Universiteit
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The Netherlands

PAH processing in space

Micelotta, E.R.

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Chapter 1

Introduction

The research described in this thesis focuses on the physical processes that Polycyclic Aromatic Hydrocarbons (PAHs) undergo during their journey through space.

On Earth, PAHs are one of the most common chemical compounds. They are naturally present in crude oil and coal deposits, arising from chemical conversion of natural product molecules, and are also formed by incomplete combustion of carbon-containing fuels such as wood, coal, diesel, fat, tobacco, or incense. Hence they are found in car exhaust, cigarette smoke and (too) well-cooked meats. This makes PAHs one of the most widespread organic pollutants, regularly under the attention of the media because some compounds have been identified as carcinogenic, mutagenic, and teratogenic. In particular one PAH compound, benzo[a]pyrene, is notable for being the first chemical carcinogen to be discovered, and is one of many carcinogens found in cigarette smoke.

In space, PAHs have been recognised as an important and ubiquitous component of the Interstellar Medium (ISM). Closely related to dust, they are formed in the outflows of evolved and dying stars. PAHs contribute substantially to the heating of the ISM and play a crucial role in the interstellar chemistry and in the cosmic life cycle. Moreover, they can be used as a diagnostic tracer of the environmental conditions within astrophysical objects.

In §1.1 we describe the various components of the ISM and how they interplay within the cosmic life cycle (Fig. 1.1), with a particular attention to supernova explosions because of their crucial role in PAH processing and evolution. In §1.2 we present an overview on PAHs, describing their structure, how they form and evolve in space, what their excitation mechanisms are and consequently how they can be identified and studied – both in the laboratory and in the ISM – through their infrared (IR) emission. The relevance of interstellar PAHs is discussed in §1.3, while in §1.4 we discuss the relevant processes for dust expected to be responsible for PAH processing as well. Finally, the importance of studying PAH processing in the ISM is highlighted in §1.5 and the content of this thesis is outlined in §1.6.

1.1 The Interstellar Medium

1.1.1 Components of the ISM

As the name already suggests, the term Interstellar Medium (ISM) indicates the material filling the volume between stars in a galaxy. It is mainly composed of tenuous hydrogen and helium gas with a contribution from heavier elements which can be

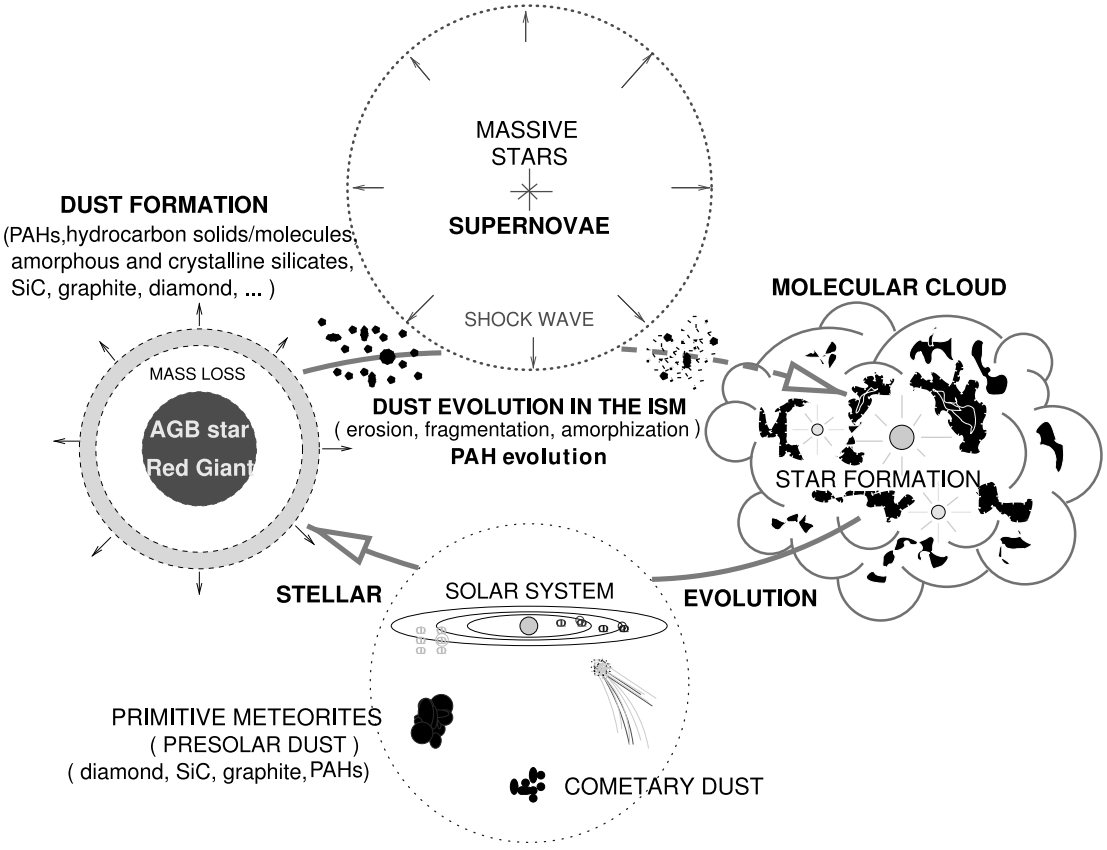


Figure 1.1 — A schematic view of the cosmic life cycle. *Figure adapted from Jones (2004).*

present in the gas phase (in atomic and molecular form) or in the solid state. In the Milky Way the total mass of the ISM gas component is 4.5×10^9 $M_\odot$ (Tielens 2005). For comparison, the mass in stars is 1.8×10^{11} $M_\odot$. The ISM is organized into a variety of phases (Tielens 2005), each characterized by specific physical properties:

- **Molecular gas**. Surveys in the CO J=1-0 transition at 2.6 mm revealed that the molecular gas in the Milky Way is localized in discrete Giant Molecular Clouds with temperatures of 10 – 20 K. This phase has a very small filling factor, only of order of 1%, but accounts for a substantial fraction of the mass, $\sim$ 30 – 60% of the total contents of the Galactic ISM. Molecular clouds are bound by their self-gravity rather than being in pressure equilibrium with other phases of the ISM. The balance of magnetic/turbulent pressure and gravity keeps them stable over timescales of $\simeq 3\times10^{\,7}$ yr, but at the same time they are nevertheless the sites of active star formation. The typical cloud size and density are $\simeq$ 40 pc and 200 cm^{-3}, with masses of 4×10^5 $M_\odot$, but they contain cores with sizes of $\simeq$ 1 pc, densities exceeding 10^4 cm^{-3} and masses in the range 10 – 10^3 $M_\odot$. The gravitational collapse of these cores leads to the formation of new stars. CO is a widely used tracer of interstellar molecular gas, but the dominant molecular species is thought to be H_2, which cannot be directly detected because of the lack of dipole transitions (the molecule is symmetric). The quantity of H_2 can be estimated from the CO using an empirical conversion factor.

- **Cold Neutral Medium (CNM)** and **Warm Neutral Medium (WNM)**. The neutral gas is traced by the 21 cm line of atomic hydrogen, and is organized into cold ($\simeq$ 100 K) diffuse H I clouds (CNM) and warm ($\simeq$ 8000 K) intercloud gas (WNM). The CNM occupies 1 – 4% of the total volume and a standard cloud has a typical density of 50 cm^{-3} and size of 10 pc. The WNM has a much lower density ($\simeq$ 0.5 cm^{-3}) but occupies a substantial fraction of the total volume ($\sim$ 30 – 60%). The mass distribution varies with the galactic latitude. Between 4 and 8 kpc from the galactic center, 80% of the H I mass in the plane of the galaxy is located in diffuse clouds, while at higher latitudes much of the H I gas is in the intercloud medium.
- **Warm Ionized Medium (WIM)**. This phase is most clearly associated with H II regions, where the gas is photoionized by hot young stars and emits in the Hα recombination line. Although most of the Hα luminosity of the Milky Way arises from distinct H II regions, almost all the mass of ionized gas (10^9 M$_\odot$) resides in a diffuse component having a low density ($\simeq$ 0.1 cm^{-3}), a temperature of $\sim$ 8000 K and a filling factor of $\simeq$ 0.25. The source of ionization remains uncertain: while photoionization from young stars seems to be the dominant mechanism near the midplane of disk galaxies, outside the galactic plane shock heating or suprathermal particle heating become probably more important.
- **Hot Ionized/Intercloud Medium (HIM)**. This hot and tenuous phase of the ISM ($T \sim 3 - 10 \times 10^5$ K and density around 10^{-3} cm^{-3}) occupies a large fraction of the volume of the halo (while the filling factor in the disk is more controversial) but has a very small mass content. The hot gas can be detected in absorption against bright background sources in highly ionized species (e.g. C IV, S VI, N V, O III, O VI), or through continuum and line emission in the far ultraviolet and X-ray wavelength range. The HIM is heated by strong shocks driven by violent stellar winds from early-type stars and supernova explosions. The hot gas detected at high latitude may have been vented by superbubbles and flown out above and below the plane through galactic chimneys.
- **Interstellar dust**. The presence of this solid state component of the ISM has been deduced from various phenomena, see e.g. Draine (2003) and references therein. Photon absorption and scattering by small dust grains results in a general reddening and extinction of the light coming from distant stars. Non-spherical dust grains may be aligned by magnetic fields or other agents such as radiation pressure or mechanical effects, resulting in the polarization of the star light when transmitted or scattered. In the proximity of bright stars, the light scattered by dust grains produces a reflection nebula. In the diffuse interstellar medium the cold dust (10 – 100 K) is heated by visible and UV radiation, and re-emits the absorbed energy as a continuum spectrum at far-infrared wavelengths. The grain size distribution as a function of the grain radius a, $n(a) \sim a^{-3.5}$ in the range a = 50 – 2500 Å (MRN distribution, Mathis et al. 1977), has been inferred from measurements of the extinction curve over a large wavelength range. Large grains dominate the total dust volume, while small grains dominate the number density and surface area. Dust grain emission is strictly related to grain size

(Draine 2003). Big grains ($a \gtrsim 1000$ Å) are in radiative equilibrium with the interstellar radiation field at temperatures of $\simeq 15 - 20$ K and re-emit the absorbed interstellar photons at infrared and sub-millimeter wavelengths. Rotating grains ('spinning dust') also give rise to radio emission (Ferrara & Dettmar 1994; Draine & Lazarian 1998). Very small grains ($a \lesssim 100$ Å) are instead quantum heated by the absorption of single UV photons, which may cause large temperature fluctuations (Draine & Li 2001), and emit at mid-IR wavelengths ($25 - 60$ μm).
Dust grains lock up the majority of the refractory elements (e.g. C, Si, Mg, Fe, Al, Ti, Ca etc), containing about 1% by mass of the gas. The composition of the interstellar dust is still under debate, but there is a general agreement to consider silicates and graphitic/carbonaceous materials as the most important dust components. It is widely accepted that dust is mainly formed at high densities and temperatures in the ejecta of evolved stars such as those populating the Red Giant Branch and the Asymptotic Giant Branch (RGB and AGB stars, Tielens 1997). Carbon-rich stars produce carbonaceus dust ("soot"), while oxygen-rich stars produce silicate dust ("sand") rich in magnesium, with a fraction of 15% at most in crystalline form (e.g. Waters 2004). During the formation of carbonaceous dust, in a process probably comparable to the formation of terrestrial soot in flames (Frenklach & Feigelson 1989a), Polycyclic Aromatic Hydrocarbons (PAHs – see §1.3) may be formed, presumably as an intermediate product when converting gas-phase C (in the form of C_2H_2) to soot. Dust grains can be also formed in the diffuse ISM itself (Draine 2009) and in the ejecta of type II supernovae (Dwek 1998), which at the same time represent the major agent responsible for dust destruction (Dwek et al. 2008).

- **Large interstellar molecules**. Besides dust grains, the interstellar medium also contains a population of large molecules which are generally identified as Polycyclic Aromatic Hydrocarbons (PAHs). Because the *processing* of these molecules in space (we will explain later on what this means) is in fact the subject of this thesis, the properties of PAHs and their importance in the interstellar environment are discussed in a dedicated section (1.3). We emphasize here that PAHs are probably the most visible representative of the molecular universe, but may be not the only one. Interstellar grains are known to contain several populations of nano-particles, whose properties differ from those of bulk materials and are much closer to those of classical large molecules. Moreover, the so-called Diffuse Interstellar Bands (DIBs), prominent absorption features observed in the visible spectra of stars, are too broad to arise from atomic transitions. Their detection implicates the presence of a large number of different molecular species, such as unsaturated carbon chains. Interstellar PAHs have often been suggested as possible carriers of the DIBs and several groups have been working on the comparison between DIBs and PAH spectra (Romanini et al. 1999; Bréchignac & Pino 1999; Salama et al. 1999; Ruiterkamp et al. 2002; Bouwman et al. 2009). Note that generally only PAH cations are considered as potential DIB carriers as neutral PAHs - at least the smaller ones - absorb more to the UV than to the visible. Nevertheless, a recent study by Kokkin et al. (2008) opens up the possibility to test neutral PAHs as carriers of the DIBs.

- **Cosmic rays**. Cosmic rays (CRs) are energetic particles consisting mainly of relativistic protons, helium (10 %), and heavier elements and electrons (1 %). The heavier elements are thought to originate from ions sputtered from dust grains in supernova shocks and subsequently accelerated through the Fermi mechanism. They seem to take about 10 % of the kinetic energy of the supernova ejecta, and their pressure provides support against gravity for the gas in the ISM. High energy ($\gtrsim$ 100 MeV/nucleon) particles contribute considerably to the energy density of the ISM ($\simeq$ 2 eV cm^{-3}). The flux of low-energy (5 – 100 MeV) cosmic rays is difficult to measure because of the *solar modulation*, i.e. the action of the solar wind which prevents low-energy CRs from entering the heliosphere or severely slows them down, with a subsequent variation (modulation) of the observed spectrum. Low-energy cosmic rays are very efficient at ionizing and heating the gas, and in fact cosmic ray ionization is the cornerstone of gas phase chemistry. Conversely, molecular observations can be used to determine the cosmic ray ionization rate, which allows us to constrain the cosmic ray spectrum at low energies. Finally, cosmic rays can induce important structural changes when impinging on dust grains and molecules.
- **Interstellar shocks**. A shock wave is defined as a pressure gradient propagating through a fluid at supersonic speed. Because of the supersonic velocity the upstream material cannot dynamically respond to the upcoming material before it arrives. The shock will then compress, heat and accelerate the medium. The heated material cools through photon emission lines, further compressing the medium. A detailed description of the physics of shock waves can be found in Zel'dovitch & Raizer (1966). Shock waves are very common phenomena in the interstellar (and intergalactic) medium, originating from supernova explosions, AGN jets, strong stellar winds from massive stars or collisions between clouds or galaxies, whenever material moves at velocities exceeding the sound speed in the surrounding medium. Two types of shocks are of interest in the interstellar medium. J-type (J for Jump) shocks, i.e. where the physical conditions (density, temperature and velocity) change abruptly between the pre-shock and post-shock regions. In this case, the gas is suddenly stopped and heated to a high temperature and insignificant radiative and non-radiative relaxation can take place. The second type of shocks occur in a magnetized medium with a low degree of ionization. These are called C-type (C for Continuous) shocks, because the physical parameters vary smoothly across the shock front. In this thesis we will consider only J-shocks in the low density interstellar/intercloud medium.
  Interstellar shocks play a crucial role in the ISM. They are the major agent responsible for the fragmentation and destruction of dust grains, with a consequent modification of the grain size distribution, which in turn may reflect on variations of the extinction curve. The fragmentation (shattering) of bigger grains will produce smaller species, possibly including PAHs which are expected to be processed as well. Interstellar shocks are also thought to be the acceleration mechanism for cosmic rays with energies below 10^{15} eV. The compression of the ISM induced by a shock can trigger star-formation, like usually observed in the spiral arms of disk galaxies. Moreover the energy injected by shock waves into the in-

terstellar – or intergalactic – medium is responsible for the heating of the gas to X-ray emitting temperatures ($> 10^6$ K).

The various phases and components of the ISM are not static and isolated from each other. At the contrary, they interact continuously through the cosmic life cycle described below.

1.1.2 The cosmic life cycle

The cosmic life cycle is summarized in Fig. 1.1. The story of a new star begins in the dark and cold cores of dense molecular clouds. As far as the pressure force is able to compensate the effect of gravity, the cloud is stable. However, if the mass of the core exceeds a critical value, gravitation will overcome the magnetic/turbulent pressure and the core will start to collapse. If the temperature and density are sufficiently high to initiate the nuclear burning of hydrogen into helium, a new star is born. In the case of low and intermediate mass stars, the energy released by the nuclear fusion will prevent the star from further collapsing during the long (10^7 – 10^{10} yr) and stable main-sequence phase of its life. Nuclear reactions in these stars can form elements up to C, O and N. After leaving the main sequence, the star will eventually move into the Asymptotic Giant Branch (AGB). In this phase, the outer layes are loosely bound to the stellar core, while thermal instabilities cause the core material (C and O) to be mixed and brought up to the stellar surface. In the end, the outer envelope will be completely stripped away, exposing the extended nebula around the star to the hot ionizing core. The result is a planetary nebula. Without further nuclear burning, the core will eventually cool down and end its life as a white dwarf.

The evolution of a high-mass star ($M_* > 8\ M_\odot$) is quite different. Massive stars burn their nuclear fuel much faster than low-mass stars. Moreover, they are able to burn C and O into heavier elements up to iron. No further burning is possible because the reaction will be endothermic, so the core will finally collapse while the outer shells will explode: the star has become a type II Supernova. The explosion may totally destroy the star or leave a relic neutron star or pulsar. Explosive nucleosynthesis can occur during the final phases of the star, producing elements heavier than Fe which will be ejected into the ISM.

During their life, stars strongly affect their surroundings, and their life cycle is intimately linked with the physical and chemical evolution of the material of the ISM. Ionizing photons from O and B stars (hot, massive and luminous) create HII regions and are able to destroy interstellar molecules. The majority of the heavy elements synthetized by stars are injected into the ISM in the form of small solid dust particles, which are mainly formed in the expanding cooling outflows of evolved or dying stars (AGB and RGB), possibly in supernova ejecta (but the amount of dust formed in SNe is not well established) and in supergiants, Wolf-Rayet stars and novae (minor production sites). Besides dust particles, the ejecta of evolved stars and supernovae also contain various molecules, from the simplest ones such as CO to much larger ones such as acetylenic chain derivatives (e.g. C_7H) and PAHs.

After injection into the ISM through stellar winds or explosions, the newly-formed stardust and molecules can cycle many times between the intercloud and cloud phases.

UV irradiation in the diffuse ISM and reactions with ions continuously break and reform molecular bonds, allowing only the most stable species to survive. In the WIM dust is mainly processed by strong shocks driven by supernova explosions. Collisions with energetic ions in the hot shocked gas can sputter atoms from the grains, while high velocity grain-grain collisions can lead to vaporization, melting, phase transformation and shattering of the colliding partners (Jones et al. 1994, 1996). In the denser media - diffuse and dense clouds - the physical conditions allow the accretion of gas phase species onto the grains, forming a mantle. In diffuse clouds, accretion seems to proceed preferentially through chemisorption[1] - partly because the high flux of FUV photons will rapidly photodesorb the physisorbed species. In molecular clouds, the mantles consist of simple molecules such as H_2O, CO, CO_2 and CH_3OH in the form of ices, which can be processed by UV photons and high energy cosmic rays into larger and more complex species more tightly bound to the cores. While these processes are experimentally well established, their role in the interstellar scenario is more controversial and not supported by strong observational evidence.

The molecular clouds hosting dust and molecules may become gravitationally unstable and then collapse, giving birth to a new generation of stars, whose elemental composition is determined by the previous stellar population. Protoplanetary disks may form around low-mass stars and likely all intersteller grains are completely vaporized and recondensed as solar system condensates. The circle is closed and the cycle starts again.

1.1.3 Supernova explosions

Supernova explosions play a crucial role in the cosmic life cycle described in the previous section. As already mentioned, they release into the ISM the heavy elements produced by the massive supernova precursor star or during explosive nucleosynthesis. Supernova driven shock waves are the major agent responsible for dust processing in the warm intercloud ISM. In addition, supernova explosions are at the origin of the coronal phase of the ISM (Hot Ionized Medium – HIM, cf. §1.1.1), where dust and molecules are processed by collisions with high velocity thermal ions and electrons in the hot gas, while the expansion of the supernova remnants into the surrounding material strongly contributes to shaping the ISM itself.

At the end of its life, a high mass star ($M_* > 8M_\odot$) ejects a significant fraction of its mass (1 – 5 $M_\odot$) in an explosive event. The ejecta have velocities of some 10^4 km s^{-1} and the typical kinetic energy associated with the explosion is some 10^{51} erg (Ostriker & McKee 1988). The ejecta will expand into the surrounding material following

[1] *Adsorption* is the accumulation of atoms or molecules on the surface of a material. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the adsorbent's surface. *Chemisorption* (or *chemical adsorption*) is adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds.
Physisorption (or *physical adsorption*) is adsorption in which the forces involved are intermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation of vapours, and which do not involve a significant change in the electronic orbital patterns of the species involved. *Photodesorption* is an increase in the desorption (depletion) of a substance from a surface in the presence of light.

a three-stage process. The first stage starts with the mass of the ejecta totally overcoming the mass of the swept-up interstellar medium and ends when these two masses becomes equal. During this phase the velocity of the ejecta does not change and at the end the kinetic energy has been thermalized and created a bubble of hot shocked gas. In the second phase, called the Sedov – Taylor phase, the bubble of hot gas will expand following a self-similar motion (e.g. McCray & Snow 1979a, and references therein). As long as the shock velocity is above ~ 250 km s^{-1} (corresponding to a temperature of the post-shock gas of 10^6 K) gas cooling is inefficient, because the most abundant atoms are fully ionized, and the expansion is then adiabatic. The accumulating mass of swept-up material will slow down the expansion but the total energy is conserved. The phase ends when the gas temperature drops below $\sim 10^6$ K because of adiabatic expansion. At this point radiative cooling becomes important, the shock becomes isothermal (for practical purposes) and the supernova remnant enters the radiative expansion phase, also called pressure-driven snowplow phase. The overpressure of the remnant with respect to the interstellar medium drives further expansion. Because of the rapid radiative cooling, the density contrast across the shock is very large, almost a factor of 100 even when limited by magnetic fields, and a dense, thin shell of shocked material will develop, which will move into the ISM as the snow in front of the snowplow. This last phase ends when the shock wave velocity approaches the ambient sound speed, $C_0 = 12$ km s^{-1}.

Supernova explosions inject energy into turbulent motions of the ISM and during their evolution will create regions of very hot but tenuous gas which cool only very slowly. When supernovae are abundant, the disks of galaxies puff up because of the turbulent motions, and part of the volume becomes filled with the hot gas, which represents a separate phase of the ISM, the HIM in which the other phases are embedded. If the supernova rate per unit volume is high, the lifetime of the remnant is long and its final volume is large, the expanding supernova remnants will then start to overlap and form a connected tunnel network filled with hot gas. Supernovae will sweep up the warm WNM/WIM phases into thin but dense walls surrounding the tenuous hot phase (HIM). Thermal instability within these walls could lead to the dense CNM phase. The effect of this SN dominated regime shows up in a carved and very filamentary interstellar medium.

Supernova remnants are not randomly distributed. Actually, many of them occur in OB associations. The effect of the many SNe exploding in OB associations, combined with the strong stellar winds of their OB progenitors, may lead to the formation of superbubbles in the ISM. The superbubbles expand and may blow out into the halo, setting up a galactic fountain (Bregman 1980). The expansion and the following explosion of the superbubble creates "chimneys" in the galactic disks through which intermediate/high velocity clouds and hot gas are vented into the halo. The clouds will fall back to the disk following ballistic trajectories, while the gas will eventually cool and condense into clouds which will rain down onto the disk again. The chimneys also provide a natural pathway for both ionizing photons (from OB associations) and heavy elements (produced by the SNe) to flow into the halo. Galactic chimneys represent a strategic mechanism to mantain the disk-halo circulation. Another example of venting into the halo is the supernova-driven galactic-scale "superwind" associated

with the starburst galaxy M82 (Fig. 1.2, Griffiths et al. 2000; Strickland & Heckman 2007). In this case there is a huge single outflow from the starburst nucleus, instead of a series of chimneys distributed over the galactic disk. In both chimneys and superwinds, material can be entrained by the outgoing flow, i.e. incorporated into the flow and transported outside the plane but retaining much of its original character (albeit with some modification). We will show in this thesis how important this mechanism is in term of PAH processing.

1.2 Polycyclic Aromatic Hydrocarbons

As already mentioned in §1.1, besides dust grains, the interstellar medium also contains a population of large molecules which are generally identified as Polycyclic Aromatic Hydrocarbons (PAHs). This identification has been carried out through the analysis of the IR emission from a variety of sources. The IR spectrum of most objects, ranging from single HII regions and reflection nebulae to galactic nuclei and entire galaxies (see Tielens 2008 for a recent review) is dominated by broad infrared emission features which show striking similarities with the features characteristic of PAH materials. These bands result from the vibrational relaxation process of FUV-pumped PAH species containing some 50-100 C-atoms. With a very high abundance of $\sim 10^{-7}$ by number relative to hydrogen, PAHs lock up about 10% of the elemental carbon and represent an important component of the ISM.

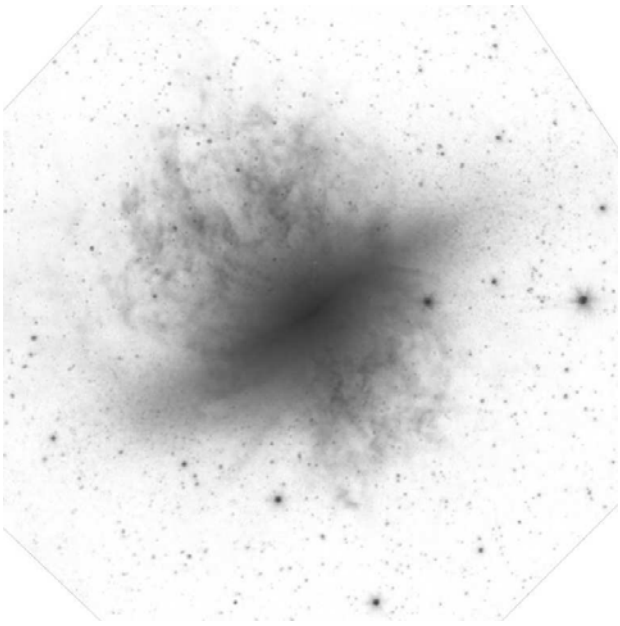
Interstellar PAHs are often "associated" with dust grains because, on the one hand, they are formed as a by-product of the formation of carbonaceous dust, and on the other hand, they seem indeed to represent, together with the other large interstellar molecules, an extension of the interstellar grain size distribution into the molecular domain. Some properties of grains can reasonably be extrapolated to PAHs taking into account a few details due to their small size, e.g. the calculation of PAH charge, see Tielens (2005). Nevertheless it is important to remember that PAHs are molecules, thus the solid state physics approach used for dust grains, for instance to treat the collisional processing in shocks, is not valid for molecules, whose physics (and chemistry) are different from that of dust in many ways.

1.2.1 Definition, characteristics and structure

PAHs belong to the family of hydrocarbons and are characterized by the arrangement of carbon atoms in a honeycombed lattice structure of fused six-membered aromatic rings with H-atoms located at the edges. Three of four valence electrons of carbon atoms are used to form covalent, σ bonds[2] with neighboring C- or H-atoms, resulting in a planar structure. The remaining electron is located in a p-orbital perpendicular to the plane. The superposition of the p-orbitals of adjacent C-atoms forms π bonds[3]

[2]The σ bond is the strongest type of covalent chemical bond. A covalent bond is characterized by the sharing of pairs of electrons between atoms and the overlap of the electron orbitals. The distinguishing feature of a σ bond is that the orbital overlap occurs directly between the nuclei of the atoms.

[3]The π bond is a covalent chemical bond where two lobes of one involved electron orbital overlap two lobes of the other involved electron orbital. While the σ bond has orbital overlap directly between the two nuclei, the π bond has orbital overlap off to the sides of the line joining the two nuclei.



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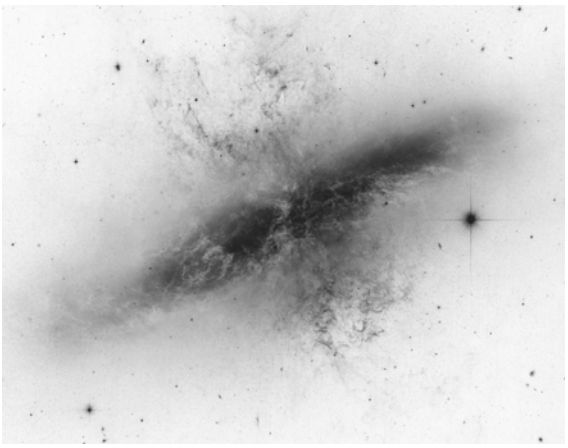

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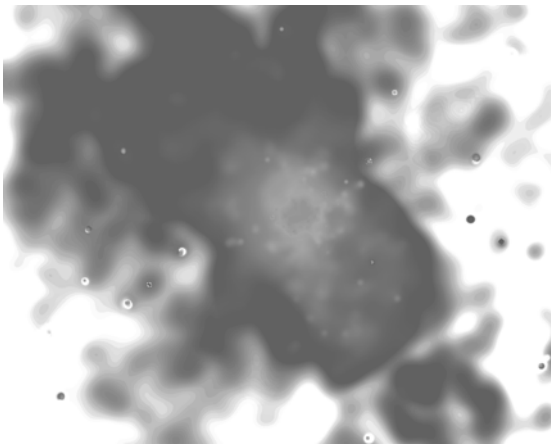


(c)

Figure 1.2 — The starburst galaxy M82 at different wavelengths. (a): infrared 3.6 μm emission from stars in the disk surrounded by infrared 8 μm PAH-dominated emission from a huge dusty halo (Spitzer IRAC). (b): optical light from stars in the galactic disk and Hα emission from filaments of glowing hydrogen blasting out of the central regions (Hubble Space Telescope). (c): X-ray emission (Chandra ACIS). The disk emission is dominated by visible light while the spectacular bipolar outflow driven by the galactic superwind is traced by the million degrees X-ray emitting gas with interwoven PAH emission. The vertical extent of the infrared emission is at least 6 kpc. *Credit – X-ray: NASA/CXC/JHU/D.Strickland; Optical: NASA/ESA/STScI/AURA/The Hubble Heritage Team; IR: NASA/JPL-Caltech/Univ. of AZ/C. Engelbracht*.

and a delocalized electron cloud above and below the plane of the molecule. The existence of such a cloud of delocalized electrons is responsible for the high stability of these species, for which reactions are possible only if the σ bonding is broken and the aromatic π ensemble is disrupted.

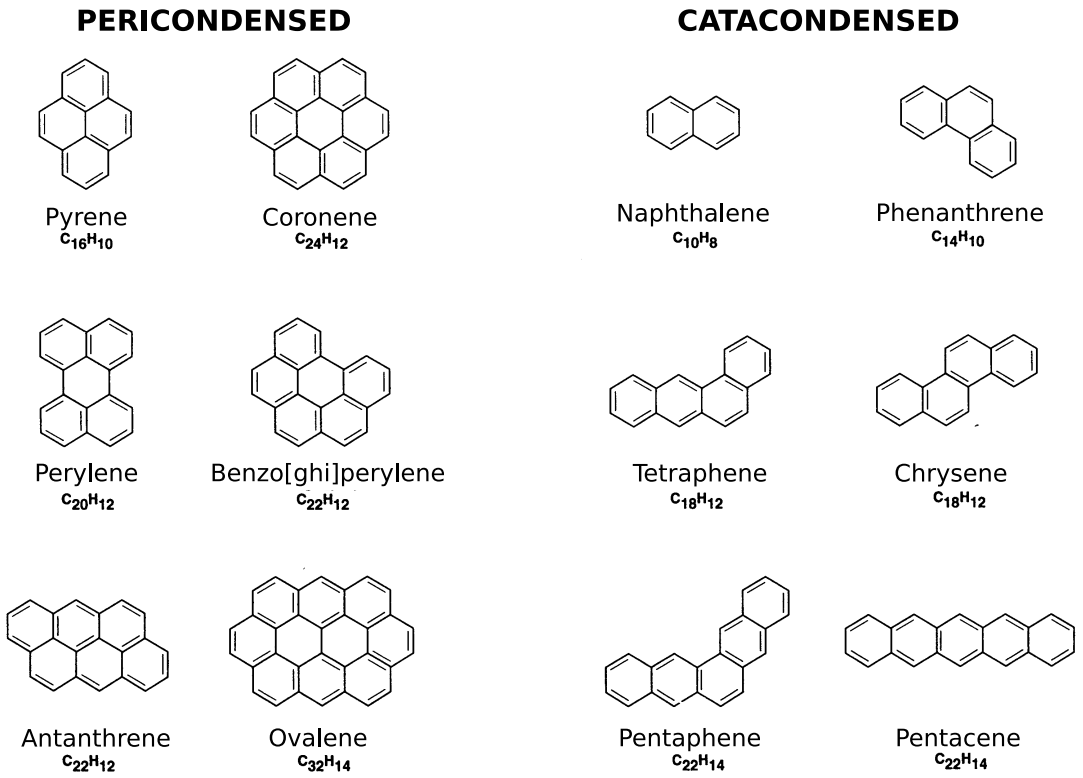


Figure 1.3 — The molecular structure of some representative PAHs. *Figure adapted from Salama et al. (1996).*

PAHs are classified into two main groups showed in Fig. 1.3. Pericondensed PAHs (left panel) have a compact structure where C-atoms are members of three or two separate rings (in the latter case only on the periphery). Within this class we find the centrally condensed, quasi-circular PAHs such as coronene and circum-coronene, where the central cycle is surrounded by a series of rings. These compact centrally condensed PAHs are among the most stable, because their structure allows complete electron delocalization and truly aromatic bonding between all adjacent carbon atoms. The radius of the pallet of a centrally condensed compact PAH is given by $a \simeq 0.9 \times \sqrt{N_C}$ Å, where N_C is the number of carbon atoms in the molecule. A typical interstellar PAH with N_C = 50 therefore has a radius of $\sim$ 6.4 Å, while dust grains typically contain many hundreds or thousands of atoms, as derived from extinction measurements. Thus, albeit that the small end of the grain size distribution is not well constrained by these studies, typical PAH sizes in the ISM are definitely smaller with respect to the 'classical' dust grains. Catacondensed PAHs (right panel) are characterized by open structures where no C-atom belongs to more than two rings. The aromatic rings are arranged in linear chains (naphthalene, anthracene, tetracene, ...) or bend rows (phenanthrene, tetraphene, ...).

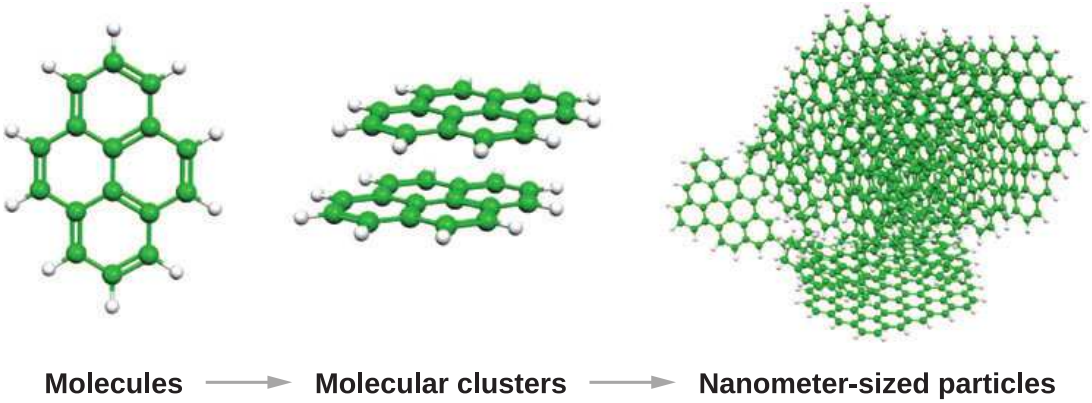


Figure 1.4 — From individual PAH molecules to amorphous carbon nanoparticles which are the constituent of carbon soot. PAH clusters form the bridge between these two aggregation states. *Figure reproduced from Tielens (2008).*

1.2.2 Formation and evolution

Interstellar PAHs are thought to originate in the envelopes of carbon-rich AGB stars, as a byproduct of the processes leading to the formation of carbonaceous dust grains ('soot'). Because of their high stability and structure, PAHs are indeed the building blocks of carbon soot. In the outflows of C-rich AGB stars, most of the carbon is locked in CO and C_2H_2 molecules. Because CO is very stable, the dominant precursors for PAHs and soot are likely acetylene (C_2H_2) and its radical derivatives. The formation of PAH molecules occurs through a two-step process: the first aromatic ring has to be built out from C_2H_2 (probably the most difficult step), afterwards the molecule grows through repeated radical formation by abstraction of a H-atom and addition of hydrocarbons. When PAH molecules are formed, they can grow and coagulate to form clusters, platelets and eventually amorphous carbon particles the solid-state branches of soot are made of (Fig. 1.4). In H-poor environments PAH formation has to occur through a different chemical pathway, which can also lead to the formation of non-planar molecules such as fullerene (Curl & Smalley 1988).

Because PAHs are closely related to dust grains, likely they will follow a similar evolution pattern. After being released into the ISM, PAHs will undergo dramatic changes. They can grow and accrete, may become part of a dust grain itself, and incorporate heavier heteroatoms such as nitrogen. In cold and dense molecular clouds, PAHs get frozen into the ice mantles covering the surface of dust grains. UV irradiation and cosmic ray bombardment trigger a rich surface chemistry with possible formation of more complex species, e.g. the substitution of a peripheal H-atom of the PAH with a methyl group (Bernstein et al. 1999). As dust grains, PAHs are also subjected to destructive processes. High energy photons, cosmic rays and strong shocks in the diffuse ISM can partially or totally destroy them, although photodestruction seems to be effective only on small PAHs ($\sim$ 20 – 30 C-atoms, Jochims et al. 1994a; Allain et al. 1996). After a protostar is born from a molecular cloud, the new complex PAHs mentioned above are easily photodestroyed by UV photons because of their minor stability with respect to the classical ones. The extremely energetic radiation field in proximity of the

newly born star will cause the complete destruction of all PAHs, including the most stable species.

1.2.3 Excitation mechanisms and IR spectroscopy

Let us now consider a small, neutral PAH molecule in the singlet electronic ground state, S_0. The absorption of UV photons with energies corresponding to the discrete electronic energy levels of the molecule will induce a transition to the upper electronic states S_1, S_2 or higher. The PAH molecule is now in an excited state which can be followed by a variety of de-excitation processes, including ionization and photodissociation. The predominant de-excitation channel depends on the environments where the molecule finds itself. On Earth, the high ambient density generally leads to collisional de-excitation. In the collision-free environment of space, instead infrared fluorescence will be dominant. The excited molecule will move to a lower-lying electronic state through internal conversion, leaving most of the initial excitation energy in the form of vibrational energy. Subsequently, the highly vibrationally excited molecule cools down, mainly by IR emission in specific vibrational modes. In order to calculate the IR emission spectrum of PAHs, we need to relate the energy of the absorbed UV photon with the temperature of the emitter. Because of their small size and small specific heat capacity, the classical approach used to determine the temperature of e.g. dust grains absorbing photons cannot be applied to PAH molecules. While dust grains reach an equilibrium temperature resulting from the balance between UV photon absorption and IR photon emission, a PAH may reach temperatures as high as 1000 K immediately after the photon absorption, but after a few seconds it may have cooled down to 10 K and remain that cold until it absorbs another UV photon after a day of so, depending on the local FUV flux (the higher the flux, the shorter the interval between two absorption). This behaviour is illustrated in Fig. 1.5, which shows the temporal evolution of the temperature of four carbonaceous grains with decreasing size. The grains are heated by the average starlight background and cooled by emission of infrared photons, over a time span of about a day. Grains with radii $a \gtrsim 200$ Å can be approximated as having a steady temperature. Grains with $a \lesssim 50$ Å , however, undergo very large temperature excursions, and the notion of "average temperature" cannot be applied (Draine 2003). Interstellar PAHs are smaller than carbonaceous grains, and they can reach peak temperatures as high as 1000 K. A PAH molecule has to be treated as a microcanonical ensemble using the methods appropriate for statistical mechanics (Tielens 2005).

We already mentioned that the IR spectrum of almost every object and region where gas and dust are exposed to UV radiation is dominated by relatively broad emission features at 3.3, 6.2, 7.7, 8.6, 11.3 and 12.7 μm (Fig. 1.6), plus various other weaker features. For almost a decade the carriers of these features remained mysterious, so they became collectively known as Unidentified InfraRed bands (UIR). Later on (Leger & Puget 1984), the comparison of astronomical spectra with laboratory spectroscopy and quantum chemical calculations of the transitions of well charactarized materials allowed the identification of PAH materials as carriers of the UIR bands. The observed features are characteristic for the stretching and bending vibrational modes of aromatic hydrocarbon materials. The 3 μm region is characteristic for C-H stretching modes: the

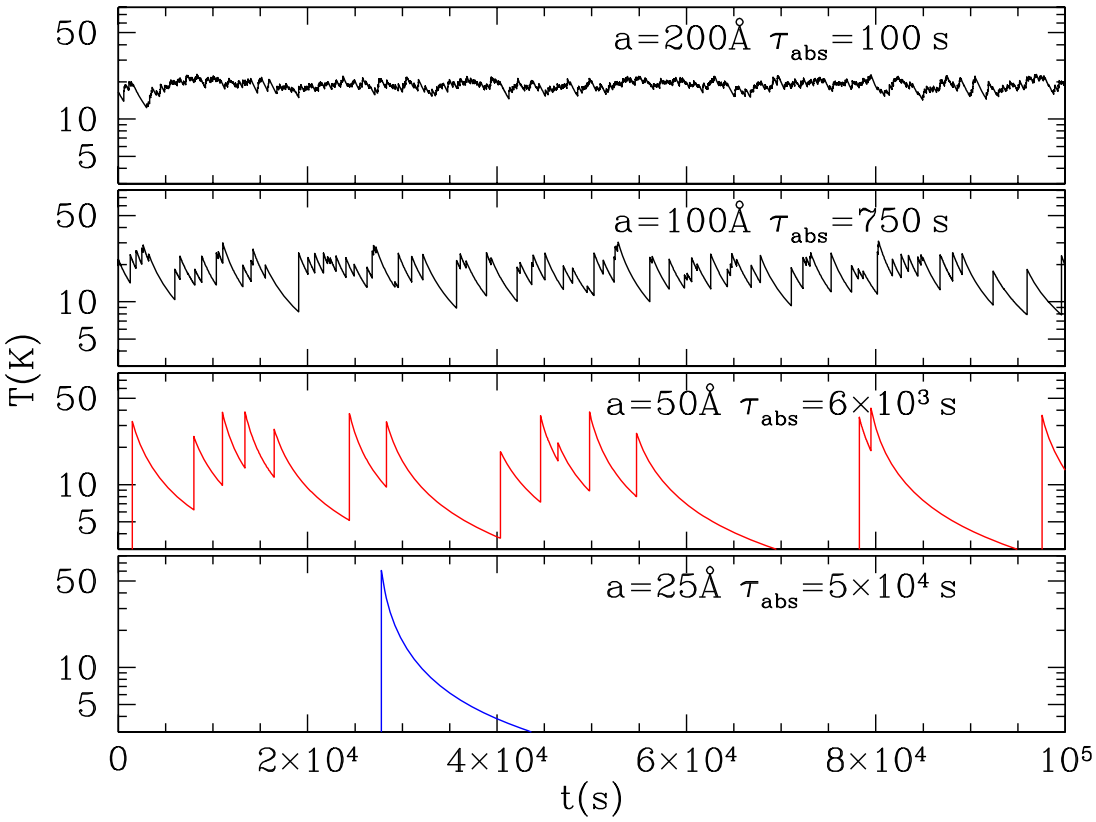


Figure 1.5 — Temporal evolution of the dust temperature for decreasing grain sizes. The dust is heated by the local interstellar radiation field, τ_{abs} is the mean time between photon absorptions. *Figure reproduced from Draine (2003).*

3.3 μm band is due to the C-H stretching mode in aromatic species, while the 3.4 μm band may arise from aliphatic groups attached as functional groups to the PAHs or to PAHs with extra H bonded to some carbons. The range 6.1 – 6.5 μm is typical for pure C-C stretching modes, while slightly longwards (6.5 – 8.5 μm) lie combined vibrations involving C-C stretching and C-H in-plane bending modes, and C-H in-plane wagging modes give rise to bands in the 8.3 – 8.9 μm range. Longward of $\sim$ 11 – 13 μm, emission bands reflect in-plane and out-of-plane ring bending motions of the carbon skeleton; hence these modes are more molecule specific, particularly at the longer wavelengths. A more detailed overview of the PAH vibrational modes, including the description of the experimental techniques and theoretical approaches involved in their study, can be found in Tielens (2008).

The charge state also has a remarkable effect on the intrinsic IR spectra of PAHs, as is illustrated in Fig. 1.7 where the absorption spectrum of a mixture of neutral PAHs is compared to the spectrum of the same species in their cationic states. It clearly emerges that ionization strongly affects the strength of the features, particularly in the 3 and 11 – 15 μm regions, while the peak frequencies are almost unchanged. Using this property it has been possible to demonstrate that the variations in the UIR spectra from a variety of astrophysical environments may arise from the presence of both neutral and charged PAHs distributed over different charge states.

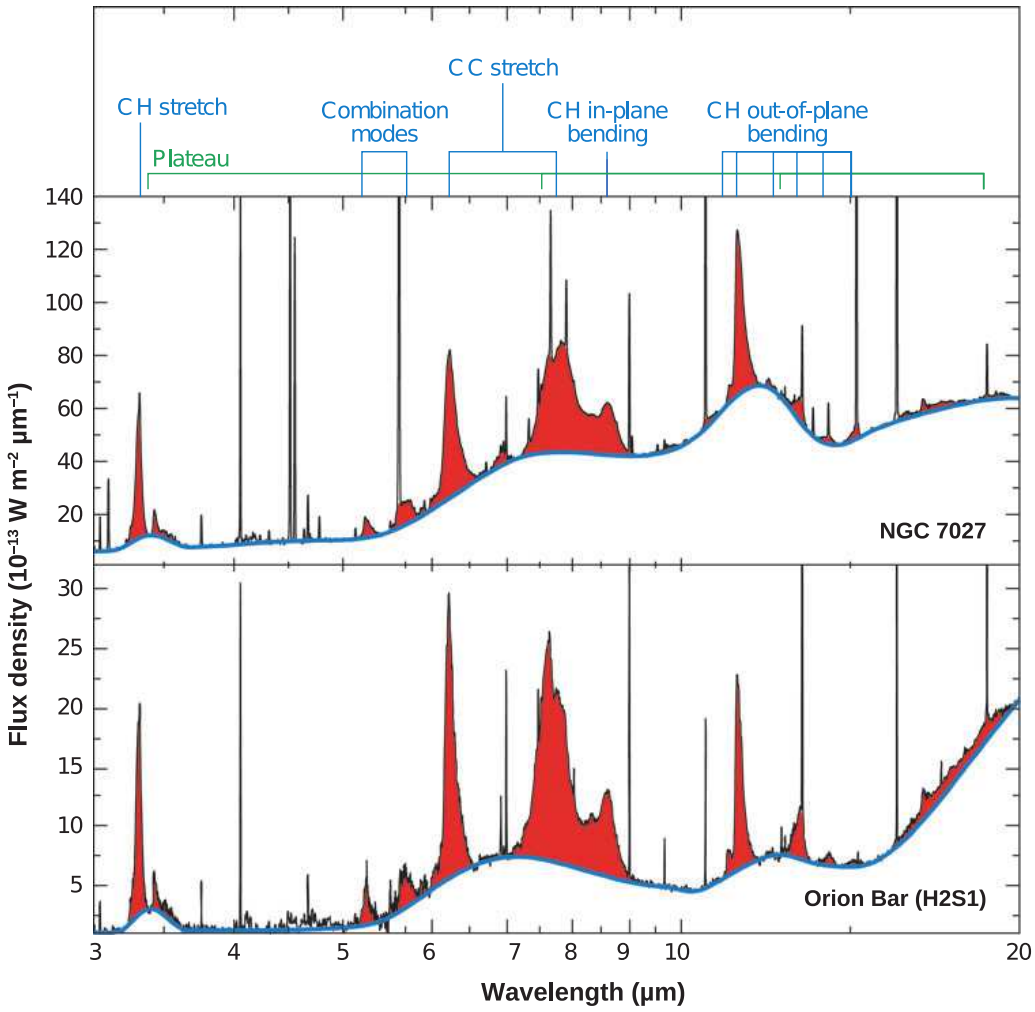


Figure 1.6 — The mid-infrared spectra of the photodissociation region in the Orion Bar and in the planetary nebulae NGC 7027. The spectra are dominated by a rich set of emission features, (almost) universally attributed to vibrational modes of polycyclic aromatic hydrocarbon molecules (top panel). The narrow features are atomic or ionic lines originating in the HII region or photodissociation region. *Figure reproduced from Tielens (2008), adapted from Peeters et al. (2002a).*

In fact, while the aromatic nature of the carriers of the UIR band is undisputed, the identification of the precise species has been the subject of a long debate. Carbonaceous solids with an abundant aromatic component – such as coal, amorphous carbon soots and chars – also show infrared emission with a general resemblance to the observed interstellar spectra. However, these are disordered materials and their features are often much broader than the observed ones. The detection of the UIR bands in photodissociation regions (PDRs, Tielens 2005) far from the illuminating star puts a strong constraint on the size of the carrier. Emission at the observed wavelengths requires temperatures that carbonaceous solids cannot apparently reach under these conditions, while small species can be heated to very high temperatures upon absorption of a single UV photon. The observed ratio of the 3.3 to the 11.3 μm band indicates a size of 50 – 80 C-atoms, while the plateau emission underneath the 6.2 and 7.7 μm

bands coupled with the absence of comparable emission in the C-H stretching mode region, suggests a size for the carrier of some 350 – 600 C-atoms. The size requirement combined with the aromatic nature of the carrier strongly favor the choice of PAHs, as molecules and/or small clusters, although no specific molecules have yet been identified. One difficulty arises from the fact that the PAHs studied in laboratory are much smaller (< 50 C-atoms) than the supposed interstellar ones. In addition, the situation is complicated for instance by the lack of a permanent dipole moment in neutral PAHs, which hence have no allowed pure rotational spectrum, by a bad partition function, by the overlapping of the fundamental vibrational modes and by the difficulty to estimate relative abundances. Nevertheless it seems more likely the presence of a family of PAHs rather than a single specific PAH molecule.

1.3 The importance of interstellar PAHs

The first striking characteristic of interstellar PAHs is that they are everywhere. The UIR bands, for which PAHs are the most accredited carriers, have been found in the mid-IR spectrum of almost every astrophysical environment where dust and gas are illuminated by UV photons, which of course does not exclude their presence in regions where they do not get the chance of being excited. Considering only the 'visible' sources, PAH features have been detected in PDRs, reflection nebulae, young stellar objects, planetary nebulae, post-AGB objects, galactic nuclei, starburst galaxies and ultraluminous infrared galaxies (ULIRGs), as well as in the IR cirrus at high galactic latitudes, on the surfaces of dark clouds, and in the general interstellar medium of galaxies - see Tielens (2008) and references therein.

In consideration of this impressive ubiquity, it is not surprising that PAHs are thought to play a crucial role in many astrophysical processes. Because of the high stability of PAHs, the high tendency of aromatic fuels to soot, and the structural similarity between their carbon backbone and that of soot, PAHs are considered the building blocks in the carbon condensation route. Through the photoelectric effect, infrared emission and gas-grain collisional cooling, PAHs (and small grains) dominate the heating and cooling of the ISM, which ultimately controls the physical conditions and the phase structure of the ISM and therefore its evolution in galaxies (Hollenbach & Tielens 1999). PAHs influence the charge balance, which reflects in the equilibrium state of chemical reactions and the gas-phase abundances in molecular clouds. They offer a large area for surface chemical reactions and so play a significant role in the interstellar chemistry. PAHs have been proposed as one possible carrier of the Diffuse Interstellar Bands (DIBs - see §1.1.1), and may also be involved in the 2175 Å feature which dominates the interstellar UV extinction curve.

Because of their characteristics, PAHs also have a promising role as a tracer for various astrophysical phenomena. The ubiquity of their emission features and their predominance in the mid-IR spectra of massive star-forming regions make PAHs a potentially powerful tool for the study of star formation throughout the universe. Essentially, the PAHs act as a dye for the presence of pumping FUV photons and hence trace the presence of massive stars (Peeters et al. 2004). The presence of PAH features has also been used to distinguish between shocked gas and PDRs (van den Ancker et al.

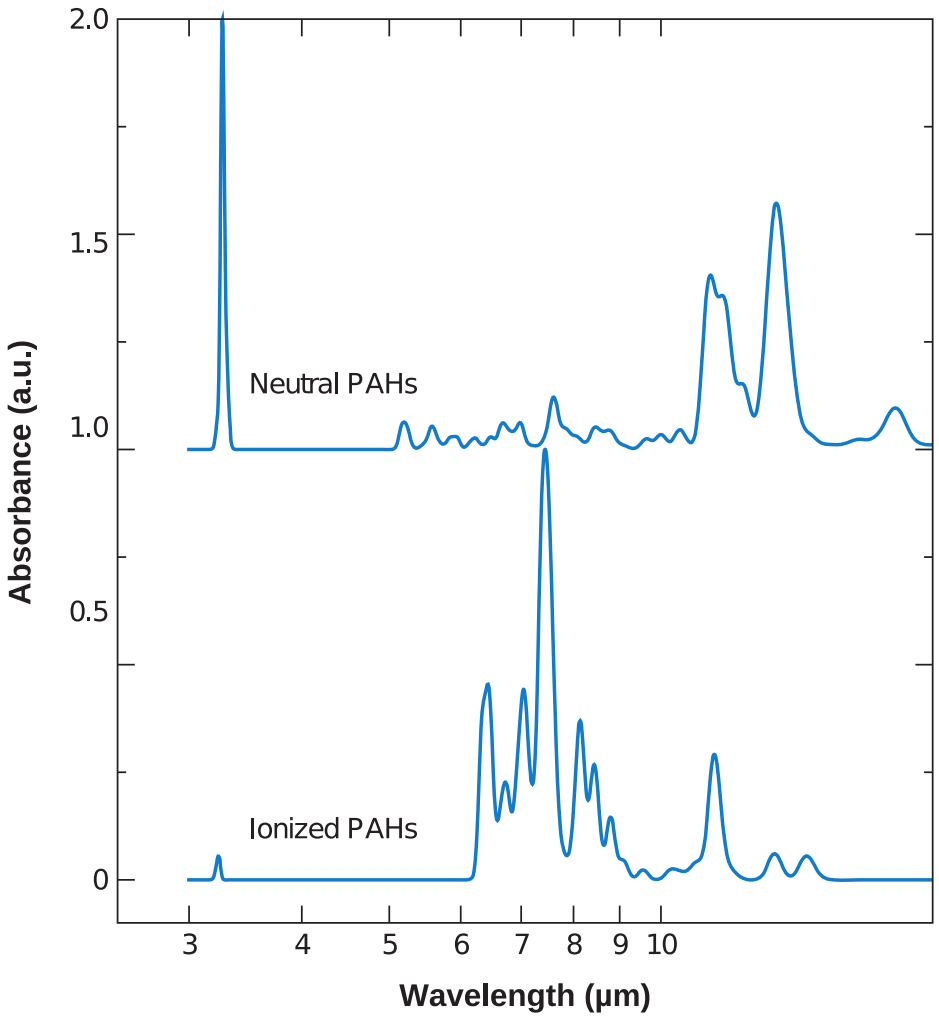


Figure 1.7 — The absorption spectrum of a mixture of neutral PAHs (top) compared with the spectrum of the same species in their cationic states (bottom). The ionization state has an extreme effect on the strength of the features, in particular the C-C modes has increased considerably relative to the C-H modes in the 3-μm and 1115-μm region, while the influence on the peak frequencies is negligible. *Figure reproduced from Allamandola et al. (1999).*

2000). In combination with the emission lines, PAHs have been employed in extragalactic studies as diagnostics for the ultimate physical processes powering galactic nuclei (e.g. Genzel et al. 1998; Tran et al. 2001). These studies show that ULIRGs are largely powered by star formation rather than active galactic nucleus activity. Consequently, the strengths of the PAH bands can also be used to probe evolutionary effects and to trace the elemental evolution in external galaxies. PAH features have also been detected in regions spatially correlated with X-ray emission from the hot gas in the star-forming region M17 and in the outflow of the starburst galaxy M82 (Engelbracht et al. 2006). Likely this emission arises from entrained gas ablated from molecular clouds and transported by superwinds or galactic fountains. PAHs could then be used as a dye for the entrained material to trace these transportation mechanisms.

1.4 Dust processing in the ISM

PAHs and dust grains are generally tightly correlated (cf. §1.2.2), thus the processes dust particles undergo during their cycling between the different phases of the ISM will also affect PAHs. In the following sections we summarize the mechanisms, able to induce structural changes, disrupt or even completely destroy dust grains. Apart from photo-processing, all the processes are *collisional* processes, i.e. based on the interaction with ions, molecules or other dust grains. Fig. 1.8 shows the results of dust processing in a typical interstellar shock with velocity of 100 km s^{-1} (Jones et al. 1996) due to the mechanisms listed below.

1.4.1 Processes affecting the dust-to-gas mass ratio

- **Sputtering** This process consists of the ejection of atoms from the grain surface, with return to the gas phase, and consequent erosion of the dust particle. The erosion is due to grain collisions with high velocity atoms and ions in energetic environments (Jones et al. 1994). Depending on the velocity distribution of the colliding partners, sputtering is defined *non-thermal* or *inertial* when collisions are determined by the relative motion between the grains and the gas, and is defined *thermal* when collisions arise from the thermal motion of the gas (Barlow 1978; Cowie 1978). Thermal sputtering is effective only for gas temperatures above 10^5 K and is dominated by collisions with H and He atoms and ions, which are the lightest and most abundant elements in the gas phase (Draine & Salpeter 1979a,c). Since thermal sputtering acts in the opposite way as accretion, a layer of equal thickness is removed from grains of any radius, resulting in the preferential destruction of the smaller grains and a less dramatic erosion of the larger ones. In grain collisions with hydrogen/protons, inertial sputtering is effective for relative velocities greater than $\simeq$ 30- 40 km s^{-1} (Tielens et al. 1994) and at lower velocities is likely dominated by collisions with the heavier projectiles (atoms and ions) in the gas (Field et al. 1997). Because the dynamics of the grains varies with their size, the effect of inertial sputtering will be size-dependent as well.
- **Vaporization** Grain-grain collisions with impact velocities above $\simeq$ 20 km s^{-1} (Tielens et al. 1994) can lead to the partial or complete vaporization of the colliding partners, followed by release of the elemental dust components into the gas phase.
- **Accretion** The adsorption and sticking onto grain surfaces of atoms, ions, radicals and molecules (possibly with the exception of the lightest species H, H_2 and He) progressively increases both the grain radius and the dust-to-gas ratio. For refractory elements such as Mg, Si and Fe, accretion can occur at temperatures as high as 1000 K, while temperatures below $\approx$ 100 K are required for species leading to icy mantles formation. Photodesorption, cosmic ray induced desorption and photoevaporation counterbalance the adsorption process. Since the adsorption rate onto a grain is proportional to the grain cross section, to a first approximation the thickness of the accreted mantle is independent of the grain radius, leading to the disappearance of the smallest grains (Guillet et al. 2008).

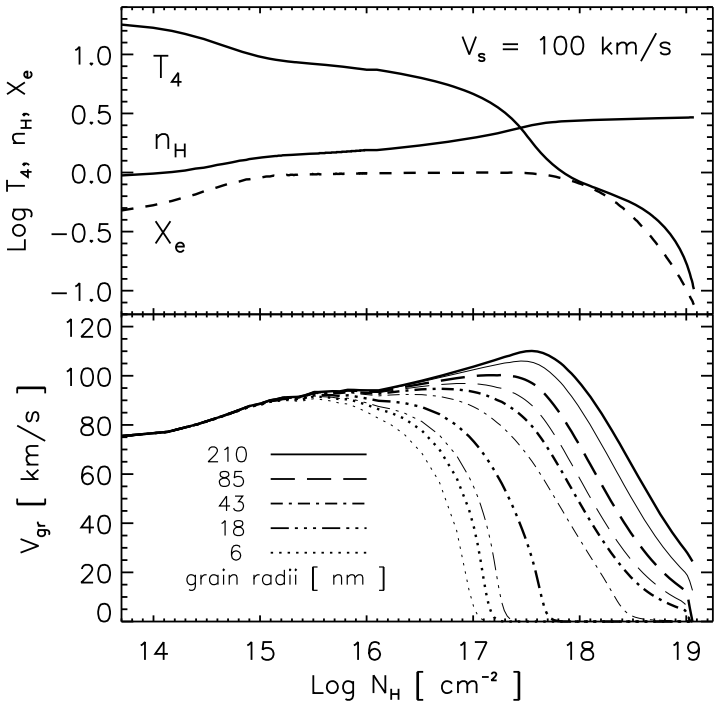
1.4.2 Processes conserving the dust-to-gas mass ratio

- **Shattering** This process occurs in grain-grain collisions with velocities above a threshold value of few km s^{-1}, and consists of the fragmentation of the dust particles into smaller fragments, with a consequent redistribution of the mass toward smaller grain sizes. The effects of shattering strongly depend on the relative velocity between the two grains, their relative sizes and physical properties, ranging from the pulverization of one or both colliding grains, to partial fragmentation or craterization of the surface of the bigger of the two (Borkowski & Dwek 1995a; Jones et al. 1996).
- **Coagulation** Grains colliding with velocities below a critical value can stick together producing conglomerates, with a consequent redistribution of the dust mass towards larger grains (Chokshi et al. 1993; Poppe & Blum 1997). The critical velocity depends on the grain composition and radius, varying from ~ 1 m s^{-1} for μm sized grains to 1 km s^{-1} for $\simeq 100$ Å -sized grains, and is enhanced by the presence of icy mantles which increase the contact surface and the interaction time during the collision.

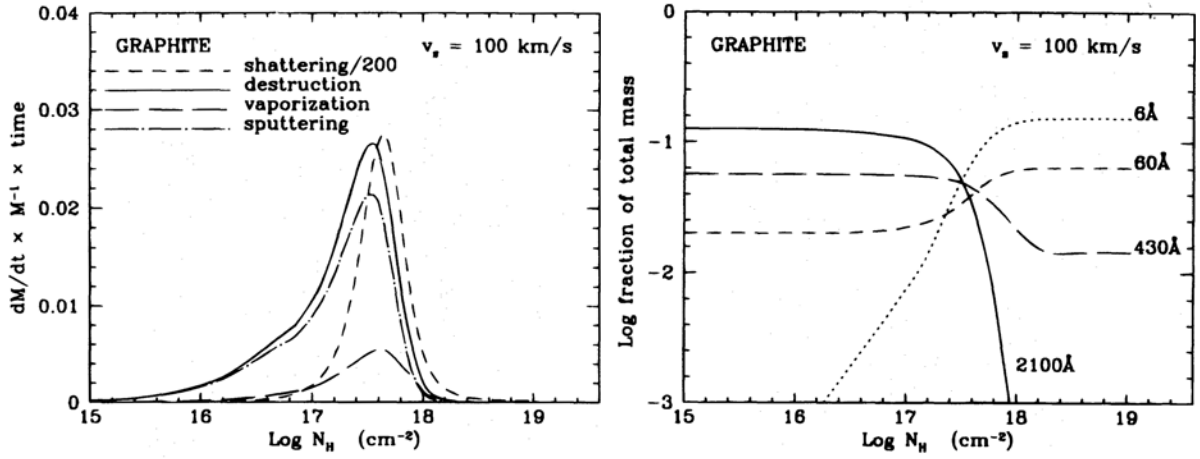
1.5 Why study collisional PAH processing in the ISM

The photophysics and photochemistry of PAHs in space have been extensively investigated. PAH photoexcitation with subsequent IR emission and photodestruction have been well studied theoretically and experimentally, and observational consequences have been evaluated. Quantum chemical calculations verified the possible vibrational modes of different PAH molecules and identified the modes measured in the laboratory. Theoretical modeling has attested to the central role of PAHs in gas chemistry and a number of theoretical studies based on unimolecular dissociation theories have assessed the importance of fragmentation of highly vibrationally excited PAHs in space (Leach 1987; Geballe et al. 1989; Allain et al. 1996; Le Page et al. 2001, 2003; Tielens 2005). Laboratory studies of molecules in conditions similar to those expected in the interstellar medium have improved the knowledge on the nature of the emitting interstellar species and on the processes involved. The ISO and Spitzer satellites have reinforced the ubiquitous nature of the UIR bands and revealed the incredible richness of the UIR spectrum and the widespread variations in the relative strength and profiles of these features, from source to source and within sources.

Concerning dust grains, their processing in the ISM has been extensively studied not only in terms of interaction with photons (e.g. scattering, extinction, photoelectric heating), but also in terms of collisional processing (§1.3), mainly by supernova shocks. Jones et al. (1996) have modelled dust shattering due to grain-grain collisions in interstellar (supernova-driven) shocks. Their calculation predicts the complete disruption of large dust grains in fast shocks propagating through the warm phase of the interstellar medium (WIM). Shocks with velocities greater than 50 km s^{-1} are able to shatter the largest grains in the MRN distribution (1000 Å $\leq a \leq$ 2500 Å) into fragments with radius smaller than $\approx$ 500 Å . The fragmentation products could also include PAH molecules which are expected to be processed as well by the shock. Unfortunately these models do not account for the destruction of PAHs by sputtering in the post-



(a)



(b) (c)

Figure 1.8 — (*a*): Profile of a shock with velocity v_s = 100 km s^{-1} (*top panel*). The temperature, $T_4 = T(\mathrm{K})/10^4$, the density, n_H and the electron relative abundance, X_e are represented as a function of the shocked column density, N_H, for the preshock density, n_0 = 0.25 cm^{-3} and the magnetic field, B_0 = 3 μG. Also shown are the graphite grain velocities (*bottom panel*) as a function of N_H for three grain radii. The column density $N_\mathrm{H} = n_0 v_s t$ is related to time through the following relation: log t (yr) = log N_H (cm^{-2}) - 13.9. (*b*): Total graphite destruction (vaporization + sputtering) and disruption (shattering) rates multiplied by time and divided by the total initial grain mass, plotted as a function of the shocked column density for the 100 km s^{-1} shock. Equal areas show equal destruction. Shattering so dominates that the shattering rate for the grains in the largest mass bin (radii = 2100 Å) is divided by 200 to fit on the figure. (*c*): Graphite grain bin masses for four grain radii plotted as a function of the shocked column density, for the shock with velocity v_s = 100 km s^{-1}. The 6 Å bin is empty at the start of the calculation. The plot clearly shows the rapid disruption of the largest grains, and the formation of small grains by shattering. *Figure reproduced from Jones et al. (1996).*

shock gas, which nevertheless may be relevant for the evolution of the interstellar PAH population.

Looking at this picture then, one can see that one important link in the chain is missing: the treatment of the collisional processing of PAHs in the ISM. PAHs and dust grains are intimately linked and they are reasonably expected to undergo the same kind of collisional processes during their lifecycle. While for dust grains the physics of these processes has been investigated and the astrophysical implications evaluated, this is not the case for PAHs. Theoretical models concerning collisional processes are missing, especially in terms of PAH damage and destruction, and this lack of information makes the interpretation of PAH observations difficult in regions subjected to such processes. From the observational point of view in fact, there is presently little evidence for the presence of PAHs in regions processed by supernova shocks. Largely, this reflects the difficulty of discerning the emission of supernova remnants against that of galactic background material. Reach et al. (2006) have identified four SNRs out of a sample of 95 whose IR colors suggest excess emission from PAHs, but most sources were too confused by the background. On the other hand, a study of the SNR N132D in the Large Magellanic Cloud revealed the presence of a steeply rising mid-IR continuum and weak emission features at 16.4 and 17.4 μm (Tappe et al. 2006). These features are attributed to relatively large carbon PAH species ($N_C \sim 4000$ C atoms). PAH emission has been detected in association with the shock-heated, X-ray emitting gas in the star-forming region M17, and the superwind driven by the nuclear starburst in M82, some 8 kpc above the plane (Engelbracht et al. 2006).

The aim of our study is to fill this key gap in our understanding of the physics behind collisional processing of PAHs and to clarify how this affects the PAH evolution in the astrophysical context. This knowledge could help to better understand the effective role of PAHs in the cosmic life cycle described in §1.1.2, particularly in terms of their relationship to dust grains. These results could also give new insights to interpret the detection – or non-detection of PAHs in specific regions and eventually provide additional arguments in favor of PAHs as a molecular dye, e.g. to trace regions of denser entrained material.

1.6 Thesis outline

The research described in this thesis aims to establish *how* the different conditions in the ISM affect PAHs, focusing on the *collisional* processing due to high velocity ions and electrons. These high velocities arise from the thermal and relative (inertial) motion induced in the gas by moderate velocity shocks, from the energy injected into the gas by very fast shocks (thermal motion), and from cosmic ray acceleration. In fact, a detailed study of the physics of the interaction between PAHs and high energy particles (ions and electrons) was still lacking, although PAHs are a key component of the ISM and these processes play a crucial role in the evolution of PAHs. In this perspective, the first key question we address in this thesis is:

What happens to PAH molecules when bombarded by high energy ions and electrons? Will they be able to survive, maintaining their character, or will they be severely damaged or even completely destroyed?

This is a general question, which is important to answer for a better understanding of the physics of PAHs.
From this it follows the second key question:

What are the astrophysical implications of PAH processing?
i.e.
What is the connection between the microscopic processes (ion/electron – PAH interaction) and the macroscopic effects on the interstellar PAH population?

This is crucial for drawing conclusions from observations: for example, to interpret the possible detection of PAHs in a (shocked) hot gas, we need to know which physical processes PAHs undergo (collisions with ions and electrons – microscopic processes) and how these processes affect the PAH population under the specific conditions of the gas (macroscopic effect). Moreover, this knowledge will contribute to a better understanding of the role of PAHs in the global ecology of the ISM.

In **Chapter 2** we present a multiwavelength study of the environment of the supernova remnant N157B in the Large Magellanic Cloud. This complex region, which besides the SNR includes a molecular cloud, dust filaments, bubbles of hot shocked gas, an OB association and a HII region, provides a very good example of the interaction between the various components of the ISM and of the variety of conditions under which PAHs can find themselves. We investigate the relative importance of shock excitation by the SNR and photo-ionization by the OB stars and the interaction between the supernova remnant and its environment, with particular attention to the dust/PAH component.

In **Chapter 3** and **Chapter 4** we present the models that we developed to describe the collisions of PAH molecules with ions and electrons and the subsequent transfer of energy, which can lead to carbon atom loss with consequent disruption and destruction of the molecules. These are the microscopic processes mentioned above. We need to develop specific models because PAHs are molecules and not small solid fragments, thus the classical approach from solid state physics cannot be applied. The results in terms of PAH destruction cannot be extrapolated from the behaviour of dust grains and strongly depend on the kind of projectile and on the energies involved. We then use our models to estimate the lifetime of PAHs (macroscopic effect) in interstellar shocks with velocities between 50 and 200 km s^{-1} (**Chapter 3**) and to evaluate the PAH survival time in a shock-heated X-ray emitting gas (**Chapter 4**), using our results to interpret existing observations. This study provides for the first time a quantitative evaluation of PAH processing in such harsh environments and gives new insights about the connection with the *dust* processing.

In **Chapter 5** we develop analogous models to evaluate the destructive effects of primary cosmic ray collisions (ions and electrons) on PAHs and estimate for how long they can survive this ubiquitous bombardment in various environments (galactic disks, galactic halos, starburst galaxy outflows and cooling flow galaxy clusters). We need specific models because the energy of cosmic rays is much higher than those of the cor-

responding particles in shocks and hot gas and the treatment of the interactions thus requires a different formalism. The resulting survival time has been compared with the previously calculated PAH lifetimes against other destruction mechanisms. This provides a map of the expected presence of PAHs as a function of the environmental conditions which can be compared with observations. Furthermore, this study allows us to check the capability of PAHs to act as molecular dye for entrained material and improves our understanding of their relationship with the other components of the ISM under a variety of conditions.

In **Chapter 6** we finally summarize our conclusions and illustrate the perspective of future research.