Laboratory studies of polycyclic aromatic hydrocarbons: the search for interstellar candidates

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Abstract. Polycyclic Aromatic Hydrocarbons (PAHs) are considered as a major constituent of interstellar dust. They have been proposed as the carriers of the Aromatic Infrared Bands (AIBs) observed in emission in the mid-IR. They likely have a significant contribution to various features of the extinction curve such as the 220 nm bump, the far-UV rise and the diffuse interstellar bands. Emission bands are also expected in the far-IR, which are better fingerprints of molecular identity than the AIBs. They will be searched for with the Herschel Space Observatory. Rotational emission is also expected in the mm range for those molecules which carry significant dipole moments.

Despite spectroscopic studies in the laboratory, no individual PAH species could be identified. This emphasises the need for an investigation on where interstellar PAHs come from and how they evolve due to environmental conditions: ionisation and dissociation upon UV irradiation, interactions with electrons, gas and dust. Insights into this question have recently been obtained from the analysis of the AIB spectra in different environments including mild UV-excited photodissociation regions, planetary nebulae and protoplanetary disks. PAH species are found - (i) - to be produced by destruction of very small grains (VSGs), -(ii)- to have an evolving charge state: neutral or cationic, and -(iii)- to undergo severe destruction in highly UV-irradiated environments, only the largest species being able to survive. There is also evidence for PAH species to contribute to the depletion of heavy atoms from the gas phase, in particular Si and Fe.

This paper illustrates how laboratory work can be inspired from observations. In particular there is a need for understanding the chemical properties of PAHs and PAH-related species, including VSGs, in physical conditions that mimic those found in interstellar space. This motivates a joint effort between astrophysicists, physicists and chemists. Such interdisciplinary studies are currently performed, taking advantage of the PIRENEA set-up, a cold ion trap dedicated to astrochemistry.

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are usually considered as the carriers of the Aromatic Infrared Bands (AIBs) observed in emission between 3 and 13 $\mu$m in many astronomical objects that are submitted to UV photon irradiation: the so-called photodissociation regions (PDRs; Léger and Puget 1984; Allamandola et al. 1983). They are expected to contribute significantly to var-
ious features of the UV-visible extinction curve such as the 220 nm bump, the far-UV rise (Joblin et al. 1992) and the diffuse interstellar bands (Salama et al. 1999). Emission bands are also expected to occur in the far-IR, that are better fingerprints of molecular identity than the mid-IR bands (Joblin et al. 2002b; Mulas et al. 2006a). They will be searched for with the Herschel Space Observatory (HSO).

PAHs (the carriers of the AIBs) appear as a major component in the cycle of dust in the Milky Way from evolved stars (planetary nebulae), to the diffuse interstellar medium (ISM) and bright PDRs associated to molecular clouds and the circumstellar environment of young stars including their disks. Their emission is also well observed in external galaxies (e.g. Smith et al. 2007; Spoon et al. 2007; Galliano et al. 2008a,b) and even in ultra-luminous IR galaxies (ULIRGs) at z=1-3 (e.g. Yan et al. 2005; Sajina et al. 2007). AIB spectra show characteristic features which fall at 3.3, 6.2, 7.7, 8.6, 11.3 and 12.7 µm. The observed spectra exhibit variations in band positions, profiles and relative intensities and also differ in their satellite features. Two general approaches can, therefore, be adopted to use these spectral features as diagnostics of the chemical and physical conditions from galaxies to circumstellar environments.

One consists in searching for groups of astronomical objects based on classification of the spectral features (Peeters et al. 2002; van Diedenhoven et al. 2004). The other one is based on a better understanding of the nature of the AIB carriers and their physical and chemical evolution due to environmental conditions. This approach is guided by experimental and theoretical studies (cf. for instance Langhoff 1996; Pauzat and Ellinger 2001; Hudgins et al. 2005; Mulas et al. 2006c; Bauschlicher et al. 2008; Joalland et al. 2009). For instance, it has been shown that the 7.7/11.3 µm band intensity ratio can be used as a tracer of the PAH+/PAH° ratio. The value of this ratio depends on the competition between ionisation and recombination with electrons, which involve the UV flux density and the electron density, respectively (cf. Figure 6.7 in Tielens 2005). This band ratio was used in a large sample of galaxies to characterise the local physical conditions (Galliano et al. 2008b).

The search for the identification of individual PAH molecules or families of species in the AIB spectra, has not been successful so far. This lack emphasises the need for an investigation on where interstellar PAHs come from and how they evolve due to environmental conditions: ionisation and dissociation upon UV irradiation, destruction in shocks, interactions with electrons, gas and dust. These questions motivate fundamental studies on analogues of interstellar PAHs in physical conditions that mimic those found in the ISM. This leads to the development of specific laboratory set-ups, such as PIRENEA, a cold ion trap dedicated to astrochemistry.

2. What can we learn from mid-IR observations?

A chemical evolution scheme for the mid-IR emission carriers

Since the IRAS mission, it is well known that there exists a population of very small particles which are transiently heated by the absorption of single UV photons and emit in the mid-IR range. PAHs were proposed to account for the AIBs and another component, called very small grains (VSGs; Désert et al. 2007).
was introduced as the carrier of the diffuse IR emission in the 25 µm IRAS band. In the last years, space missions, and in particular the European Infrared Space Observatory and the NASA Spitzer Space Telescope, have gathered a wealth of spectral data that allows us to better characterise the various mid-IR emission features and their variations. One can consider either a large sample of individual objects that are not spatially resolved, or study the spatial variations of these bands within extended objects. In the first approach, the objects can be quite compact which implies that the spectrum integrated in the spectrometer beam is likely to include the contribution from different types of regions. The exciting central source may also be difficult to characterise (e.g. PNe, compact H II regions, disks, etc.). In the case of extended objects on the other hand, one can hope to access chemical frontiers (gradients in the abundances of species).

Spectro-imagery of extended PDRs has become possible in the mid-IR (5-16 µm) with ISOCAM in CVF mode (Cesarsky et al. 1996). A striking result from these observations is the presence of continuum emission in PDRs far from exciting sources (Abergel et al. 2002). This reveals the presence of VSGs transiently heated by single UV photons. The continuum relative to the bands is highly variable, showing that VSGs are a dust component that differs in nature from PAHs (Compiègne et al. 2008). Further analysis of the data using principal component analysis (Rapacioli et al. 2005b) allows us to extract three fundamental spectra, the various mixtures of which create the observed spectral variations. Two of the spectra carry only band emission (they are assigned to PAH cations and neutrals) and the other one has band and continuum emission (it is assigned to VSGs). Interestingly, the drop of the VSG emission at the cloud edge appears to be correlated with the increase in the PAH emission, strongly suggesting that free PAHs are produced by destruction of VSGs under UV irradiation. This idea is fully consistent with the strong spatial variations observed in the IRAS 12/100 µm ratio at the surface of molecular clouds (Boulanger et al. 1990; Bernard et al. 1992). These studies continued then taking advantage of the IRS spectrometer onboard the Spitzer telescope (Houck et al. 2004). In particular, the SPECPDR programme was dedicated to the study of the evolution of the mid-IR emission spectrum, by performing 5-35 µm spectro-imagery of mild-excited PDRs (Joblin et al. 2005). Berné et al. (2007) analyzed these data using blind signal separation (BSS) analysis. They confirmed the results previously obtained by Rapacioli et al. (2005b) and extended them to a larger set of regions and a larger spectral range. The two spectra assigned to PAHs were shown to contain bands only whereas the VSG spectrum to carry the continuum, up to 25 µm. In cool PDRs, as the ones considered in this study with a UV field of the order of a few 100 G0 or less, the continuum emission is dominated by stochastically heated dust particles and not by larger grains at thermal equilibrium.

The studies on PDRs by Rapacioli et al. (2005b) and Berné et al. (2007) led to two important results. The first one is that free PAHs are efficiently produced by destruction of VSGs, most likely under exposure to UV photons. This led Rapacioli et al. (2005b) to propose PAH clusters as good candidates for these VSGs. The second important result is the fact that the mid-IR emission in these regions can be well accounted for by a very limited number of components: 3 different spectra from 3 different populations, namely neutral PAH0, cationic PAH+ and VSGs. It is of interest to consider these spectra to analyze
the spectra of other types of objects in particular those in which UV-excitation conditions are more extreme. This was the motivation to study the mid-IR emission spectra of planetary nebulae (PNe), H II regions [Joblin et al. 2008] and protoplanetary disks [Berné et al. 2009]. In these objects, grains at thermal equilibrium are likely to contribute to the mid-IR continuum. The description of this continuum would require detailed modelling for each source, with variations in dust temperature producing variations in its spectral shape. It cannot, therefore, be reproduced by a simple linear superposition, with varying weights, of a small number of fixed spectra, which is the very assumption underlying the applicability of BSS. A continuum combining two slopes was, therefore, subtracted from the observations keeping an appropriate level for band wing emission. Three PDR-type spectra were built by taking an average spectrum of each species from the spectra extracted by Rapacioli et al. and Berné et al. in NGC 7023, Ced 201, and the ρ-Ophiucus filament. The continuum from VSG spectra was removed since only bands are fitted. Each average spectrum is then fitted using a combination of Lorentzians and normalised to their 6-14 µm integrated intensity. The resulting template spectra are shown in Figure 1. All major features have been included except a plateau at λ ≥ 12 µm for VSGs which was difficult to reproduce due to contamination by the H2 line at 12.3 µm and underlying continuum.

The basis consisting of the three PDR components was found to be insufficient for obtaining a satisfactory fit of the observed spectra in highly-excited objects. First, in all classes of objects, PNe, H II regions and disks around A stars, the presence of another PAH population was evidenced and called PAHx. The PAHx spectrum was built empirically to account for the mid-IR emission observed in PNe and compact H II regions [Joblin et al. 2008] but was inspired by quantum chemistry calculations [Bauschlicher et al. 2008]. The main characteristic of this spectrum is that it has a strong feature at 7.9 µm significantly redshifted with respect to the 7.6 µm feature of PAH0 and PAH+. The theoretical calculations by Bauschlicher et al. (2008) show that such redshift can be explained if one considers compact PAHs which are large (of the order of 100 or more carbon atoms) and ionised (cations or anions). Second, broad emission features (BFs) had to be considered: BFs at 8.2 and 12.3 µm that are inspired from post-AGB spectra (type C objects of Peeters et al. 2002), and a dBF (for disk broad feature) at 8.3 µm was extracted from T-Tauri spectra (Bouwman et al. 2008). These features are thought to be associated to material that is rich in aliphatics and easily destroyed by UV irradiation [Sloan et al. 2007].

The set of the 6 template spectra displayed in Figure 1: PDR-type (3), PAHx, 8.2 and 12.3 µm BFs, were successfully used in Joblin et al. (2008) to interpret the mid-IR emission arising from PNe and H II regions both in the Galaxy and Small and Large Magellanic Clouds. Similarly, the set of the 5 template spectra: PDR-type (3), PAHx, and 8.3 µm dBF were successfully used to analyze the spectra of some protoplanetary disks (Berné et al. 2009). The obtained results are in line with the photodestruction of VSGs leading to free PAHs and the survival of only the largest ionised PAHs, the PAHx in highly irradiated environments. The BFs in PNe are only observed in young sources, which is in line with efficient destruction of their carriers by UV irradiation.
Figure 1. The 7 mid-IR template spectra that are used to fit the observed emission in mild UV-excited PDRs (Rapacioli et al. 2005b; Berné et al. 2007), protoplanetary disks (Berné et al. 2009), planetary nebulae (PNe) and H II regions (Joblin et al. 2008). The various PAH mixtures are displayed on the left: PAH$^0$, PAH$^+$ and PAH$^x$ (large ionised species only clearly observed in highly UV-irradiated environments). The right panel displays the spectrum from VSGs after continuum subtraction as well as some broad features that are only observed in specific classes of objects: the broad features at 8.2 and 12.3 µm in PNe (8.2BF and 12.3BF), and the feature at 8.3 µm (dBF) in disks.

One of the implications of this work is that the mid-IR emission can be used to trace the local UV irradiation conditions. The observation of the PAH$^x$ component reveals strong irradiation conditions. In protoplanetary disks, Berné et al. (2009) show that the relative abundance of the different components: VSG, PAH$^0$ and PAH$^+$, and PAH$^x$ can be used to characterise the central object. The authors also noticed that PAH$^x$ are not observed around hot Be stars, which strongly suggests that in these objects the observed emission is dominated by the nebula surrounding the star and not by the disk. This work also provides a rather simple chemical evolution scheme for mid-IR emitters through the cycle of dust from evolved stars (PNe), to PDRs associated to molecular clouds and to the circumstellar environment of young stars including their disks. The PAH$^0$, PAH$^+$ and VSG components are found in evolved stars and in PDRs as well. VSGs appear as loose aggregates of PAHs. They could be dissociated in UV-irradiated conditions and reformed in the denser and more shielded environments of molecular clouds (Rapacioli et al. 2006). However, there is no obvious chemical scenario to rebuild PAH molecules in molecular clouds. This, therefore, puts a constraint on the lifetime of PAH species considering that at least part of them has to survive the processing by shocks in the diffuse ISM before being incorporated in molecular clouds (cf. Jones et al. 1996, and A. Jones in this volume for a description of the processing of carbon dust in shocks). Our study suggests that some PAHs have to survive against these shocks and constitute the building blocks to regenerate VSGs in molecular clouds.

There is still some effort to be done to explore the conditions in which the PAH$^x$ component is observed. It was assigned to very large compact ionised PAHs. As discussed in Joblin et al. (2008), these species are likely to be present
Figure 2. Examples of the analysis of the mid-IR spectra of planetary nebulae (left panel; from Joblin et al. 2008) and protoplanetary disks (right panel; from Berné et al. 2009). The spectra after continuum subtraction have been smoothed at the resolution of $\lambda/\Delta \lambda = 45$ (dashed line) and fitted using the template spectra displayed in Figure 1 (solid line). The PAH components are displayed in colour lines: PAH neutrals (green dashed line), cations (blue dash-dot line), and PAH$^+$ (red continuous line). The broader components have been shifted for clarity: VSGs (diamonds), 8.2, and 12.3 $\mu$m BF, and dB/ (dash-dot line). The ionic gas lines have been removed from the PNe spectra.

in mild-excited PDRs as well, but their emission is revealed in highly irradiated environments as due to the combined effect of destruction of the smaller PAHs (the PAH$^0$ and PAH$^+$ components) and higher excitation conditions that bring these very large PAHs to higher temperatures. In lower irradiation environments, efficient emission in the 6-9 $\mu$m range arises from PAHs of diameter less than 10 Å (Draine and Li 2007). Assuming a compact shape for these species, this leads to sizes of less than 120 carbon atoms (cf. Eq. 2 in Omont 1986). Larger PAHs will emit efficiently in this range if they can reach higher internal temperatures, e.g. contain more than 13.6 eV of internal energy. This is possible under high enough UV flux, leading to the absorption of multiple UV photons; the UV absorption rate is then fast enough to make it likely that one or more UV photons can be absorbed before the energy from the previously absorbed ones has been completely reemitted. PAH$^+$ could absorb multiple UV photons when very close to the central star, which is clearly the case in protoplanetary disks (Berné et al. 2009). In the case of PNe or H II regions, the rise of internal temperature could be also due to the absorption of extreme UV (EUV) photons ($h\nu > 13.6$ eV) if PAH$^+$ are located inside the ionised region or very close to it. Compiègne et al. (2007) measured some PAH emission in the H II region facing the Horsehead nebula, suggesting that these species could indeed be excited by EUV photons. Further studies at high spatial resolution are, however, necessary.
to conclude on the exact location of PAH\textsuperscript{x} in the compact objects studied in Joblin et al. (2008) and Berné et al. (2009).

Figure 3. Lowest energy structural isomers for the cationic complexes of silicon with pyrene C\textsubscript{16}H\textsubscript{10} and corresponding IR spectra, calculated using a version of the density functional theory (cf. Joalland et al. 2009). The Si-C bond lengths are given in Å.

3. The identification of PAHs (and VSGs)

3.1. The spectroscopic view

The identification of interstellar and circumstellar PAHs and VSGs relies on the match between their spectroscopic fingerprints and bands that are observed in astronomical spectra. The mid-IR range reflects mainly chemical bonds and, therefore, provides information on the composition and some trends about the size and structure, but is not well suited to identify individual species. As discussed in Section 2., three main populations were extracted by Rapacioli et al. (2005b), Berné et al. (2007) and Joblin et al. (2008): the PAH\textsuperscript{0}, PAH\textsuperscript{+} and PAH\textsuperscript{x}. Detailed studies on the positions and shapes of specific bands can also provide insights into the nature of the emitting species. For instance,
Hudgins et al. (2005) showed that the blueshifted position of the 6.2 µm band cannot be accounted for by PAHs, neutrals or cations. The authors put forward an alternative explanation involving N atoms inserted within the C-skeleton. Recently, Joalland et al. (2009) proposed another scenario in which this band is the signature of [SiPAH]^+ π-complexes in the ISM, emphasising the importance of the interaction of heavy atoms with PAHs (cf. Figures 3 and 4).

Figure 4. The IR spectrum of the Red Rectangle nebula observed with SWS and retrieved from the ISO archive. Joalland et al. (2009, see also Figure 3) showed that [SiPAH]^+ π-complexes have specific mid-IR fingerprints that can provide an explanation for -(i)- the 6.2 µm component of the “6.2 µm” AIB and -(ii)- the presence of satellite bands observed on the blue side of the 6.2 and 11.2 µm AIBs. From this assignment, it is deduced that typically 1% of the cosmic silicon is attached to PAHs.

In the UV range, PAHs and VSGs are expected to contribute to both the 220 nm bump and the far-UV rise. Cecchi-Pestellini et al. (2008) have shown that the two spectral features and their variations can be accounted for by mixtures of PAHs in different ionisation states. Whereas the composition of the mixtures is not unique, the trend given by the variation of the charge state is robust. However, this model only considers free PAHs due to the lack of spectral data on VSGs whether they are PAH clusters or of another nature. Diffuse interstellar bands (DIBs) that fall essentially in the visible range (Herbig 1995) are a way to identify individual PAH molecules by their low-lying electronic transitions, which are very characteristic. The fishing for candidates has not been successful so far (see for instance Salama et al. 1999). Only Iglesias-Groth et al. (2008) recently claimed a tentative identification of ionised naphthalene C_{10}H_{8} along one line of sight. Rotational spectroscopy is another way to identify specific candidates with the limitation that this applies only to species with a significant value of their dipole moment. Lovas et al. (2005) proposed that corannulene, C_{20}H_{10}, is a good candidate considering the large value (for a PAH) of 2.07 D for its dipole moment. A recent study (Pilleri et al. 2009) combines spectroscopic results obtained in the laboratory (Herbeth, Giesen, in preparation), numerical simulations of the emission of corannulene in astronomical environments using a dedicated Monte–Carlo code (Mulas et al. 2006a), and astronomical observations at the IRAM 30 m telescope. An upper limit for the abundance of corannulene in the Red Rectangle was derived. It amounts to 10^{-5} for the carbon abundance in this species relative to the total carbon contained in PAHs.
An alternative for the spectroscopic identification of PAHs is a search for their emission features in the far-IR range, these features being much more specific to the exact molecular identity than the ones in the mid-IR. The far-IR bands are emitted during the cooling cascade of UV-excited PAHs, mainly at the end of the cooling (Joblin et al. 2002b). The emission spectrum of a large sample of PAHs in different charge states ( neutrals and cations) and in specific objects (such as the Red Rectangle nebula) has been computed by Mulas et al. (2006a). The Monte–Carlo code takes as an input molecular parameters that are available in the theoretical on–line spectral database of PAHs (Malloci et al. 2007): the positions and intensities of all vibrational modes and

Figure 5. Calculated infrared emission spectrum from a sample of 20 PAHs ranging in size from $C_{10}H_8$ to $C_{48}H_{20}$, each in two charge states for a total of 40 distinct spectra, compared with the estimated dust continuum in the Red Rectangle nebula. Different panels correspond to different assumptions for the band profiles, $\sigma_{PR}$ representing the width of the P and R rotational branches and $\sigma_Q$ the width of the central Q branch, which is assumed to depend on the band frequency $\omega$ (see Mulas et al. 2006a) for details. (a) $\sigma_{PR} = 5.5 \text{ cm}^{-1}$, $\sigma_Q/\omega = 0.7\%$, (b) $\sigma_{PR} = 5.5 \text{ cm}^{-1}$, $\sigma_Q/\omega = 0.07\%$, (c) $\sigma_{PR} = 0.7 \text{ cm}^{-1}$, $\sigma_Q/\omega = 0.7\%$, (d) $\sigma_{PR} = 0.7 \text{ cm}^{-1}$, $\sigma_Q/\omega = 0.07\%$. The operation ranges of the relevant astronomical facilities are overlaid for reference. The HSO will open the possibility to identify PAHs by their far-IR bands.
the photo–absorption cross–sections up to the vacuum–UV. The results presented in Mulas et al. (2006a) concern the intensities emitted in the different bands. In Figure 5 different widths have been assumed to account for the PQR rotational structures of the bands. Comparison with the observed spectra however requires a detailed calculation of the emission profile. During the cooling cascade of the excited PAH, all but the very last one of the transitions are not a fundamental (i.e. 1 → 0) transition, but instead happen between two vibrationally excited states. The peak position of the IR bands is a function of both the coupling between modes leading to a cross-anharmonic shift and the quantum numbers in the emitting vibrational mode leading to an anharmonic shift (Oomens et al. 2003). The effect of vibrational anharmonicity on band shape for each band requires then the knowledge of all the molecular parameters, which are not easy to access by experiment or theory (Mulas et al. 2006b). A recent study has been performed on naphthalene, C\textsubscript{10}H\textsubscript{8} (Pirali et al. 2009), that illustrates the interplay between high-resolution spectroscopy and numerical simulations of the photophysics of PAHs. The authors have shown that the model developed by Mulas et al. is able to predict the overall band shape when rotational structure and hot band sequences are introduced in the modelling. Extension of this work to larger molecules is expected, in the future, to benefit on the experimental side from the AILES far-IR beamline at the SOLEIL synchrotron facility. From an observational point of view, the future will be the search for the far-IR bands of PAHs with the HSO. The best strategy to detect these bands is to search for the Q branches associated to these out-of-plane modes. The PACS and SPIRE instruments provide the best compromise between resolving power and sensitivity to evidence these features. Follow-up observations at very high resolution with the heterodyne spectrometer HIFI will allow us to resolve the hot band structure of the Q branches and may be also some structure in the P and R branches. From these data, detailed information on the emitting molecule will be retrieved.

3.2. On the nature of dissociating VSGs

As discussed in Section 2, free PAHs are produced by destruction of VSGs. This process is observed in regions where UV photons are present, including PDRs with mild excitation conditions, in which the chemical frontier between PAHs and VSGs can be resolved (cf. for instance Figure 6). This implies that VSGs dissociate quite easily and are, therefore, rather loose aggregates. Rapacioli et al. (2005b) proposed that they are clusters of PAHs with a minimum size of typically 400 carbon atoms per cluster. Taking into account the fact that these VSGs are the carriers of the continuum up to 25 µm in these regions (Berné et al. 2007), some of the dissociating VSGs could contain up to a few thousands of carbon atoms.

The formation and destruction mechanisms of (C\textsubscript{24}H\textsubscript{12})\textsubscript{4} and (C\textsubscript{24}H\textsubscript{12})\textsubscript{13} have been modelled in detail by Rapacioli et al. (2006) in the northern PDR of NGC 7023. This study provides a description of the formation mechanism by molecular dynamics simulations and of the photodissociation by using a statistical theory (phase space theory). The description of the photophysics of a specific cluster in the astronomical environment considered is then provided using a kinetic Monte–Carlo code that follows Joblin et al. (2002b). This work
led to the conclusion that the studied neutral PAH clusters are destroyed more rapidly than they are formed in the NGC 7023 northern PDR. This is consistent with emitting VSGs being quite larger than the studied species. There are also several other factors that can reinforce the stability of the clusters including a larger size for the PAH units (Rapacioli et al. 2005a) and charge effects (Rapacioli and Spiegelman 2009). There is also the possibility for a continuous source of production of VSGs in PDRs due to advection processes bringing unprocessed matter from the molecular cloud into the UV-exposed layers. All this leads to different scenarios that have to be explored, putting forward both fundamental data and astronomical models.

Figure 6. Spatial distribution of the emission of the PAH ($\text{PAH}^0$, $\text{PAH}^+$) on the left panel and VSG (right panel) components extracted in Ced201 by Berné et al. (2007). Contours represent the integrated mid-IR (5-35 $\mu$m) emission. This illustrates the chemical evolution from VSGs to PAHs due to UV radiation from the star situated in the center of the field of view.

The idea for the presence of PAH clusters has been strengthened by the observed spatial correlation between the region where VSGs dissociate and that where extended red emission (ERE) arises (Berné et al. 2008). This suggests that PAH clusters are ERE carrier precursors. Furthermore, theoretical studies (Rhee et al. 2007) show that charged PAH dimers ($\text{PAH}_2^+$) can fluoresce efficiently in the 600 to 1000 nm range. Although this concerns only some specific dimers that are closed-shells, Berné et al. (2008) have shown that this is still consistent with the observations, considering that ERE carriers contribute typically to only a few % of the mid-IR emission. They also discussed the fact the charged PAH dimers are quite likely to be present in PDRs since they constitute the last step in the dissociation cascade of PAH clusters and they can be reformed efficiently by collision between neutral and cationic PAHs. Furthermore their stabil-
ity is increased relative to their neutral counterpart (Rapacioli and Spiegelman 2009).

Serra et al. (1992) and Chaudret et al. (1991) suggested that interstellar PAHs can coordinate efficiently to metal atoms and in particular to iron. Modelling work by Marty et al. (1994) suggests that VSGs made of PAHs and Fe atoms can be formed and survive in PDRs at least in some rather shielded conditions ($A_V \sim 4-5$). This work however suffers from the lack of data on the fundamental properties (photodissociation, reactivity) of these systems. In a recent work, Simon and Joblin (2009) found that the presence of Fe atoms in coronene clusters increases the stability of the aggregate. The bonding dissociation energy (BDE) of the coronene dimer ($C_{24}H_{12})_2$ is calculated to be $\sim 1$ eV (Rapacioli et al. 2005a) and $\sim 1.3$ eV for its positively charged counterpart (Rapacioli and Spiegelman 2009). This BDE was found to be 1.7 and 2.0 eV for $[Fe(C_{24}H_{12})_2]^+$ and $[Fe_2(C_{24}H_{12})_2]^+$, respectively (Simon and Joblin 2009). The presence of Fe atoms in the ionised aggregates is, therefore, expected to further increase their stability compared to the homogeneous clusters, and consequently increase their lifetime in PDRs.

### 3.3. The depletion of heavy elements

Several authors suggested that part of the iron and other heavy metals is in the form of atoms that attach and desorb from very small carbonaceous grains (Weingartner and Draine 1999; Rodríguez 2002; Whittet 2003; Rodríguez and Rubin 2005, see also contributions from B. Draine and S. Zhukovska in this volume). The photodissociation of very small iron-PAH grains was proposed to account for the increased abundance of atomic iron in H II regions (Rodríguez 2002). The abundances of Fe and Si in translucent lines of sight were recently discussed (Miller et al. 2007). This work shows that more of these elements are in the dust phase when the non-linear far-UV rise of the extinction curve increases, giving support to the fact that they are accreted by the smallest grain populations, e.g. PAHs and VSGs which are responsible for this rise (Cecchi-Pestellini et al. 2008).

Abundances of gas-phase elements have been derived in the diffuse ISM by UV absorption measurements (Sofia et al. 1994; Fitzpatrick 1996; Savage and Sembach 1996; Miller et al. 2007) and in PDRs by analysis of mid-IR emission in atomic forbidden lines (Fuente et al. 2000; Kaufman et al. 2006; Okada et al. 2008). The general conclusion is that the abundance of Fe in the gas-phase is typically a factor of 5-10 less than that of Si. This means that the probability of collision of a PAH with a Si atom is about one order of magnitude larger compared to a collision with an Fe atom. But this does not tell how much of Fe (or Si) is indeed attached to PAHs or VSGs since this results from the competition between attachment and dissociation, which requires a proper description of the physical conditions in the studied regions and some knowledge on the fundamental properties of the involved species.

Recently, the presence of Si-PAH$^+\pi$-complexes in PDRs was proposed on the basis of spectroscopic fingerprints (Joalland et al. 2009). The formation of these complexes is expected to occur without any barrier by simple radiative association releasing 3.0 eV energy. A different question is that of the substitution of C atoms by Si atoms in the PAH skeleton which has still to be addressed. The Si-PAH$^+\pi$-complexes would involve about 1% of the cosmic abundance of Si in
the Red Rectangle nebula. Despite detailed theoretical study, no specific mid-IR spectroscopic fingerprints were found that could be used to reveal the presence of Fe-PAH$^+$ species in the ISM (Simon and Joblin 2007). The main effect of iron was found to be a charge effect, leading to changes of the band intensity ratios. Still Fe-PAH$^+$ are expected to live longer in the ISM conditions, considering that the associated BDE is typically 2.6 eV (Simon and Joblin 2007) to be compared to 1.5 eV for Si-PAH$^+$ (Joalland et al. 2009). In addition, we have to consider that Fe atoms have a lot of electrons available for chemical bonding and the formation of larger [Fe$_x$PAH$_y$] clusters with $x$ and $y > 1$ is expected. This is not the case for Si. Experimental studies show a fast formation in the gas-phase of the [Fe(C$_{24}$H$_{12}$)$_2$]$^+$ complex and no formation of the [Si(C$_{24}$H$_{12}$)$_2$]$^+$ complex (Pozniak and Dunbar 1997). Therefore [Fe$_x$PAH$_y$] clusters are good candidates to consider for interstellar VSGs and deserve some studies to characterize their properties including their IR spectroscopy.

A crude estimate of the composition of Fe-PAH complexes can be made as follows. In H II regions, both VSGs and PAHs are expected to be destroyed and, therefore, Fe atoms attached to these species entirely released in the gas phase. (cf. the results of Clark et al. 1995 on the Rosette Nebula and λ Orionis H II regions and the recent work of Povich et al. 2007 on the massive star formation region M17). Currently available values for gas-phase Fe abundance in H II regions are quite inaccurate: 2-30% (Rodríguez 2002) and < 22% (Okada et al. 2008) of the solar abundance. If we take a value of 5% for Fe attached to PAHs and VSGs, which is in fact consistent with the value given earlier by Klotz et al. (1995), we obtain an average proportion of 2 Fe atoms for one PAH in Fe-PAH complexes (assuming an abundance of 7 $10^{-7}$ for PAHs: Joalland et al. 2009).

4. The laboratory approach

The analysis of space observations shows that further studies are mandatory to characterize the properties of PAHs and VSGs and related species including [Si-PAH]$^+$ and [Fe-PAH]$^+$ complexes in conditions which mimic those found in interstellar space. The PIRENEA set-up in Toulouse has been developed for this purpose (Joblin et al. 2002a). It combines the electromagnetic trapping and the mass spectrometry performances of an ion cyclotron resonance (ICR) cell with cryogenic cooling. The achieved ultra-high vacuum ($\sim 10^{-10}$ mbar) and the cold temperatures (30 K on the trap) allow us to approach the physical conditions of isolation encountered in interstellar space. The set-up is equipped with (i) a gas injection interface for reactivity studies and (ii) photon sources including tunable lasers and a Xe arc lamp that provides continuous radiation from 200 nm to the near-IR. The ions are produced by laser ablation-ionisation from a solid target and are trapped in the ICR cell under the conjugated action of a magnetic field provided by a 5 T superconductor magnet and electrical potentials applied on the trapping plates. The ion signal that is used for mass analysis is generated by exciting coherently the ion cloud with an alternating electric field that contains the cyclotron frequencies of the ions. The ion motion induces an image charge signal on the detection electrodes and this transient signal is recorded and analyzed by Fourier Transform (FT) to retrieve the cyclotron frequencies of the ions and therefore allowing to derive their mass-
over-charge ratio, m/z (Marshall and Schweikhard 1992). Another advantage of the excitation technique is the ability of isolating, in the ICR cell, only the species of interest at a given m/z ratio by selective ejection of the other trapped species (Guan and Marshall 1996). Very often, the laser ablation technique generates a mixture of species including isotopomers and fragments. It is, therefore, mandatory to isolate the ions of interest for a specific study of their physical and chemical properties. The ions of interest are ions at a given m/z ratio that can include different isomeric forms (species with the same chemical formula but different structures). The experimental procedure consists, therefore, in (i) the production and isolation of the ions of interest, (ii) cooling down of the ions either radiatively in the environment of the cold walls or by collisions with a buffer gas, and (iii) photon irradiation or gas injection depending on the process that is studied.

Figure 7. Production and isolation of the coronene dimer [(C_{24}H_{12})_2]^+ (m/z=600 and 601, 602 for the ^{13}C isotopomers) in PIRENEA (a) and dissociation under irradiation with the Xe arc lamp and the \( \lambda_c = 475 \) nm filter (b). The dissociation results in the production of the monomer C_{24}H_{12}^+ (m/z=300 and 301 for the ^{13}C isotopomer).

We report here some results that have been obtained on the photodissociation of laboratory analogues of VSGs by irradiation with the Xe arc lamp. The general question is whether the considered species can easily release PAHs units under photon irradiation in the gas-phase. The wavelength range of the Xe lamp can be adjusted by using longpass colour filters whose cut-off wavelength \( \lambda_c \) is defined at 50\% of transmission. In the experiments discussed below, we used the \( \lambda_c = 475 \) nm filter. The dissociation products are recorded by mass spectrometry and kinetics curves can be obtained by reporting the relative abundances of the parent ion and its photofragments as a function of the irradiation time which varies from hundreds of milliseconds to several seconds.

The first species that are considered are PAH clusters. Bréchignac et al. (2005) reported the formation of coronene clusters containing up to 13 units in a gas aggregation source. The clusters were ionised before detection in a time-offlight mass spectrometer. The limitation of this experiment is that the formed
clusters cannot be handled for further studies. Still, there was the possibility to irradiate the flying clusters with a focused laser light at $h\nu = 4$ eV, which induces both ionisation and heating of the clusters. Interestingly, the authors suggest that this process induces a growth mechanism for the aromatic network. The process was reconsidered by Schmidt et al. (2006) who concluded that the destruction of the cluster should proceed through evaporation of van-der-Waals bond coronene units and not by intrachannel chemical reactions. More experimental data is, therefore, needed to study the dissociation process under better controlled conditions. The PIRENEA set-up is not equipped with an aggregation source. The dimer $[(\text{C}_{24}\text{H}_{12})_2]^+$ was formed in situ in the ICR cell by reactivity of trapped $\text{C}_{24}\text{H}_{12}^+$ with a neutral vapour of coronene. The formed dimer was isolated (Figure 7 - left panel) and irradiated using the Xe arc lamp and the $\lambda_c = 475$ nm filter (Figure 7 - right panel), showing that the dissociation occurs through evaporation of a coronene unit.

Figure 8. Production and isolation of the $[\text{Fe}(\text{C}_{24}\text{H}_{12})_2]^+$ complex ($m/z = 656$) in PIRENEA (a) and dissociation under irradiation with the Xe arc lamp and the $\lambda_c = 475$ nm filter (b). The dissociation results in the production of the $[\text{Fe}(\text{C}_{24}\text{H}_{12})]^+$ complex ($m/z = 356$) that produces $\text{C}_{24}\text{H}_{12}^+$ by dissociation (right panel). The derived photodissociation pathway is given in Figure 9. The lowest energy structural isomers for the $[\text{Fe}(\text{C}_{24}\text{H}_{12})_2]^+$ and $[\text{Fe}(\text{C}_{24}\text{H}_{12})]^+$ complexes were calculated using a version of the density functional theory (cf. Simon and Joblin 2009).

The other species that are considered are clusters made of PAHs and Fe atoms. Formation of $[\text{FePAH}]^+$ and $[\text{FePAH}_2]^+$ by radiative association in an ICR cell was performed by Dunbar et al. (1994) and Pozniak and Dunbar.
A comparable technique could be used in PIRENEA, as for coronene dimers. Instead, an ablation-ionisation technique was used with a solid target made of a mixture of trirundodecayne Fe$_3$(CO)$_{12}$ and coronene C$_{24}$H$_{12}$ deposited onto a thin layer of nanoparticles of silica (Simon and Joblin 2009). [FeC$_{24}$H$_{12}$]$^+$ and [Fe$_x$(C$_{24}$H$_{12}$)$_2$]$^+$ ($x=1$-3) complexes were formed. We discussed in Section 3.3 that VSGs could contain an average proportion of 2 Fe atoms for one PAH. Therefore the species, which have been produced in PIRENEA can be considered of astrophysical interest. Their photodissociation was recorded under irradiation of the Xe lamp with the $\lambda_c=475$ nm filter. As an example, Figure 8 shows the isolation (left panel) and photodissociation (right panel) of [Fe(C$_{24}$H$_{12}$)$_2$]$^+$, which fits with the general photodissociation pathway reported in Figure 9. [Fe$_x$(C$_{24}$H$_{12}$)$_2$]$^+$ ($x=1$-3) complexes are found to sequentially photodissociate by losing iron atoms and coronene units under visible irradiation. The carbon skeleton of coronene is preserved with C$_{24}$H$_{12}^+$ as the smallest photofragment (Simon and Joblin 2009). The authors show that (i) the stability of the complex increases with the number of iron atoms, and that (ii) the presence of iron atoms induces efficient electronic excitations likely to be responsible for a significant increase of the heating efficiency in the experiments conducted with the PIRENEA set-up.

All these experimental results fit into a scenario in which [PAH$_n$] and [Fe$_x$PAH$_n$] complexes are formed efficiently in molecular clouds as described by Marty et al. (1994) and Rapacioli et al. (2006) and get easily dissociated upon UV-visible irradiation to produce free PAHs (and Fe atoms/ions). These are only first results. This work will be pursued by using in particular photon sources that are more relevant to interstellar conditions. In the experiments described above, we used visible continuous irradiation, which allows us to build internal energy in the irradiated species by successive absorption of photons. The dissociation occurs when the dissociation threshold is reached (Boissel et al. 1997). To mimic photodissociation in PDRs, it is more relevant to use the absorption of far-UV photons and that will be possible soon in PIRENEA. It is important to mention that for these large species, the timescale for relaxing the absorbed energy by IR emission can be larger than the timescale for absorption of UV-visible photons even in mild UV-excited PDRs. This is indeed this process that is expected to govern the photodissociation of large PAH clusters in PDRs (Rapacioli et al. 2006).

5. Summary: The future of PAHs

The AIBs are a major signature of UV-irradiated environments and, therefore, could be a valuable tool for astronomers to trace the local physical and chemical properties in these environments. In the recent years, some progress has
been done in the understanding of the processing in circumstellar and interstellar environments of the proposed carriers for AIBs: PAHs and related species (VSGs). These observational results provide guidelines for laboratory studies. For instance, an important result is the production of free PAH molecules by photodissociation of VSGs, which provides insights into the nature of these VSGs. A still open question is the contribution of PAHs to the depletion of heavy atoms, such as Si and Fe. Although there is some spectroscopic evidence for the presence of Si-PAH$^+$ complexes in PDRs, the proof for the adsorption of Fe on PAHs and its inclusion in VSGs is still lacking. This should be further investigated considering the potential implication it has in element depletion, charge balance as well as chemistry (possibility of a catalytic chemistry) in astronomical environments.

A key question remains the identification of individual PAHs through spectroscopic fingerprints. The identification of electronic transitions by comparison to the DIBs is one way. Another way will be opened in the near-future with the launch of HSO providing the possibility to explore the far-IR range where the bending modes of the carbon skeleton are found. Clearly this subject has some exciting years to go. Important enough is, from space to the laboratory, to be open-minded in order to consider different kinds of PAH-related species since the question is not solved yet. There is still a lot to do at the interface between astronomy and physical chemistry.

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