PAHs and the Universe
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THE PAH-DIB HYPOTHESIS

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Abstract. In this contribution I review the PAH-DIB hypothesis. Firstly, I list several properties of PAHs and their behaviour and expected signatures in space. Next, I give an overview of the current observational insights on the DIB carriers. I conclude with a brief description of recent results on the search for the DIB carriers and the prospects we have for identification.

1 Introduction: The diffuse interstellar band problem

The discovery of stationary absorption lines toward spectroscopic binaries prompted the discovery of the interstellar medium (Hartmann 1904). In the 1930s an increasing number of the narrow absorption bands were identified with *e.g.* ionized titanium, neutral potassium, CH and CH^+. However, a handful of broader bands could not be identified. Merrill *et al.* (1938) presented the first detailed study of several of these so-called “diffuse” interstellar bands (DIBs). They found these absorption features to correlate roughly with the amount of interstellar dust inferred from the apparent reddening of stars. Also, they found a good correlation with atomic gas phase species. Based on their observations they concluded that indeed these DIBs could not be due to atoms but their carriers would likely be either related to grains or to larger gas-phase molecules (see also Snow & Destree, elsewhere in this volume). Despite many efforts over the last decades, to this date the carriers of the DIBs remain an illusive component of the diffuse interstellar medium (ISM).

2 The PAH-DIB hypothesis

In the May 1985 issue of *A&A* both Van der Zwet *et al.* and Léger *et al.* stipulated explictly the so-called PAH-DIB hypothesis. Shortly afterwards, June 1st 1985,

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Crawford *et al.* published a paper in similar vain in ApJ. The basic idea of the PAH-DIB hypothesis proposed by these authors states that:
polycyclic aromatic hydrocarbons (PAHs) are predicted to be the carriers of (some of) the diffuse interstellar bands[1].

Essentially this was a direct follow-up on the pioneering work by Allamandola *et al.* (1985) and Puget *et al.* (1985) in which it was shown that PAHs emit in the unidentified infrared (UIR) bands due to excitation upon absorption of optical-UV photons. In this contribution on the connection between PAHs and the DIB carriers I will also consider related large molecules such as fullerenes, nanotubes and carbon rings. Next, I will highlight the different arguments for this connection.

3 Properties of PAHs and their behaviour in space

The arguments favouring PAHs as DIB carriers follow directly from the properties of PAHs (many of which were already listed in the three seminal papers mentioned above):

- PAHs (or more generically aromatics) are very abundant in space as evidenced from the ubiquitous presence in space of the UIR emission bands.
- PAHs, in particular if compact, can be very stable against photo- and thermo-dissociation. Therefore, a significant number density could survive in the harsh ISM.
- PAHs and their ions (cations or anions) have transitions in the near-UV, visible to near-infrared. Wavelengths of the strongest bands depend strongly on the size, the symmetry (shape) and ionization state of the considered PAH. Small to medium sized ionized PAHs have spectra dominated by one strong transition. This can be a broad & strong UV/visible band or a narrow & weak visible/near-IR band, depending whether the ionized PAH is compact or not. This can explain the distribution of DIBs between broad/strong and weak/narrow bands.
- Laboratory spectroscopy of PAHs in Ne/Ar matrix isolation shows indeed strong bands in the DIB range. However, inaccuracies in position and band broadening due to the matrix environment make it impossible to assign specific bands in observations; Theoretical calculations support this conclusion but also lack sufficient accuracy. Unfortunately, laboratory gas-phase spectra of PAHs in interstellar conditions are still very difficult to obtain (Pino *et al.*, elsewhere in this volume).
- Possibly many stable PAH configurations could be formed, and thus give rise to many absorption lines.

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[1] Historical note: Interestingly, Platt (1956) and Donn (1968) already proposed "PAHs" to explain the reddening curve. Several others proposed polyatomic molecules "carbon chains/rings" as DIB carriers; *e.g.*: Merrill (1938), Danks & Lambert (1976), Smith *et al.* (1977), Douglas (1977). In addition, much was already known about UV/visible spectra and molecular properties of PAHs (*e.g.* Clar 1964; Birks 1970).

- Diffuse cloud models show that PAH ionization and hydrogenation levels are sensitive to the local physical conditions, dust extinction properties, and the effective radiation field (Bierbaum *et al.* and Montillaud *et al.*, elsewhere in this volume). A significant fraction of PAHs will be singly positively ionized (typical ionization potentials of PAHs are between 5 to 8 eV). This provides a natural explanation for the lack of correlation between DIBs.
- PAHs and/or related carbonaceous material can also account for the 2175 Å UV bump (Mulas *et al.*, elsewhere in this volume).

From the inferred presence of PAHs in space (through the UIR emission bands) and the particular chemical and physical properties of PAHs listed above one could already predict that these molecules should also give rise to electronic absorption lines in the UV/visible/near-IR range.

4 Observational insights on the DIB carriers: Are they PAHs?

There is growing observational support to assign the DIB carriers to PAHs (and/or other closely related molecules). This section present the insights on the DIBs from an observational point of view. The reader is also referred to the excellent reviews by Herbig (1995) and Sarre (2006) for additional details and references.

- DIBs show a large variety of profiles. Widths range from 0.5 to 30 Å (or 2–80 cm^{-1}). These widths exclude atomic or diatomic carriers and suggest polyatomics. Several narrow DIBs have a pronounced substructure. Broad DIBs are not known to show substructure. The 6613 Å DIB substructure (peak separation) changes consistently with temperature. DIB linewidth and line shape can be explained by rovibronic contours and line broadening due to internal conversion for medium sized molecules (*i.e.* PAHs containing 20–30 carbon atoms or the C_{60} fullerene).
- Searches for polarisation of the DIB profiles have set stringent upper limits to the polarization efficiency of the carriers. This is indicative of a carrier that is not attached or part of (*i.e.* an impurity) the dust grains causing the continuum polarization.
- The signature of these bands can be observed to stunning similarity in galactic and extragalactic regions. DIBs have been observed to reside in most Local Group galaxies (*e.g.* LMC, SMC, M 31, M 33), as well as in more distant spiral galaxies and starburst galaxies and even beyond toward Damped Lyman-Alpha systems (*e.g.* Cox & Cordiner 2008). DIB carriers are therefore ubiquitous (just as the UIR emission bands) throughout the Universe (in space and time). Formation routes and conditions are clearly universal.
- Most DIBs show only a marginal correlation with each other. One of the few exceptions seems to be the 6196 Å and 6613 Å DIB pair. This implies that there is a unique carrier for each diffuse band (*i.e. 1 DIB for 1 PAH*; where the latter can be a specific – ionization/hydrogenation – state of a particular PAH structure).

- DIB strengths are only loosely correlated with the total amount of dust and gas. There appears to be one exception to the rule. The 8620.4 Å "Gaia" DIB shows a strong correlation with reddening, E($B-V$), although some intrinsic scatter is still observed. Possibly its carrier is more closely related to dust grains than others. DIB strengths have been compared to many other environmental parameters that give information on the interstellar clouds. Positive correlations are observed for most cases although this may often be simply the result of averaging several individual clouds along distant sightlines. Large variations in DIB strength are observed between single clouds that contain similar amounts of gas and dust.
- Band strength ratios are affected by the effective UV field. In particular the 5780/5797 ratio can be used as a tracer of the effective interstellar radiation field (ISRF) strength.
- DIB families (*i.e.* bands that behave in a similar sense) reflect the interstellar conditions which determine locally the relative importance of neutrals, cations and anions.
- Until this date the DIBs are only observed to reside in the diffuse-to-translucent ISM (probed by sightlines toward stars). No DIBs have been conclusively found to be present in other astrophysical environments. For example, evolved stars are known factories of dust and complex molecules and could therefore contribute to the production of PAHs. However, recent studies show that DIB carriers are very weak, if not absent, in circumstellar environments of post-AGB stars - thus the carriers do not form or conditions to excite these transitions are not met.

5 Search for DIB carriers

The success of laboratory efforts to measure spectra of molecules in the gas-phase has driven the search for carbon chains in the ISM. Maier *et al.* (2001, 2002) obtained laboratory spectra of C_3 and C_5 but only detected the former in a few translucent clouds. In addition, the diacetylene cation (HC_4H^+) is proposed to match with the 5069 Å DIB (Krelowski *et al.* 2010). There have been no other positive results yet for other neutral, cationic and anionic linear carbon-chain radicals measured in gas-phase (Tulej *et al.* 1998; Motylewski *et al.* 2000). Increasingly sensitive astronomical spectra could well reveal these intrinsically weak bands in the future. Further progress in laboratory experiments have yielded the first gas-phase spectra of small PAHs. Iglesias-Groth *et al.* (2008, 2010) found (new) absorption features, toward an interstellar region with anomalous microwave emission, at wavelengths predicted for both naphthalene (${C_{10}H_8}^+$) and anthracene (${C_{14}H_{10}}^+$) cations. The conclude that 0.008% of the carbon budget is contained in the two molecules. Linnartz *et al.* (2010) studied an acetylene plasma and found a band coinciding with the 5849 Å DIB. A specific molecular assignment of the carbon based carrier could not be made. Similar results by Reilly *et al.* (2007) showed that radical species produced by discharge of benzene give rise to an absorption band coincident with a strong DIB at 4760 Å.

One of the more tentative assignments is perhaps that of C_{60}^{+} to two near-infrared bands at 9577 and 9632 Å. Early after its discovery C_{60} was proposed as contributing both to the UIR bands and the DIBs (*e.g.* Kroto *et al.* 1985; Léger *et al.* 1988). Sellgren *et al.* (elsewhere in this volume) report detection and assignment of C_{60} in the IR. Optical laboratory spectra of $C_{60}^{+/-}$ in the gas-phase are needed to detect this molecule in the visual range.

However, it is important to note here that despite identifying several new interstellar features none of the over 200 diffuse bands observed in the visible spectrum has been identified yet.

6 Prospects

- The PAH-DIB proposal provides a plausible working hypothesis to approach the issue of identifying the DIB carrier(s).
- Alternative candidate carriers can not be dismissed, although the carriers are very likely large carbonaceous gas phase molecules that are stable, UV resistant, but sensitive to the local cloud conditions, in particular the ISRF.
- Spectroscopic signatures in both the UV and the near-IR are predicted for many (neutral/cation) PAHs. Surveys with COS/HST (see Snow & Destree, elsewhere in this volume) and X-Shooter/VLT are underway. The presence of electronic absorption bands in the near-IR would be a direct test of the presence of large ionized molecules in space. At present only two interstellar absorption band detections, at 1.18 and 1.32 μm (Joblin *et al.* 1990), have been put forward. The lack of near-IR/UV signatures of PAHs could put severe constraints on the properties of PAHs in the diffuse/dense ISM.
- It is crucial to explore environments other than diffuse/translucent clouds. In particular, circumstellar envelopes of evolved stars ("PAH" factories) are interesting objects.
- Identification of specific PAHs in far-IR could be directly verified in the UV to near-IR (or *vice versa*) as discussed in Joblin *et al.* (elsewhere in this volume).
- The conditions for efficient formation of PAHs are not yet understood. Either this could occur via evolved stars or supernovae that produce the dust content of the Universe or, alternatively, these are produced in-situ in the ISM. The formation process could either happen bottom up starting with small building blocks (C, CH, C_2H_2, etc.) or alternatively, top down, as fragments from large carbonaceous structures (very small grains).
- Weeding out impossible isomers is another key element to the PAH-DIB hypothesis. Another important point in this respect is the PAH size distribution. Is it dominated by small or larger PAHs, by peri- or catacondensed PAHs?

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