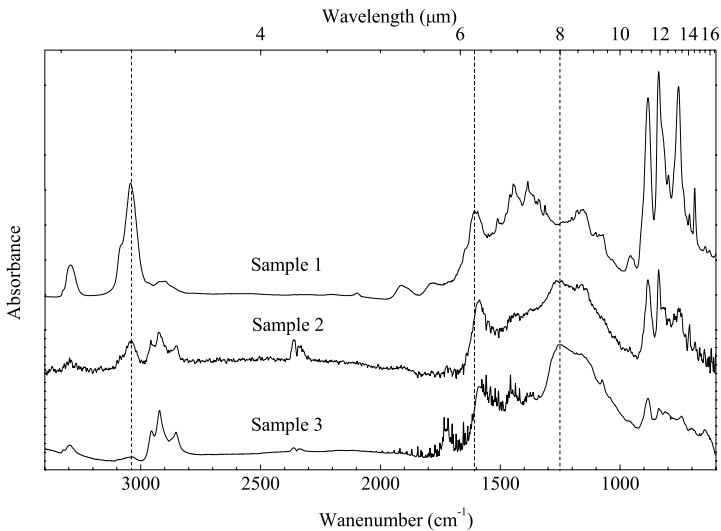

Fig. 1. IR absorption spectra of three soot samples after continuum subtraction. The spectra were normalized altogether in order to match the intensity of the band at 1600 cm^{-1}. CO_2 spectral contamination at about 2400 cm^{-1} for sample 2 and H_2O spectral contamination in the 1800–1400 cm^{-1} range for sample 3 may be seen due to slight variations of the purge of the spectrometer. Note the shift of the band at about 1600 cm^{-1} and the presence or absence and shift of the band at about 1250 cm^{-1}.

We have recently shown that the $6.2\,\mu$m band position traces the intimate cross-linkage of the polyaromatic units composing the soot (Pino *et al.* 2008). Such evolution is accompanied by an evolution of the band at about $8\,\mu$m. We tentatively attribute this band to defect-like modes of the polyaromatic units, as outlined in Figure 1, either at the edge and cross-linking the units together or within the unit and shaping the unit away from planarity. Such nanostructural characteristics are, in combustion processes, related to the growth mechanism of the soot (D'Anna 2009). Similarly, different interstellar emitters could have experienced different formation pathways.

4   Conclusion

The study of soot analogues of the cosmic dust allows us to analyse the spectral characteristics of AIB spectra that were classified from A to C. The role of the

defects in the carbonaceous particles appears to be at the core of the variations of the spectral features, in particular those related to the aromatic carbon skeleton, the band at about $6.2\,\mu$m and that at about $8\,\mu$m. Progress on the understanding of the nanostructuration of the emitters will be essential to decipher the growth and lifecycle of this component of interstellar matter, as proposed in Carpentier *et al.* (2012).

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